UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

Prime Time Toys LLC, Prime Time Toys Ltd.
and Easebon Services Ltd.
Petitioners

v.

Spin Master, Inc.
Patent Owner

Case IPR2023-1461
PATENT NO. 8,596,255

DECLARATION OF MATTHIEU HAUSIG

In support of Petitioner's Motion to Motion to Correct Exhibits 1016 and 1017, I, Matthieu Hausig, hereby declare:

1. I am Senior Counsel at Amster Rothstein & Ebenstein, LLP.

2. In August 2023, I assisted counsel of record in the IPR, Kenneth George and Brian Comack, in the preparation and filing of Petitions in connection with IPR2023-1339 and IPR2023-1348 (collectively "The Prior IPR Petitions"), including the preparation and filing of the exhibits to the Petitions.

3. The Prior IPR Petitions each included an expert declaration from Joel Delman and an expert declaration from Dr. Maureen T. F. Reitman. In the Prior IPR Petitions, the Declaration of Joel Delman was designated as Petitioner's Exhibit No. 1016 and the Declaration of Dr. Maureen T. F. Reitman was designated as Petitioner's Exhibit No. 1017. See IPR2023-1339; IPR2023-1348.

4. In the Prior IPR Petitions, the Delman and Reitman Declarations submitted as Exhibit Nos. 1016 and 1017 referenced and attached various exhibits or appendices. I was tasked with creating the PDF documents for each of Exhibit Nos. 1016 and 1017 in the Prior IPRs, and in this regard took the following steps:

a) adding divider pages to each exhibit or appendix;

b) digitally stamping each exhibit or appendix with a page and exhibit number;

c) combining the exhibits or appendices into a single PDF document; and

d) combining the PDF document containing the exhibits to the Delman Declaration with the Delman Declaration (Ex. 1016) and the PDF document containing the appendices to the Reitman Declaration with the Reitman Declaration (Ex. 1017).

5. As a result of the steps in Paragraph 4, for each of the Prior IPRs, I created a single PDF document containing Mr. Delman's Declaration and all of his referenced exhibits (see Ex. No. 1016). I then filed this PDF document as Exhibit 1016 in the Prior IPRs. Mr. Delman's Declarations in those IPRs included his exhibits as attachments.

6. As a result of the steps in Paragraph 4, for each of the Prior IPRs, I likewise created a single PDF document containing Dr. Reitman's Declaration and all of her appendices (see Ex. No. 1017). I then filed this PDF document as Exhibit 1017 in the Prior IPRs. Dr. Reitman's Declarations in those IPRs included her appendices as attachments. The Reitman Declaration in IPR2023-1348 included one extra appendix, namely the challenged '282 Patent, but otherwise had the same appendices as the corresponding declaration in IPR2023-1339.

7. In the Prior IPRs, I served counsel for Patent Owner with: (a) the Delman Declaration with all attached exhibits; and (b) the Reitman Declaration with all attached appendices.

8. The Petition for the present case was filed about a month after the Prior IPR Petitions. I again assisted Kenneth George and Brian Comack with the preparation and filing of the Petition and related exhibits.

9. In the present case, declarations were again prepared for Joel Delman and Dr. Maureen T. F. Reitman. These declarations were very similar to the declarations filed in the Prior IPRs, and the exhibits and appendices were identical. The Delman Declaration in this IPR referenced the same exhibits as his declarations submitted in the Prior IPRs. Similarly, the Reitman Declaration referenced the same appendices as her declarations submitted in the Prior IPRs.

10. By way of background, we initially received the Delman and Reitman Declarations for this IPR without the attached exhibits and appendices. I was tasked with attaching the exhibits and appendices to these declarations and then filing them in this IPR.

11. Just like in the Prior IPRs, for this IPR, the Delman Declaration was designated as Petitioner's Exhibit No. 1016 and the Reitman Declaration was designated as Petitioner's Exhibit No. 1017. In this IPR, the exhibits

numbers for the Delman Declaration and the appendices for the Reitman Declaration were identical to those used in Prior IPR Petitions.

12. It was my understanding that Mr. Delman and Dr. Reitman intended that the same exhibits and appendices that were used in the Prior IPR Petitions were to be included as attachments to their respective declarations in this IPR. I also understood that Kenneth George intended that I file the Delman and Reitman Declarations in this IPR so that they included such exhibits and appendices, and he instructed me to do so.

13. Based on my understanding and Mr. George's instructions, I created combined PDF versions of the Delman and Reitman Declarations for this IPR that included as attachments the relevant exhibits and appendices. To do so, I used the same steps described in Paragraph 4 above.

14. However, unbeknownst to me, a clerical error occurred in connection with my creation of these files. Due to a misconfiguration that I did not notice at the time, the combined PDF files that I created to include the Delman Declaration and exhibits, and the Reitman Declaration and appendices were not saved in the correct location on my computer.

15. Because the combined declarations were opened automatically as PDFs when I created them, the Delman and Reitman Declarations appeared to include as attachments their respective exhibits and appendices. However, I did not notice that these combined declarations were not saved in the

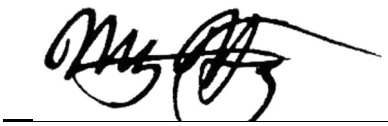
location that I intended to save them. As a result, when the Delman and Reitman Declarations were filed as Exhibits 1016 and 1017 in this IPR, I unintentionally uploaded and filed versions of the declarations that did not include the attached exhibits and appendices. As a result of this clerical error, the Delman and Reitman Declarations that I filed in this IPR did not include as attachments their respective exhibits and appendices.

16. Upon learning of this clerical error, I was tasked with submitting corrected versions of the Delman and Reitman Declarations so that they include their respective exhibits and appendices as attachments. The corrected versions of these declarations are attached hereto as Attachment A and Attachment B. I will file these corrected declarations in this IPR should the PTAB grant Petitioner's motion to file same.

I hereby declare under penalty of perjury under the laws of the United States of America that the foregoing is true and correct, and that all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true.

Date: Sept. 11, 2024

Respectfully submitted,



Attachment A

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

Prime Time Toys LLC, Prime Time Toys Ltd.
and Easebon Services Ltd.
Petitioners

v.

Spin Master, Inc.
Patent Owner

U.S. PATENT NO. 8,596,255

Case IPR2023-01461

DECLARATION OF JOEL DELMAN UNDER 37 C.F.R. § 1.68 IN SUPPORT OF PETITION FOR *INTER PARTES* REVIEW OF U.S. PATENT NO. 8,596,255

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I, Joel Delman, do hereby declare as follows:

I. Introduction

1. I am the founder and Chief Design Officer at Informed Innovation. My business address is 2176 W 24th Street, Los Angeles CA 90018, and I have been involved in the industrial design field for 28 years. I am over 18 years of age and I would otherwise be competent to testify as to the matters set forth herein if I am called upon to do so at trial, hearing or deposition.

2. I have been retained as an expert witness on behalf of Prime Time Toys LLC, Prime Time Toys Ltd., Easebon Services Ltd. for the above-captioned Petition for Inter Partes Review ("IPR") of U.S. Patent No. 8,596,255 (the "'255 Patent").

3. I have been asked to provide my opinions regarding whether Claims 1, 2, 13 and 15-20 of the '255 Patent ("the Challenged Claims") would have been obvious to a person having ordinary skill in the art at the time of the alleged invention.

4. The '255 Patent issued on December 3, 2013, from U.S. Patent Appl. No. 12/973,897 ("the '897 application"), filed on December 20, 2010. The '897 application is a continuation-in-part of U.S. Patent Appl. No. 12/777,134, filed on May 10, 2010, and issued as US Patent No. 8,371,282 ("the Parent Patent"). Ex. 1001 at Cover.

5. Claims 8, 19 and 20 of the '282 Patent are the subject of a proceeding in the United States International Trade Commission entitled *In the Matter of Certain Soft Projectile Launching Devices, Components Thereof, Ammunition, and Products Containing Same,* Investigation No. 337-TA-1325 ("the ITC Case"). In the ITC Case, the Patent Owner claimed dates of invention for some of the claims that preceded the May 10, 2010 filing date of the Parent Patent. For the purposes of my Declaration, I have used the earliest alleged invention date claimed by Patent Owner in the ITC Case, namely, February 21, 2010. Whether the date of alleged invention is February 21, 2010 or May 10, 2010 has no impact on the opinions I offer in this Declaration.

6. The face of the '255 Patent names Keith G. Meggs as the purported inventor, and identifies Hobbeezone, Inc. as the purported assignee. Ex. 1001 ('255 Patent) at Cover. I understand that Spin Master, Inc. alleges it currently owns the '255 Patent.

7. In preparing this Declaration, I have reviewed the '255 Patent, the file history of the '255 Patent, prior art references, and other references from the time of the alleged invention.

8. In forming the opinions expressed in this Declaration, I relied upon my education, training, knowledge, and experience in the relevant art, and have considered the viewpoint of a person having ordinary skill in the relevant art as of

February 21, 2010 (a "POSITA," defined below in Section VII). I have further considered and relied upon the materials cited in this Declaration, as well as a conversation with Dr. Maureen Reitman. My opinions are based, at least in part, on the following references, as well as the art and publications cited throughout this declaration: (1) Bulgarian Patent No. BG110343 to Peev ("Peev") (Ex. 1003) published July 31, 2009, (2) ThinkGeek Spitballs ("Spitballs") (Ex. 1002) published November 27, 2009 and (3) U.S. Patent No. 4,834,059 to Moorhouse ("Moorhouse") (Ex. 1006) issued May 30, 1989.

II. Background and Qualifications

9. I earned a Master of Industrial Design from Pratt Institute in New York, and have been an industrial designer, design strategist, and inventor for the past 28 years. I most recently worked with the design consultancy Product Development Technologies LLC (PDT) since 1999 and served as PDT's Los Angeles Creative Director from 2007.

10. Since PDT's acquisition in December 2017, I have continued my design practice through my consultancy Informed Innovation Inc. My work encompasses a broad range of activities related to product design and development, including strategic user research (to guide clients toward optimal design solutions), aesthetic and functional innovation, and high-level program management. I also

provide expert witness and litigation support services in matters related to patent litigation.

11. Prior to joining PDT, I worked as a staff designer at the New York based design consultancies Henry Dreyfuss Associates and Cousins Design, then upon moving to Chicago as Senior Designer with Zenith Electronics Corp. I currently serve as Chair of the Industrial Designer's Society of America's (IDSA) Design Protection Committee, and as an Associate Professor at ArtCenter College of Design in Pasadena, California.

12. My CV is attached to this report as Exhibit A.

13. Throughout my career in industrial design and product development, I have been engaged in assisting clients with a wide variety of design challenges, including numerous programs focused on the development of toys and games. My clients and royalty-based entrepreneurial work for such designs have included Fisher Price, Learning Resources, Little Kids, Vtech, Crayola and others, for whom I designed everything from infant products to action figures and electronic learning games.

14. Among my many projects for this market, I invented and designed "Light 'N Strike Math" for Learning Resources, an award-winning electronic activity game which has remained among the most successful products in its category for the past 15 years. I also invented and licensed the "Bubble Bugs" line

of bubble blowing toys for Little Kids Inc., incorporating air- powered bubble blowing mechanisms that have successfully sold at big box retailers and independent toy shops without interruption for the past 24 years.

15. My work in the toy industry has been recognized with Gold Awards from Doctor Toy and the Toy Industry Association.

16. I have more than a year of experience developing projectile launchers, including conceiving, designing, and prototyping toy projectile launchers. For example, I conceived, designed and prototyped projectile toys including "Team Stomp Rockets" (in which two or more children simultaneously provide the air pressure to launch foam rocket projectiles) and gun-like launchers for toy cars and "Ice Riders."

17. I have likewise assisted in the design and development of an advanced, spring-loaded diabetes lancing device incorporating a launch mechanism with many similarities to mechanisms powering spring-powered projectile toy guns (and for which Nerf gun mechanisms were modified to serve as initial prototyping test beds).

18. For that project (and all design programs on which I have been engaged) I gained a comprehensive understanding of the intended users for each product I design, how they will use the product, and how my designs will be compared to other designs that consumers evaluate in their purchasing decisions.

19. On a personal level, I am the father of two boys with whom I have extensive hands- on experience in the purchase, use and maintenance of our family's large collection of airguns. We own approximately 30 airguns, vintage and contemporary, comprising most every mechanism available – multi-pump, spring piston, gas piston, electric, CO2 and PCP – which I regularly maintain and occasionally repair. These guns utilize BBs, pellets and airsoft ammunition.

20. I have also purchased, broken down, and modified toy projectile launchers, including for example Nerf blasters, of all kinds. I have engaged with the active online community of Nerf "modders" to employ more powerful springs and other aftermarket components to modify and improve the firing qualities – power and accuracy – of the toy guns I purchased for my sons.

21. Through my professional and personal experience described above, I thus bring to this engagement the understanding and perspective of a designer and inventor, as well as a parent, who is intimately familiar with the category of toys which form the subject matter of this litigation, including how they operate and how they are played with by children. I am very familiar with the design and development of projectile launchers such as those at issue in this matter, and possess a solid understanding of the mechanisms and play patterns relevant to the development of projectile launching devices.

22. I have been named as inventor on over 40 issued and applied for U.S. Patents. The complete list of these patents and published applications is attached as Exhibit B. My design work has received awards and recognition from the Industrial Designers Society of America (which awards include, among others, the "IDSA 20/20 Award" recognizing twenty designers who contributed to the advancement of the design profession in 2020), the Chicago Athenaeum, the Consumer Electronics Association, the Toy Industry Association, ID Magazine and the Wall Street Journal, and has been featured in books aimed at educating design students about the profession.

23. In addition to my work in product design consulting, I have frequently offered my expertise as mentor and advisor to technology and hardware-focused startups via Los Angeles based incubator and accelerator programs, and served as a member of the Board of Directors for the 3D printed medical device manufacturer MetaMason Inc. for five years.

24. Given the foregoing range of professional and personal experience over the course of my career as an industrial designer, I believe I am well qualified to opine on the matters covered in this report, and to offer opinions from the viewpoint of one skilled in the art with respect to the alleged inventions at issue in this case.

25. During the previous five years, I have testified as an expert either at trial or by deposition in 15 cases. The complete list of these matters is attached as Exhibit C.

26. During the previous 10 years, I have authored approximately 25 articles and publications. Attached as Exhibit D is the list of articles and publications I have written.

27. Prior to entering the profession of industrial design, I graduated from Harvard Law School and practiced corporate and securities law. I have not practiced or been barred as an attorney for the last 27 years.

28. I have been informed by counsel for Petitioners about the relevant provisions of patent law to be applied for purposes of this report, which are summarized in Section V below. I have applied those principles to the facts of this case. I offer no opinions on the law related to the matters in this case.

29. I do not provide any guidance or opinion as to the law, which I understand is the purview of the court. Rather, the opinions expressed and reasoning applied are those of an experienced industrial design consultant, viewing the relevant questions from the relevant perspectives (e.g., a person having ordinary skill in the art at the time of the alleged invention, i.e., in the February-May 2010 timeframe) and applying (as necessary) the law as it has been explained to me by counsel for Petitioner.

III. Compensation

30. I am being compensated for work on this matter pursuant to my agreement with Rubin Anders at my normal rate of $350 per hour. For non-working travel time I am being compensated pursuant to my agreement with Rubin Anders at my normal rate of $200 per hour. My compensation is in no way based on the outcome of this investigation or on the opinions that I provide. I have no interest, financial or otherwise, in the outcome of this matter. I have no financial interest in, or affiliation with, any of the parties in this matter.

IV. Summary of Opinions

31. In my opinion, Claims 13 and 15-20 of the ’255 Patent are rendered obvious by the combination of Peev and Spitballs.

32. In my opinion, Claims 1 and 2 of the ’255 Patent are rendered obvious by the combination of Peev, Spitballs and Moorhouse.

V. Legal Principles

33. I am not an expert in patent law and am not offering any opinions on the legal standards. In this section I provide my understanding of the law as it has been explained to me by counsel for Petitioners, and I applied this understanding when rendering my opinions in this Declaration.

34. I understand that claims in an IPR are construed using the same claim construction standard that would be used to construe the claim in a civil action,

including construing the claim in accordance with the ordinary and customary meaning of such claim as understood by one of ordinary skill in the art and the prosecution history pertaining to the patent. I also understand that the ALJ in the related ITC case has construed certain claim terms in the parent patent and I have used her constructions.

35. I understand that a claim is invalid if it is obvious. Obviousness of a claim requires that the claim be obvious from the perspective of a person having ordinary skill in the relevant art at the time the alleged invention was made. I understand that a claim may be obvious in view of a single prior art reference, or may be obvious based on a combination of two or more prior art references.

36. I understand that an obviousness analysis requires an understanding and consideration of the scope and content of the prior art, any differences between the alleged invention and the prior art, the level of ordinary skill in evaluating the pertinent art, and any secondary considerations of nonobviousness (if any).

37. I understand that when there is a design need or market pressure to solve a problem and there are a finite number of identified, predictable solutions, a person of ordinary skill has good reason to pursue the known options within his or her technical grasp. If this leads to the anticipated success, it is likely the product not of innovation but of ordinary skill and common sense.

38. I further understand that a claim is obvious if it unites old elements with no change to their respective functions or alters prior art by mere substitution of one element for another known in the field, and that combination yields predictable results. While it may be helpful to identify a reason for this combination, common sense should guide the analysis and no rigid requirement of finding a teaching, suggestion, or motivation to combine is required. When a product is available, design incentives and other market forces can prompt variations of it, either in the same field or a different one. If a person having ordinary skill in the relevant art can implement a predictable variation, obviousness likely bars its patentability.

39. I also understand that for the same reason, if a technique has been used to improve one device and a person having ordinary skill in the art would recognize that it would improve similar devices in the same way, using the technique is obvious. I understand that a claim may be obvious if common sense directs one to combine multiple prior art references or add missing features to reproduce the alleged invention recited in the claims.

40. With respect to secondary considerations, I understand that certain factors may support or rebut the obviousness of a claim, and these are often referred to as "secondary considerations." I understand that such factors include, among other things, (i) commercial success of the alleged invention, (ii) skepticism of those having ordinary skill in the art at the time of the alleged invention, (iii) unexpected

results achieved by the alleged invention, (iv) any long-felt but unsolved need in the art that was satisfied by the alleged invention, (v) the failure of others to make the alleged invention, (vi) praise of the alleged invention by others having ordinary skill in the art, and (vii) copying of the alleged invention by others in the field. I also understand that contemporaneous and independent invention by others is a secondary consideration tending to show obviousness.

41. I understand that there must be a nexus—that is, a connection between the merits of the claimed invention and any submitted secondary considerations evidence—in order for the evidence to be pertinent to the obviousness inquiry. I understand that if there is not a nexus between the secondary considerations evidence and the claimed invention, that is not indicative of nonobviousness.

42. I understand that even if there is secondary considerations evidence that has a nexus to the Challenged Claims, that does not mean that the patent claims must be nonobvious. Rather, it is one element that must be considered in the overall obviousness analysis. I understand that weak secondary considerations evidence may not overcome a strong showing of obviousness in view of the prior art.

VI. The '255 Patent

43. The '255 Patent relates to "soft-projectile launching devices" for "super absorbent polymer projectiles." Ex.1001, 1:14-19. The 255 Patent recognizes projectile launching devices were well-known and included "a variety of different

types of launching toys," including Nerf "blasters." *Id.*, 1:23-33. The '255 Patent also recognizes other toy projectile launchers, like paint ball and airsoft guns, were well-known "small projectile systems for gaming and professional training purposes." *Id.*, 1:66-2:3.

44. The '255 Patent indicates "[s]uper absorbent polymers (SAPs) were first invented "in the 1960s and are commonly used in personal disposable hygiene products such as diapers, protective underwear, and sanitary napkins" and "are polymers that can absorb an extremely large amount of liquid relative to their own mass." *Id.,* 4:54-59.

45. During prosecution of the application that became the '255 Patent, the Patent Examiner issued an Office action on December 10, 2012 rejecting pending claims 1-2 "under 35 USC 103(a) as being unpatentable over Zuloff (US 7004813 B2) modified by Bartlett (US 6386293 B1), Vanmoor (US 5697179 A) and Moorhouse (US 4834059 A). Ex. 1018, 97.

46. The Examiner explained that Zuloff disclosed a device for projecting soft-projectiles which included a firing mechanism and a magazine interface. The Examiner acknowledged that Zuloff did not "explicitly teach a device for projecting a soft-projectile wherein the soft-projectile is made from super absorbent polymer" and did not teach a magazine interface with a locking mechanism or a safety mechanism at one end of the barrel designed to prevent access thereto. *Id.* The

Examiner relied on Vanmoor for its teaching of a magazine interface with a locking mechanism and Moorhouse for its teaching of a safety mechanism at the end of a barrel. Ex. 1018, 98.

47. With respect to the missing teaching in Zuloff of a soft-projectile "made from super absorbent polymer", the Examiner relied on Bartlett (Ex. 1014) which teaches a "device (Figs. 1, 3, 6 and 8) for projecting super absorbent polymer" and argued that it would have been obvious "to use the super absorbent polymer material of Bartlett with the disclosure of Zuloff to launch a projectile comprised of super absorbent polymer." Ex. 1018, 98.

48. The Examiner made similar obviousness rejections for remaining claims 3-5 utilizing the same references (Zuloff, Vanmoor and Moorhouse), together with an additional reference (Lee (US 5285765)), to show that the components of the claimed device were old. The Examiner again used the Bartlett reference to show that launching a projectile made of super absorbent polymer was old. Ex. 1018, 100-102.

49. The Applicant filed an Amendment in response to the Office Action on May 10, 2013. The Applicant amended claim 1 and added 15 new claims. Ex. 1018, 109-113. The Applicant traversed the rejections arguing that "[n]either Zuloff nor Bartlett teach, suggest or make obvious soft-projectiles made from a super absorbent polymer as required by claim 1." As to Bartlett, the Applicant explained that it

"teaches methods for delivering a fire retardant solution of super absorbent polymers to either protect the surface from fire, or extinguish the fire when it has begun. . . Bartlett teaches storing the super absorbent polymer in a pressurized reservoir and mixing it with ordinary tap water prior to spraying the mixture either to protect a surface from fire, or extinguish a fire." Ex. 1018, 114-115.

50. The Applicant argued that it would not be obvious "to take a material [SAP] used as part of a fire retardant solution and use it to make soft-projectiles because they are completely different fields of endeavor." Ex. 1018, 115. The Applicant stated:

> The field of fire retardants has nothing to do with the field of soft-projectiles. Bartlett does not teach, suggest, or make obvious "a plurality of soft-projectiles having the same shape, each soft projectile being formed from a hydrated super absorbent polymer" but rather discloses an adapter for a fire hose to spray a mixture or slurry that includes super absorbent polymer onto a surface. There is absolutely no relationship between the fire retardant patent of Bartlett, and the claimed soft-projectiles for a projection device. Furthermore, the super absorbent polymer in Bartlett is slurry and is not "a plurality of soft-projectiles having the same shape."

Ex. 1018, 115, emphasis in original.

51. In response, the Patent Examiner issued a Notice of Allowability of all pending claims. Ex. 1018, 122-125. However, soft-projectiles for use with a projection device having the same shape (spherical) and made from SAP were old. The prior art taught "Spitballs," a soft, spherical superabsorbent polymer ammunition for use in a blow gun. See Ex. 1002, 14-25. Applicant did not disclose and the Examiner did not cite Spitballs (or Peev) during prosecution.

VII. Person of Ordinary Skill in the Art (POSITA)

52. I have been advised by counsel that there are multiple factors relevant to determining the level of ordinary skill in the pertinent art, including (1) the educational level of the inventor; (2) the type of problems encountered in the art; (3) the prior art solutions to those problems; (4) the rapidity with which innovations are made; (5) the sophistication of the technology; and (6) the educational level of active workers in the field.

53. In a proceeding before the International Trade Commission (ITC), Petitioner and I proposed that a person of ordinary skill in the art ("POSITA") at the time of the alleged invention of the Parent Patent (US Patent No. 8,371,282) would be someone who (i) had a Bachelor's degree in Industrial Design or Mechanical Engineering or (ii) a toy designer with at least five years' experience designing toys (including launchers), with both of (i) and (ii) having access to a chemist knowledgeable regarding super absorbent polymers.

54. I understand that Patent Owner proposed, in the same proceeding before the International Trade Commission (ITC), that a person of ordinary skill in the art at the time of the alleged invention ("POSITA") of the parent patent would (1) have had a Bachelor's degree in mechanical engineering, industrial design, or an equivalent, with at least one year of relevant experience designing projectile launching systems and (2) be a member of a team, which would include a person with a Bachelor's in materials science, chemistry, or equivalent, or has at least one year experience working with materials for use in consumer products.

55. Patent Owner's and Petitioner's definitions of the POSITA are similar, and my opinions in this Declaration would not change if I used Patent Owner's definition of the POSITA rather than Petitioner's definition.

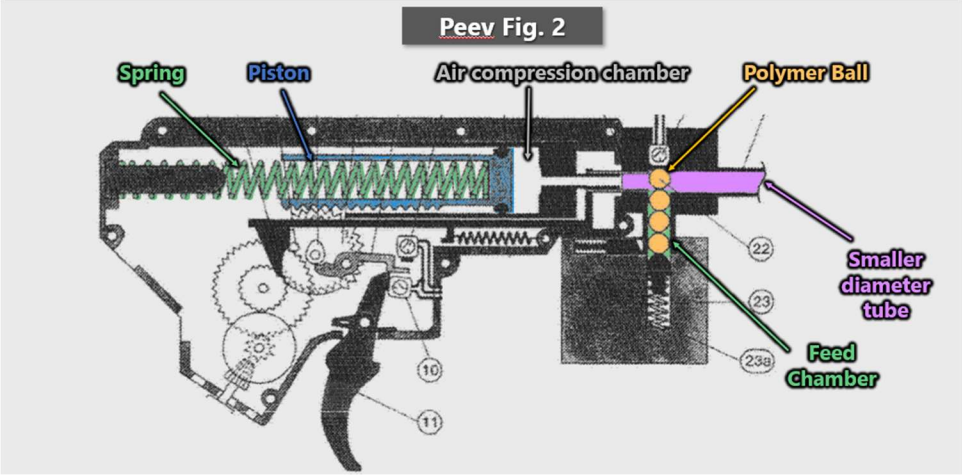
VIII. Scope and Content of the Prior Art

A. Peev

56. Peev discloses electric airsoft guns that "find application in the sporting gun industry and are used for military emulations or training ***or for fun [and entertainment] when conducting airsoft games***." Ex. 1003, 23. As explained by Peev, one advantage of its airsoft gun is that it improves airsoft game ***play*** by using techniques that "increase[] the number of shots that can be ***played*** on one full battery charge." Ex. 1003, 27.

57. Figures 1-3 of Peev respectively show the airsoft gun in the different stages of firing the ammunition. Ex. 1003, 38-40. Figure 1 shows the "SAFE" mode, when the gun cannot be fired. *Id.* Figure 2 shows the trigger pulled and the ammunition 22 ready to be fired. *Id.* Figure 3 shows the ammunition launched into free flight from the gun. *Id.*

58. Reference is made to Figure 2 of Peev (annotated below) to illustrate the components and operation of the airsoft gun:



Ex. 1003, 39 (annotations added).

59. Peev's projectiles are a plurality of polymer balls 22 (see yellow shading) that are the same shape and are launched from an airsoft gun. Ex. 1003, 31-32. As shown in the above drawing, these balls are held in a feed chamber and then loaded to a firing position. Ex. 1003, 23. The topmost ball 22 is in the smaller diameter tube (shaded in purple), ready to be fired. Ex. 1003, 31, 32 and 39. Once in the firing position, a firing mechanism accelerates the projectile down the barrel.

60. Peev's firing mechanism includes: (1) an air compression chamber (see the gray arrow); (2) a piston (shaded in blue) disposed within and axially aligned with the air compression chamber; and (3) a spring (shaded in green) operatively arranged to bias the piston toward a rest position (Figures 1 and 3) from a cocked position (Figure 2) within the air compression chamber. Ex. 1003, 31-32 (". . .the sector wheel 5 pulls back the ***piston 47,*** tightens ***the spring 46,*** pulls back the nozzle 45 . . . and allows the ball 22 . . . to enter the chamber 20 of the ***barrel 21*** (Fig. 2). . . . [T]he piston 47 . . . under the pressure of the spring 46 accelerates forward and ***compresses the air in the cylinder 48*** inserting it through the nozzle into the barrel 21 and ***firing the ball 22.***").

61. The feed chamber of the airsoft gun of Peev is a removable magazine. During game play, Peev describes replacing an empty magazine with a full one. Ex. 1003, 34 ("In order to resume firing, after replacing an empty magazine with a full one, the shutter stop button 27 must be pressed . . .").

62. The firing mechanism of Peev uses air pressure to launch the projectiles and applies a force (i.e., air) directly to the projectiles. Ex. 1003, 32. Peev's device is a toy that is in the shape of a gun. Ex. 1003, 23, 39-41.

B. Spitballs

63. Spitballs describes "Spitballs" as a toy projectile that can be launched using a launcher and that was listed for sale and described by toy retailer ThinkGeek

by at least November 27, 2009. Ex. 1002. I reviewed printouts of the product packaging and description from the Wayback Machine, dated November 27, 2009 and November 30, 2009. Ex. 1002, 14-22. I understand that the Wayback Machine archives webpages as they existed on a given date, and includes within the URL the exact year/month/day/hour/minute/second on which the webpage was archived, such that the webpages in Ex. 1002 are saved versions of the webpages as they existed at the identified date and time. Ex. 1002, 1.

64. In my opinion, prior to February 21, 2010, POSITAs interested and ordinarily skilled in the art of projectile launchers, exercising reasonable diligence, could have located the Spitballs publication. Before 2010, ThinkGeek was a well-known toy retailer, in particular with respect to airsoft and nerf-type foam rocket launchers.

65. I understand that in October of 2009, Thinkgeek.com featured a separate category for "Cube Warfare" (cube being short for cubicle) that included 20 items, including an airsoft gun, a foam rocket launcher, a rubberband-powered launcher, a catapult, an indoor paintball simulator, an air-powered marshmallow shooter, and other launchers. Ex.1002, 26-28. A POSITA visiting the Thinkgeek website would have understood the website category "Cube Warfare" as containing warfare themed toys that could be used in an office environment.

66. Once at Thinkgeek.com, a POSITA could have navigated to "geek toys" and from there to either "Cube Warfare" or "Science Toys" to find the Spitballs listing. Ex.1002, 4-25. The page contained an image of the Spitballs packaging image and text which is available by clicking an image box. Ex.1002, 20-22. A POSITA would recognize the box contains an image that is part of the Spitballs listing by virtue of the "Zoom" icon beneath the image and the image icon in the upper left corner, and "Additional Images." Ex.1002, 17-19. Both captures are from November 30, 2009, showing these materials were published together. Ex.1002, 17-22.

67. Spitballs are soft spherical SAP projectiles that can be launched out of projectile launchers. The picture of the Spitballs product packaging shows both un-hydrated balls (in plastic bag, lower middle) and hydrated balls (picture on packaging, bottom left, and in front of the packaging, bottom right) (Ex. 1002, 18):



68. The packaging shows a projectile launcher in the form of a cylindrical tube, shown on the packaging in a background cartoon with a child launching a Spitball. Ex. 1002, 18. The child's blue eyes are at the top with her or his nose between them and a hand in front of their nose. The hand is holding a white Spitball projectile launching tube to the child's mouth. And shown immediately behind the plastic containing the Spitballs, the tube launches a cartoon spit ball. Id. The

Spitballs product packaging also says that the balls "grow[] 200x their size," that they "slip, slide, bounce, and explode," and that they are "fun to throw."

69. The description of Spitballs explains that "Spitballs start out as tiny balls and expand 200 times when stuck in water." Ex. 1002, 21. After hydration, "[t]hey are slimy and squishy." Id. Spitballs "[w]ill bounce and/or explode into mushy parts on impact (depending on the force you throw them)" and that the balls are "spherical polymers." Id. "Spitballs grow to about 0.6" in diameter (the longer they absorb water, the bigger they grow)." Id.

70. The description of Spitballs also shows multiple Spitballs in a person's hand and a bowl of spitballs, Ex. 1002, 21 as reproduced below:



71. As shown above, the Spitballs packaging included a plastic packet that contains over 150 dehydrated SAPs. See Ex. 1002, 18, 21 (packet is located directly above "They Slip, Slide, Bounce & Explode"); The Spitballs packaging teaches to

hydrate the dehydrated Spit Balls by emptying them into a bowl or cup of water. See Ex. 1002, 21. The product listing teaches that the dehydrated Spitballs can "grow up to 200 times their original size" as they absorb water. Ex. 1002, 21.

72. The packaging teaches to launch the hydrated SAP Spitballs through a tube, just as is done with conventional wadded up paper spitballs. As shown by the yellow highlighting below, the front of the packaging includes a drawing of a person holding a straw and launching a hydrated SAP Spitball from a tube.



Ex.1002, 18 (annotated and cropped).

C. Moorhouse

73. Moorhouse is directed to an air gun with safety features. Specifically, the gun of Moorhouse compresses a spring during cocking and uses the air accelerated by the spring to propel a projectile during firing. To prevent unintended projectiles from being inserted into the barrel, the front of the barrel is blocked except during firing. Ex. 1006, Abstract.

74. Moorhouse teaches blocking means (see 340 in Fig. 4) disposed adjacent the front end of the barrel for preventing the insertion of objects into the barrel from the front thereof. The blocking means is movable between an operative position, wherein it extends substantially across the barrel (see item 340 in Figs. 4, 5 and 6) and in the travel path of the projectile, and an inoperative position, wherein it is spaced from the travel path of the projectile (see item 340 in Figs. 20 and 21). The blocking means are operative in response to movement of the trigger between its rest position and its firing position, which moves the blocking means to its inoperative position (see item 340 in Figs. 20 and 21) when the trigger is in its firing position and to its operative position when the trigger is not in its firing position. Ex. 1006, 2:14-26, 13:51-14:6. The above is illustrated in the annotated, excerpted portions of Figs. 4 and 21, shown below. Ex. 1006, Figs 4 and 12.

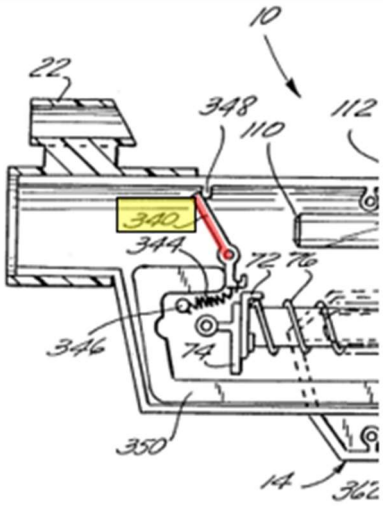


FIG. 4 (excerpted and annotated)

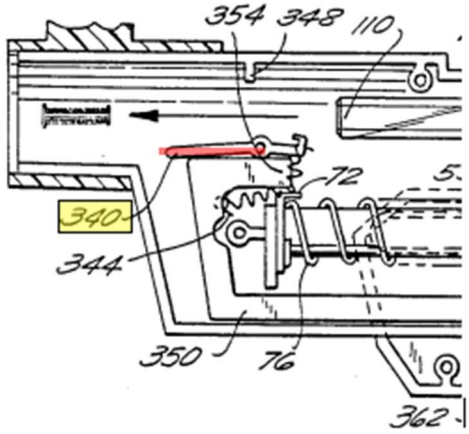


FIG. 21 (excerpted and annotated)

IX. Peev In Combination With Spitballs Renders Claims 13 and 15-20 Obvious

A. Motivation to Combine Peev and Spitballs

75. Peev discloses an airsoft gun. Prior to 2010 it was known that while airsoft guns are a lot of fun to play with, they fire hard plastic ammunition, and that this ammunition can hurt and even cause injury. In a 2008 article from Bleacher Report, entitled "Airsoft Guns: A Double Edge Sword", the author acknowledges that airsoft guns are fun to play with, but at the same time there is a risk of injury because the rounds are made of hard plastic and they can "crack the skin and even cause minor bleeding." Ex. 1005, pg. 3.

76. Prior to 2010, Spitballs were softer projectiles ("Will bounce and/or explode into mushy parts on impact." Ex. 1002, 21) that could be used in place of the hard spherical plastic ammunition to address the injury problem.

77. There was a finite number of ammunition options that a POSITA could have considered that would have a reasonable expectation of success in an airsoft gun such as Peev, including rubber, cork, foam, and soft plastics, such as SAPs. Based on my discussions with Dr. Reitman I understand that SAPs were known to be easily adjustable as to size, shape and softness. This is a significant advantage in adapting SAPs for use with airsoft guns. For example, the gel strength may be adjusted to ensure that the SAP ammunition does not break apart when loaded into and launched from the barrel of the gun.

78. Replacing hard plastic projectiles in an airsoft gun with soft SAP projectiles was well within the technical grasp of a POSITA as of 2009. In addition to (or as an alternative to) adjusting the SAP, a POSITA would have also known that airsoft guns could be easily adjusted. A POSITA could change the spring pressure to avoid any premature breakage of SAP projectile or could change the size of the air compression chamber to regulate the amount of force that would be exerted on the SAP projectiles.

79. In view of the foregoing (see Pars. 76-79), it is my opinion that, by February 21, 2010, a POSITA would have expected that replacing the harder injury

causing ammunition of Peev with softer, safer Spitballs ammunition would have been a success.

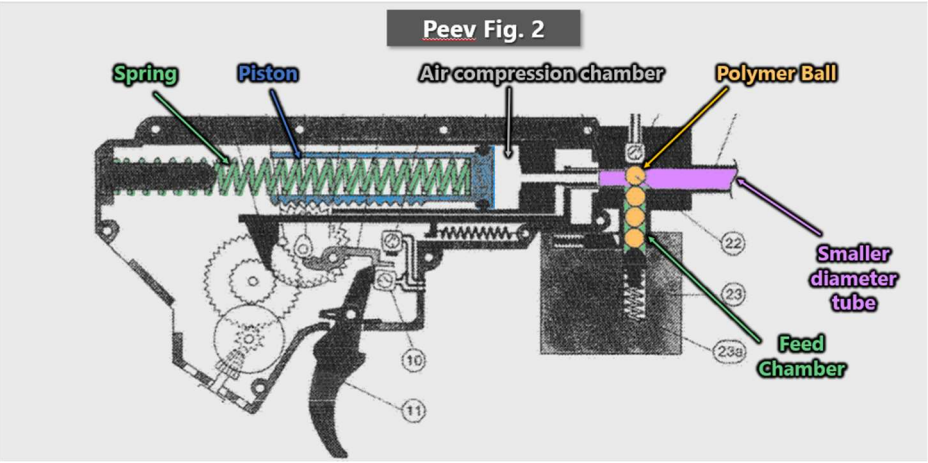
80. Peev and Spitballs are in the same field of endeavor, namely, launchers and ammunition used for fun. Peev teaches an airsoft gun that can be used for fun in games that launches spherical bullets. Spitballs teaches spherical ammunition that can be launched for fun and games. In fact, airsoft guns and Spitballs were both found in the Cube Warfare section ("Cube" is short for cubicle) of the Thinkgeek website. See Paras. 63-66, *supra.*

81. A POSITA would have recognized that combining air guns, such as Peev's toy gun with Spitballs' hydrated SAP projectiles, is a simple substitution of one known element (spherical hydrated SAP soft-projectiles) for another known element (Peev's spherical hard bullets) to obtain predictable results (a safer air gun that preserves the fun of the gun).

B. Claim 13

82. Claim 13 recites "A device for projecting a soft-projectile made from a super absorbent polymer, the device comprising: a feed chamber including a plurality of soft-projectiles having the same shape, . . ." Peev teaches a device for projecting a plurality of projectiles having the same shape, namely, spherical. Ex. 1003, 31-32. As shown in the annotated drawing below 22 is a spherical "ball".

Ex. 1003, 23, 39. The device of Peev also includes a feed chamber (highlighted in green) which holds a plurality of projectiles. See Ex. 1003, 31-32.



83. Spitballs discloses a plurality of soft spherical projectiles. Ex.1002, 21 ("awesome spherical polymers."). Spitballs' packaging depicts numerous dehydrated Spitballs in a bag and several hydrated spherical Spitballs in the bottom-left corner of the package, and eight hydrated spherical Spitballs placed in front of the bottom right corner of the package. Ex. 1002, 18. The ThinkGeek listing also includes images of many hydrated SAP spheres resting in the hand of a person, and placed in a bowl. These images all show that Spitballs are a ***plurality*** of small, clear beads having a ***substantially spherical shape***. Ex.1002, 21 ("Contains: 2g of Spitballs (about 150 or so).").



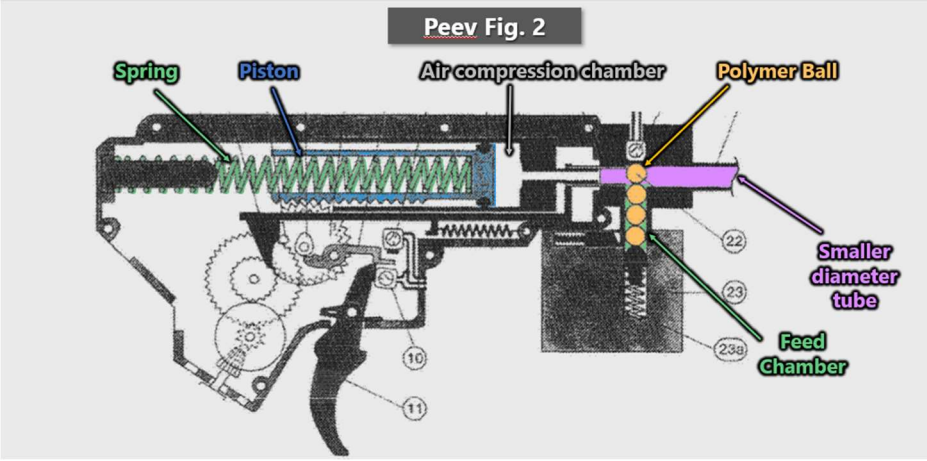
84. Spitballs also teaches soft-projectiles. Ex.1002, 21 ("Spitballs start off as small hard little spheres. Soak them in water for about 4 hours (or overnight for best results) and they will absorb water and grow up to 200 times their original size."). After soaking in water, Spitballs become "slimy and squishy," and "[i]f you throw them gently, they will bounce" or "[i]f you throw them hard enough, they will explode into mushy pieces." Ex.1002, 21. A POSITA would have understood that a "squishy" sphere that bounces and can "explode into mushy pieces" when it hits a target is a "soft-projectile." The "squishy" and "mushy" nature of the projectile and the ability to "explode" on impact will reduce the force of the impact, such that a POSITA would have understood it is soft.

85. For the reasons set forth in paragraphs 76-82 above, a POSITA would have been motivated to use the plurality of soft projectiles having the same spherical

shape (Spitballs) in place of the plurality of hard projectiles of Peev having the same spherical shape.

86. Claim 13 goes on to state ". . . each soft-projectile being formed from a hydrated super absorbent polymer, . . ." In the ITC Case the ALJ construed "super absorbent polymer" to mean a "polymer that can absorb an extremely large amount of liquid relative to its own mass." Ex. 1015,14. First, Spitballs are "spherical polymers." Ex.1002, 21. Second, Spitballs can "Grow[] 200x Their Size!" when hydrated. Ex.1002, 18, 21 (when soaked "in water for about 4 hours (or overnight for best results)," they "will absorb water and grow up to 200 times their original size."). Further, based on my discussions with Dr. Reitman, I understand that Spitballs have the well-known properties associated with SAPs and absorb an extremely large amount of liquid relative to their own mass.

87. Claim 13 goes on to state ". . . wherein the device is adapted to load a soft-projectile from the feed chamber to a firing position; . . ." The device of Peev includes a feed chamber which holds a plurality of projectiles. See Ex. 1003, 31-32. As shown below in annotated Fig. 2 of Peev, a feed chamber (highlighted in green) containing projectiles includes a spring 23 for loading the projectiles 22 (highlighted in yellow) into a firing position within the barrel of the launcher. See Ex. 1003, 31-32, 39.



88. Claim 13 goes on to state ". . . and a firing mechanism operatively arranged to accelerate the soft-projectile made from a super absorbent polymer, from the firing position, down a barrel." Peev's firing mechanism (shown above) includes: (1) an air compression chamber (see the gray arrow); (2) a piston (shaded in blue) disposed within and axially aligned with the air compression chamber; and (3) a spring (shaded in green) operatively arranged to bias the piston toward a rest position (Figures 1 and 3) from a cocked position (Figure 2) within the air compression chamber. Ex. 1003, 31-32 (". . .the sector wheel 5 pulls back the piston 47, tightens the spring 46, pulls back the nozzle 45 . . . and allows the ball 22 . . . to enter the chamber 20 of the barrel 21 (Fig. 2). . . . [T]he piston 47 . . . under the pressure of the spring 46 accelerates forward and compresses the air in the cylinder 48 inserting it through the nozzle into the barrel 21 and firing the ball 22.").

89. As of February 21, 2010, it would have been obvious to a POSITA to replace the hard spherical balls in Peev's feed chamber with soft-spherical SAP

ammunition (Spitballs) to reduce the risk of injury and for the other reasons set forth in paragraphs 76-82 above. As Dr. Kudrowitz admits, it would have been well within the technical grasp of a POSITA to modify Airsoft guns such as Peev to launch soft SAP projectiles. Ex. 1004, 529:21-530:12, 532:15-23.

90. In my opinion, Peev in combination with Spitballs renders Claim 13 obvious.

C. Claim 15

91. Claim 15 states "The device of claim 13, wherein the feed chamber is a removable magazine." During game play, Peev describes replacing an empty magazine with a full one. Ex. 1003, 34 ("In order to resume firing, after replacing an empty magazine with a full one, the shutter stop button 27 must be pressed . . .").

92. In my opinion, Peev in combination with Spitballs renders Claim 15 obvious.

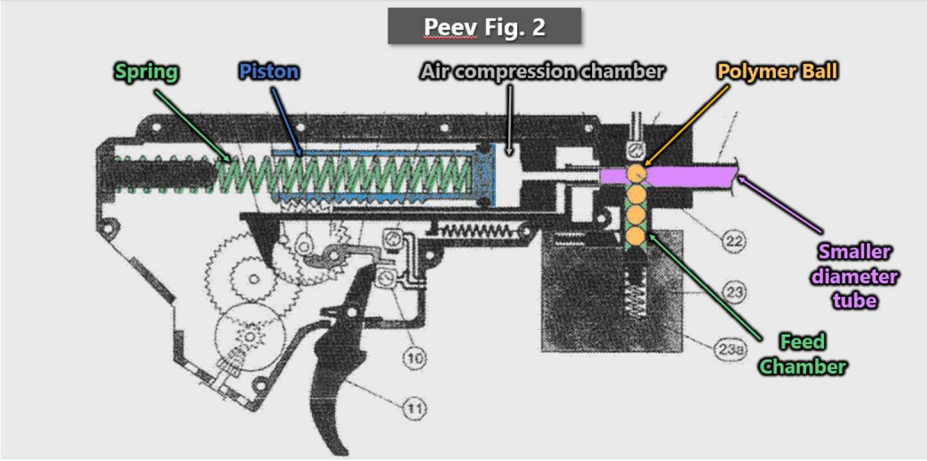
D. Claim 16

93. Claim 16 states "The device of claim 13, wherein the soft-projectiles have a diameter of 10 millimeters or less." Peev teaches an airsoft gun, described as using polymer balls with a diameter of 6 mm. Ex. 1003, 23. Based on my discussions with Maureen Reitman, a POSITA would have known how to adjust the size of hydrated Spitballs to obtain soft projectiles having a diameter of less than about 10 mm.

94. In my opinion, Peev in combination with Spitballs renders Claim 16 obvious.

E. Claim 17

95. Claim 17 states "The device of claim 13, wherein the device is designed to use air pressure to launch the soft-projectiles." As shown below in annotated Fig. 2 of Peev, Peev discloses that upon firing a "piston 47, under the pressure of spring 46, accelerates forward and compresses the air in the cylinder 48, inserting it through the nozzle into the barrel 21 and firing ball 22." Id., 32, 39.



96. In my opinion, Peev in combination with Spitballs renders Claim 17 obvious.

F. Claim 18

97. Claim 18 states "The device of claim 13, wherein the firing mechanism applies a force directly to the soft-projectile located in the firing position to accelerate the soft-projectile, from the firing position, down the barrel." Peev

teaches a firing mechanism that directly applies a force to a projectile. Specifically, "piston 47, under the pressure of spring 46, accelerates forward and compresses the air in the cylinder 48, inserting it through the nozzle into the barrel 21 and firing ball 22." Ex. 1003, 32.

98. Patent Owner's position in the ITC Case with respect to Claim 14 of related US Patent No. 8,640,683 is that using a spring, piston, and air compression chamber to compress air to launch a projectile constitutes a "direct" application of force. Ex.1021, 21-23, 26-28. The air pressure generated by the piston in the airsoft-type firing mechanism of Peev directly applies a force to the "spherical bullets" under Patent Owner's interpretation.

99. In my opinion, Peev in combination with Spitballs renders Claim 18 obvious.

G. Claim 19

100. Claim 19 states "The device of claim 13, wherein the device is a toy." Peev discloses that electric airsoft guns can be used for fun in airsoft games. Ex. 1003, 23. An airsoft gun used for fun and games, as described in Peev, is a toy.

101. In my opinion, Peev in combination with Spitballs renders Claim 19 obvious.

H. Claim 20

102. Claim 20 states "The device of claim 13, wherein the device is in the shape of a gun." Peev discloses a projectile launcher in the shape of a gun Ex. 1003, 23 ("Electric airsoft guns [1] externally represent a copy of real firearms"). Further, Figures 1-3 of Peev depict a gun-shaped projectile launcher. See Ex. 1003, 39-41

103. In my opinion, Peev in combination with Spitballs renders Claim 20 obvious.

X. Peev In Combination With Spitballs and Moorhouse Renders Claims 1 and 2 Obvious

A. Motivation to Combine

104. The motivation to combine Peev and Spitballs is discussed above and includes reducing the risk of injury and the fact that Peev and Spitballs are in the same field of endeavor, namely, projectile launchers and ammunition used for fun. See paragraphs 76-82, above. Moorhouse is also in this same field of endeavor. It is directed to air guns used in paint ball games and describes various safety features for such guns, all with the goal of reducing the risk of injury. Ex. 1006, 1:10-65. A POSITA seeking to reduce the risk of injuries would be motivated to use one or more of the safety features described in Moorhouse.

B. Claim 1

105. Claim 1 states "A device for projecting a soft-projectile made from a super absorbent polymer, the device comprising: a feed chamber including a

plurality of soft-projectiles having the same shape, . . .” As discussed in paragraphs 83-85 above, Peev teaches a device for projecting a plurality of projectiles having the same shape, namely, spherical. The device of Peev also includes a feed chamber which holds a plurality of these projectiles. The projectiles of Spitballs are also of the same shape and are soft.

106. For the reasons set forth in paragraphs 76-82 above, a POSITA would have been motivated to use the plurality of soft projectiles having the same spherical shape (Spitballs) in place of the plurality of hard projectiles of Peev having the same spherical shape.

107. Claim 1 goes on to state “. . . each soft-projectile being formed from a hydrated super absorbent polymer, . . .” As discussed above in paragraph 87, Spitballs teaches soft-projectiles formed from a hydrated super absorbent polymer.

108. Claim 1 goes on to state “. . . wherein the device is adapted to load a soft-projectile from the feed chamber to a firing position; . . .” As discussed above in paragraph 88, Peev teaches a device that loads projectiles from the feed chamber to a firing position.

109. Claim 1 goes on to state “. . . and a firing mechanism operatively arranged to accelerate the soft-projectile made from a super absorbent polymer, from the firing position, down a barrel; and . . .” As discussed above in paragraph 89,

Peev teaches a firing mechanism that accelerates projectiles from a firing position down a barrel.

110. As of February 21, 2010, it would have been obvious to a POSITA to replace the hard spherical balls in Peev's feed chamber with soft-spherical SAP ammunition (Spitballs) to reduce the risk of injury and for the other reasons set forth in paragraphs 76-82 above. As Dr. Kudrowitz admits, it would have been well within the technical grasp of a POSITA to modify Airsoft guns such as Peev to launch soft SAP projectiles. Ex. 1004, 529:21-530:12, 532:15-23.

111. Claim 1 goes on to state ". . . a safety mechanism obstructing an end of the barrel and designed to prevent access to the interior of the barrel but allow a soft-projectile accelerated by the firing mechanism to exit the barrel." Moorhouse teaches blocking means (see 340 in Fig. 4) disposed adjacent the front end of the barrel for preventing the insertion of objects into the barrel from the front thereof. The blocking means is movable between an operative position, wherein it extends substantially across the barrel (see item 340 in Figs. 4, 5 and 6) and in the travel path of the projectile, and an inoperative position, wherein it is spaced from the travel path of the projectile (see item 340 in Figs. 20 and 21). The blocking means are operative in response to movement of the trigger between its rest position and its firing position, moving the blocking means to its inoperative position (see item 340 in Figs. 20 and 21) when the trigger is in its firing position and to its operative

position when the trigger is not in its firing position. Ex. 1006, 2:14-26, 13:51-14:6. The above is illustrated in the annotated, excerpted portions of Figs. 4 and 21, shown below. Ex. 1006, Figs 4 and 12.

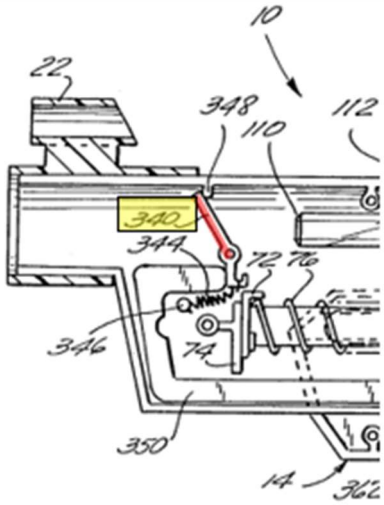


FIG. 4 (excerpted and annotated)

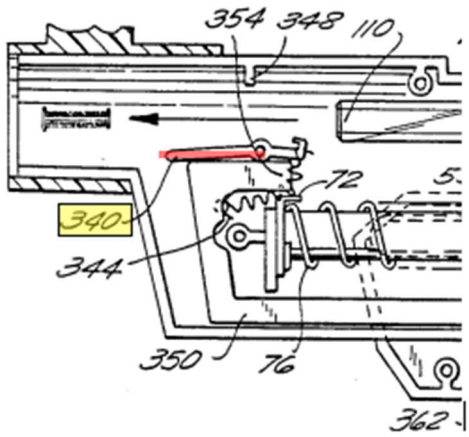


FIG. 21 (excerpted and annotated)

112. At the time of the alleged conception date, it would have been obvious to a POSITA to utilize the safety mechanism of Moorhouse in the device of Peev to reduce the risk of injury and for the other reasons provided above in paragraphs 76-82 and 105.

113. In my opinion, Peev in combination with Spitballs and Moorhouse renders Claim 13 obvious.

C. Claim 2

114. Claim 2 states "The device for projecting a soft-projectile made from a super absorbent polymer of claim 1, wherein the feed chamber is a removable magazine." During game play, Peev describes replacing an empty magazine with a full one. Ex. 1003, 34 ("In order to resume firing, after replacing an empty magazine with a full one, the shutter stop button 27 must be pressed . . .").

115. In my opinion, Peev in combination with Spitballs and Moorhouse renders Claim 2 obvious.

D. Secondary Considerations

1. Simultaneous Invention

116. Korean Patent Publication No. 20-2010-0004855 to Kim (Ex. 1022) is evidence of simultaneous invention and supports a finding of obviousness.

117. According to Kim, it was filed in the Korean Intellectual Property Office on November 1, 2008, long before the earliest alleged invention date of February 21, 2010. Ex. 1022, 7. It was published on May 11, 2010, one day after the May 10, 2010 earliest filing date of the '255 Patent. Id. Under the heading "Prior Art", Kim explains that "[c]onventional bullets are made of hard materials and some people become disabled." *Id*., 8. Kim solves the problem of "injury to the human body" by forming toy bullets from "gel or gel material". *Id*., 7. The toy gun of Kim uses air pressure to fire the gel bullet, which is "safer to use than a bullet of a

conventional rigid material structure and does not cause injury to the human body." *Id.* Claim 1 of Kim broadly covers all gel materials (*Id.*, 8), which are soft and prevent injury, just like SAP projectiles such as Clear Spheres and Spit Balls. Dependent Claim 2 specifies that gel material is made of a cleaning substance and dependent Claim 3 specifies that the gel material is luminous. *Id.*

118. Kim recognized the same problem at the same time as the named inventor on the '255 Patent. Kim arrived at the same solution for the same reasons. This evidence of simultaneous invention supports a finding that the Challenged Claims of the '255 Patent are obvious and therefore invalid.

119. A video posted by Vat19 to YouTube (Ex. 1023) is also evidence of simultaneous invention and supports a finding of obviousness.

120. I understand that by December 20, 2010, Vat19 posted a video to YouTube featuring Spitballs and depicting two men launching Spitballs at each other. Ex.1023. The video explains, "Spitballs are fascinating little projectiles perfect for launching at just about anything," while inserting a Spitball into a straw and launching it at his colleague. Ex.1023. The video explains how long you leave them in is up to you, and adjusts the size:



121. The Vat19 video states "Bigger Spit Balls will explode easily," "while smaller Spit Balls are durable and bouncy." Ex. 1023. "They're also perfect for shooting from a straw or tube." *Id*.



2. Commercial Success

122. In the ITC Case Patent Owner's expert Dr. Kudrowitz testified that the Xploderz products sold by the Maya Group (the former owner of the '255 Patent)

were commercially successful, relying on sales of the Maya Group blasters in 2011 and 2012, and certain testimony of Mr. Ron Brawer, a Maya Group executive and one of the named inventors on the Parent Patent.

123. However, Patent Owner's marketing expert, Lynn Rosenblum, testified "that the packaging and advertising focus of the Xploderz and Blaster Pro products was on the apparent product differentiators of these products, i.e., their firing distance, ammunition capacity, and ease of use." Ex. 1004, 581:17-582:9. None of the Challenged Claims cover "firing distance, ammunition capacity, and ease of use."

124. Mr. Brawer testified that the commercial success of the Xploderz products was the result of the ability of these products to hold more ammunition and to shoot the ammunition twice as far as competitive Nerf products, and that both of these features resulted from the use of SAP ammunition. As also discussed below, ultimately Mr. Brawer testified that the use of SAP as ammunition was the primary force driving demand and was the "foundation of the line". Ex. 1013, 293:16-20. However, as discussed above, SAP ammunition (Spitballs) was in the prior art.

125. As to the important "more ammunition" feature, Mr. Brawer testified that it was the result of using SAP as ammunition:

> Q. There's a second bullet here that says, "***Holds More Rounds*** in the Magazine!" Do you see that?

A. Yes, I do.

Q. And what is this reference to being able to hold more rounds in the magazine a reference to?

A. Well, if you were to take 70 rounds and develop them for shooting in the Xploderz/Blasterz product, it was a container smaller than a soda can. And if you were to try and take 70 rounds of foam darts, you would be running around with something the size of a shoebox. And so ***the physical quality of the SAP as an ammunition, because it was much smaller, allowed for you to*** easily maneuver and hold and ***carry with you a much larger number of rounds*** of ammunition.

Q. So, again, this use of the ***SAPs as the ammunition*** was part of what ***enabled the Xploderz*** products to ***hold more rounds*** in the magazine, which is one of the most important features in this focus group study?

A. ***Yes***.

Ex. 1013, 267:7-268:8.

126. As to the important "more distance" feature, Mr. Brawer testified that it was the result of using SAP as ammunition:

Q. What was the characteristic of the Blasterz prototype that became the Xploderz product that

> contributed to that important feature of being able to ***shoot twice as far*** as comparable products like NERF?
>
> A. A ***different ammunition*** system.
>
> * * *
>
> Q. And in your mind, the ***use of the SAPs as the ammunition*** was part of what enabled the Xploderz products to shoot ***twice as far as*** comparable NERF products?
>
> A. ***It was by far the most important thing***.

Ex. 1013, 266:3-8; 267:2-6; 275:4-275:9; 293:16-293:20.

127. Mr. Brawer also testified that the primary force driving demand of the Xploderz products was the use of SAPs as ammunition.

> Q. Is it fair to say that ***all of the features*** of the [Xploderz] product that you used to create excitement in your TV advertising ***were directly linked to the use of SAPs as ammunition*** in your projectile launcher?
>
> A. ***Absolutely***.

Ex. 1013, 275:4-275:9; 293:16-293:20.

128. In summary, the testimony of the Maya Group executive, Mr. Brawer, identifies three factors that drove sales of the Xploderz products; the ability to hold more ammunition, to shoot the ammunition further, and the use of SAP ammunition.

The first two features are unclaimed. Ammunition capacity and shooting distance appear nowhere in the Challenged Claims. It is my understanding that commercial success due to unclaimed features cannot provide a nexus to the Challenged Claims.

129. The third feature identified by Mr. Brawer as driving sales, SAP ammunition, was in the prior art (Spitballs). It is my understanding that commercial success due to a feature that was known in the prior art cannot provide a nexus to the Challenged Claims.

I hereby declare under penalty of perjury under the laws of the United States of America that the foregoing is true and correct, and that all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true. I understand that willful false statements are punishable by fine or imprisonment or both. *See* 18 U.S.C. Section 1001.



Joel Delman

Dated: September 30, 2023

Exhibit A

JOEL DELMAN | InformedInnovation
2176 W. 24th Street, Los Angeles, CA 90018 773.517.1862 joel@informedinnovationinc.com

Formerly a corporate lawyer, I graduated Harvard Law School and later earned a Master's in Industrial Design at Pratt Institute. From toys to complex medical devices, I've spent the past 27 years guiding innovation through strategic product development, and have helped hundreds of clients bridge the gap between creative insight and commercial success.

EDUCATION

Pratt Institute Master of Industrial Design, 1995
Harvard Law School J.D. 1991
New York University B.S. Economics, 1988

PROFESSIONAL EXPERIENCE

Design Director
Informed Innovation Inc.
Los Angeles, CA 2018 – Present

- Strategic consulting agency focused on the application of design thinking to clients' most challenging business opportunities

Creative Director
Product Development Technologies LLC
Los Angeles, CA 1999 – 2018

- Promoted effective user-centered design processes in a fast-paced, multidisciplinary consulting environment
- Managed all issues related to intellectual property, licensing of technology, and the many legal facets of design and development
- Founded and directed PDT's Informed Innovation division, charged with generating proprietary products for license to leading manufacturers; delivered over 300% ROI
- Responsible for multiple large scale programs for a diverse range of clients, from complex medical devices to mass market consumer electronics

Associate Professor
ArtCenter College of Design
Pasadena, CA August 2019 – Present

- Graduate level class in portfolio development and professional practice

Board of Directors
Metamason Inc.
Pasadena, CA 2013 – Present

- Healthcare focused startup capitalizing on 3D printing technologies to automate the creation of custom-fit medical devices
- Engage, advise and take part in decisions impacting all aspects of corporate strategy, fundraising and governance

Mentor & Advisor
Make in LA
Los Angeles, CA 2016 – Present

- Provide guidance to startups, from the perspective of product development and design strategy, at Los Angeles' first dedicated hardware accelerator

Mentor & Advisor
The Design Accelerator
Pasadena, CA 2013 – Present

- Partnership among Art Center College of Design, Caltech and Idealab implimenting low-cost management techniqes to help design-driven tech startups grow into scalable technology businesses

Principal **Twenty Twenty Thinking Inc.**
Chicago, IL 1997 – 1999

- Invented, developed and licensed magical toy concepts, including the award-winning Bubble Bugs[tm] and Exclamation! Pen[tm]
- Built successful licensing revenue stream, leveraging background in business, law and design to go head-to-head with established toy development firms

Designer **Zenith Electronics Corp.**
Chicago, IL 1995 – 1997

- Managed brand development through design of next gen televisions, remotes and media devices for giant American electronics manufacturer challenged by Asian competition

Designer **Cousins Design**
New York, NY 1993 – 1995

- Responsible for all phases of design process at renowned boutique firm, from initial concept development through client presentations

Attorney **Gunster, Yoakley & Stewart**
West Palm Beach, FL 1991 – 1993

- Creative problem solving for a variety of complex corporate, banking and securities matters, focused on the legal needs of entrepreneurial businesses

HONORS

Chair, IDSA Design Protection Committee
(Industrial Designers Society of America)
IDSA 20/20 Award
Recognizing twenty designers who contributed to the advancement of the design profession in 2020
40+ US Patents and Patents Applied For
Dr. Toy Best New Toy, *Gold Award*
ID 40 Award, *ID Magazine*
Good Design Award, *Chicago Athenaeum*
CES Innovation Award, *Consumer Electronics Association*
Industrial Design Excellence Award (IDEA), *Industrial Designers Society of America*
Wall Street Journal "Form + Function" Column, *Featured Designer*
Becoming a Product Designer, *Profiled by author and distinguished designer Bruce Hannah*

SELECT CLIENTS



Exhibit B

JOEL DELMAN | InformedInnovation
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US Patents and Applications on Which I am Named Inventor

US Utility Patents

10,631,678
6,578,725
6,976,605
6,997,342
6,997,345
7,047,585
7,207,461
7,306,131
7,571.537
7.882,840

US Design Patents

D389,516
D468,224
D474,087
D503,320
D503,877
D511,507
D512,290
D512,617
D514,410
D515,317
D522,329
D551,665
D554,636
D555,649
D557,338

US Patent Applications

20180014681
20160250363
20160249760
20110213399
20090149804
20090137859
20070277741
20070277740
20070267333
20060076309
20050242153
20050242151
20050242150
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20040251590
20040245267
20040245266
20030182749
20020108952

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Joel Delman | Expert Witness Testimony

Facet Technologies, LLC v. ***Lifescan, Inc.*** *(Utility Patent Infringement)*
Date of engagement: January, 2023
Central District of California, Case No. 2.22-cv-01717-MCS-MAR
Expert for Defendant Lifescan, Inc., engaged by Carter Ledyard & Milburn LLP
Patent evaluation, Expert reports, Deposition

In the Matter of Certain Soft Projectile Launching Devices, Components Thereof, Ammunition, and Products Containing Same *(Utility Patent Infringement)*
Date of engagement: October, 2022
United States International Trade Commission Inv. No. 337-TA-1221
Expert for Defendant Daisy Manufacturing Company, engaged by Kirkland & Ellis LLP
Patent evaluation, Expert reports, Deposition, Trial testimony (ITC Hearing May 2023)

Geigtech East Bay LLC v. ***Lutron Electronics Co., Inc.*** *(Trade Dress Infringement)*
Date of engagement: July, 2022
Southern District of NY, Case No. 1:18-CV-05290
Expert for Defendant, engaged by Arnold & Porter LLP
Trademark evaluation, Expert report, Deposition

Proslide Technology Inc. v. ***Whitewater West Industries Ltd****. (Design Patent Infringement)*
Date of engagement: August, 2021
Middle District of Florida, Case No. 6:20-cv-02189-CEM-DCI
Expert for Defendant, engaged by Buchalter PC
Patent evaluation, Expert reports, Deposition

Panasonic Corporation v. ***Getac Technology Corporation*** *(Design Patent Infringement)*
Date of engagement: April, 2021
Central District of California, Case No. 8:19-cv-01118-DOC-DFM
Expert for Defendant, engaged by King & Spalding LLP
Deposition, Trial testimony (Jury trial, June 2022)

Glam and Glits Nail Design Inc. *v. iGel Beauty, LLC (Design Patent, Trade Dress Infringement)*
Date of engagement: December, 2020
Central District of California, Case No. 8:20-cv-00088-JVS-DFM
Expert for Plaintiff, engaged by Lapple Ubell IP Law, LLP
Deposition

Shure Inc. v. ***ClearOne Inc.*** *(Design Patent Infringement)*
Date of engagement: May, 2020
District of Delaware, Case No. 19-1343 (RGA) CJB)
Expert for Defendant, engaged by Hueston Hennigan LLP
Multiple depositions, Trial testimony (Jury trial, November 2021)

In the Matter of Certain Electronic Stud Finders, Metal Detectors and Electrical Scanners *(Utility Patent Infringement)*
Date of engagement: December, 2020
United States International Trade Commission Inv. No. 337-TA-1221
Expert for Plaintiff Zircon Corp., engaged by Palo Alto Legal Group
Deposition, Trial testimony (Bench trial, June 2021)

JOEL DELMAN | InformedInnovation
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Town and Country Linen Corp. v ***Ingenious Designs LLC et al***
(Design Patent Infringement, Trade Secret Misappropriation)
Date of engagement: January, 2020
Southern District of New York, Case No. 1:18-cv-05075-LGS
Expert for Defendant, engaged by Baker & Hostetler LLP
Deposition

Lanard Toys Ltd. v. ***Anker Play Products LLC*** *(Design Patent, Trade Dress, Copyright Infringement)*
Date of engagement: June, 2020
Central District of California, Case No. 2:19-cv-04350-RSWL-AFM
Expert for Defendant, engaged by Seyfarth Shaw LLP
Deposition

MGA Entertainment, Inc. v ***Zuru LLC*** *(Trade Dress Infringement)*
Date of engagement: January, 2020
California Superior Court, Case No. 19-chc-00599
Expert for Defendant, engaged by Dentons LLP
Deposition, Trial testimony (Bench trial, March 2020)

Rhino Metals Inc. v. ***Sturdy Gun Safe, Inc.*** *(Trade Dress and Design Patent Infringement)*
Date of engagement: August, 2019
Idaho District Court, Case No. 1:18-cv-00474-EJL
Expert for Defendant, engaged by Givens Pursley LLP
Deposition

LILLEbaby LLC v. ***BabySwede LLC et al*** *(Utility Patent Infringement)*
Date of engagement: June, 2019
In the Matter of Certain Child Carriers and Components Thereof
United States International Trade Commission Inv. No. 337-TA-1154
Ohio Northern District Court, Case No. 1:19-cv-00504-JG
Expert for Defendant, engaged by Dorsey & Whitney LLP
Deposition

Spigen Korea Co., LTD. *v. Ultraproof, Inc. et al (Design Patent Infringement)*
Date of engagement: August, 2018
California Central District Court, Case No. 2:17-cv-01161-DOC-DFM
United States Court of Appeals for the Federal Circuit, Case: 19-1435
Expert for Plaintiff, engaged by Lewis Brisbois Bisgaard & Smith LLP
Deposition

C&A Marketing, Inc. (dba Polaroid) v. ***GoPro Inc.*** *(Design Patent Infringement)*
Date of engagement: January, 2017
District Court of New Jersey, Case No. 1:15-7854-RMB-JS
Expert for Defense, engaged by Kilpatrick Townsend & Stockton LLP
Deposition

Exhibit D

JOEL DELMAN | InformedInnovation
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General Articles and Publications

Going In Blind: Redesigning the Next Generation Perkins Brailler, Product Design & Development Magazine, November 11, 2010

Are Amazon, Netflix and Google Making Too Many Decisions for Us?, Forbes, November 24, 2010

Design in 2010: Four Emerging Trends in Technical Product Design, Engineering Exchange Magazine, April 5, 2010

4 Reasons Why 3D TV is Years Away from Adoption, MediaShift, May 18, 2010

Economic Recession Doesn't have to Halt Innovative Product Development, Design Manufacturing News, March 31, 2011

Cost vs. Quality: The Dangers of Outsourcing Design Overseas, Appliance Design Magazine, August 10, 2011

The Consumerization of Medical Products, Medical Product Outsourcing Magazine, August 31, 2011

Design that Transforms the Eating Experience, Bloomberg.com, January 5, 2012

The Los Angeles Perspective on CES: Guest Blogger CES 2013, LAObserved, January 2013

Does Design + Celebrity = Innovation? Innovation Excellence Magazine, March 12, 2013

Publications by Product Development Technologies Inc.

Asian Design: A Look at the Landscape, PDT Pulse June 2008

PDT Pulse: CES Trends 2013, February 2013

PDT Pulse: E3 Electronic Entertainment Expo Trends 2013, June 2013

PDT Pulse: CES Trends 2014, February 2014

PDT Pulse: E3 Electronic Entertainment Expo Trends 2014, June 2014

PDT Pulse: CES Trends 2015, February 2015

PDT Pulse: NAFEM Trends 2015, March 2015

PDT Pulse: E3 Electronic Entertainment Expo Trends 2015, June 2015

PDT Pulse: Trends in Medical and Healthcare Solutions, August 2015

PDT Pulse: CES Trends 2016, February 2016

PDT Pulse: POC Medical Diagnostics Trends, April 2016

PDT Pulse: E3 Electronic Entertainment Expo, Virtual Reality Past, Present and Future, June 2016

PDT Pulse: CES Trends 2017, February 2017

*PDT Pulse: E3 Electronic Entertainment Expo Trends 2015*7 June 2017

Speaking Engagements

The Future of Food Preparation, California State University Long Beach Duncan Anderson Lecture Series, November 10, 2011

Research as the Foundation to Great Design, Southern California Biomedical Council MedTech Design Forum, May 31, 2012

Design Patents and Defining the Article of Manufacture: An Expert Witness Plays Devil's Advocate; Orange County Intellectual Property Law Association, April 19 2018.

Design Patents and Defining the Article of Manufacture: An Expert Witness Plays Devil's Advocate; CLE Webinar for The TASA Group, February 21, 2019.

The Good, The Bad and The Ugly: How Recent Design Patent Cases Impact Design Protection; Webinar for IDSA, August 25, 2020

Legal Contracts for Designers: (Almost) Everything You Need to Know; Presentation at the IDSA International Design Conference, September 17, 2020

Interviews

Delivering Realizable Solutions Through Informed Innovation, Market News First (MN1), March 9, 2007

How are you Influencing ER and Surgical Devices?, Medical Design Technology Magazine, November 17, 2010

Live from the Medical Design and Manufacturing Expo: The Latest Trends in Medical Devices, CBS Los Angeles Newsradio KNX10.70, February 2015

Navigating CES and Passenger Experience Trends, Airline Passenger Experience Association, January 8 2016

JOEL DELMAN | InformedInnovation
2176 W. 24th Street, Los Angeles, CA 90018 773.517.1862 joel@informedinnovationinc.com

Design Mysteries with Bruce Hannah
Apple Podcast, January 2022

Attachment B

ED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

Prime Time Toys LLC, Prime Time Toys Ltd.
and Easebon Services Ltd.
Petitioners

v.

Spin Master, Inc.
Patent Owner

U.S. PATENT NO. 8,596,255

Case IPR2023-TBD

DECLARATION OF DR. MAUREEN T.F. REITMAN, SC.D., F.S.P.E., P.E. UNDER 37 C.F.R. § 1.68 IN SUPPORT OF PETITION FOR *INTER PARTES* REVIEW OF U.S. PATENT NO. 8,596,255

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I, Dr. Maureen T.F. Reitman, do hereby declare as follows:

I. INTRODUCTION

1. I have been retained as an expert witness on behalf of Prime Time Toys LLC, Prime Time Toys Ltd., Easebon Services Ltd. for the above-captioned Petition for Inter Partes Review ("IPR") of U.S. Patent No. 8,596,255 (the "'255 Patent").

2. I have been asked to provide my opinions relating to issues concerning super absorbent polymers (SAP) recited in Claims 1, 2, 13 and 15-20 of the '255 Patent ("the Challenged Claims").

3. The '255 Patent issued on December 3, 2013, from U.S. Patent Application No. 12/973,897 ("the '897 application"), filed on December 20, 2010. The '897 application is a continuation-in-part of U.S. Patent Appl. No. 12/777,134, filed on May 10, 2010, and issued as US Patent No. 8,371,282 ("the Parent Patent"). Ex. 1001 at Cover. For the purposes of my Declaration, I have used the earliest alleged invention date claimed by Patent Owner in a related ITC Case involving the Parent Patent. I understand that in the ITC Case, Patent Owner alleged that certain claims of the Parent Patent were conceived no later than February 21, 2010.

4. In preparing this Declaration, I have reviewed the '255 Patent, scientific literature, and certain prior art.

5. In forming the opinions expressed in this Declaration, I relied upon my education, training, knowledge, and experience in the relevant art, and have considered the viewpoint of a "Chemist" knowledgeable regarding super absorbent polymers as of February 21, 2010. I understand "Chemist" to include professionals with degrees in chemistry, material science, polymer science, or another related field who have knowledge regarding the chemistry of super absorbent polymers. I have further considered and relied upon the materials cited in this Declaration, and have had conversations with Joel Delman regarding my opinions. My opinions are based, at least in part, on ThinkGeek Spitballs ("Spitballs") (Ex. 1002) published November 27, 2009.

II. BACKGROUND AND QUALIFICATIONS

6. I am a Principal Engineer and the Vice President of two groups at Exponent, Inc. ("Exponent"), including the Polymer Science and Materials Chemistry Practice. Founded in 1967, Exponent is a multi-disciplinary engineering and scientific consulting firm that brings together more than 90 different disciplines to solve engineering, science, regulatory, and business issues facing our clients.

7. I hold a Bachelor of Science in Materials Science and Engineering from the Massachusetts Institute of Technology (MIT), and a Doctor of Science in Materials Science and Engineering, with a thesis in the field of polymers and fibers,

from MIT. I am a licensed Professional Engineer in the state of Maryland. I have been practicing in the field of polymer science and engineering for more than 30 years as a researcher at MIT, in a variety of technical roles at the 3M Company, and as a consultant with Exponent.

8. I have formal training and practical experience related to the chemistry, manufacture and performance of a wide range of natural and synthetic polymers, including polyacrylates, polyacrylamides, polyesters, polyolefins, polyamides, polyvinyl alcohol, polyacrylonitrile, polysaccharides, polypeptides, linear and graft copolymers, charged polymers, and other compositions. I have specific experience with superabsorbent polymers, hydrogels, oleogels, and other crosslinked polymer systems for the uptake of fluids. I provide consulting engineering services in all aspects of the field of polymer materials science, including, but not limited to, materials selection, polymer formulation, process improvement, testing, product design and development, failure analysis and intellectual property analysis. I am a Fellow of the Society of Plastics Engineers.

9. I have attached a copy of my curriculum vitae as Appendix A.

III. COMPENSATION

10. While I am a salaried employee of Exponent, Exponent is being compensated for my work on this matter at my customary hourly rate of $875 per

hour in 2023. My compensation does not depend in any way on the contents of my report or the outcome of this matter. I have no interest, financial or otherwise, in the outcome of this matter. I have no financial interest in, or affiliation with, any of the parties in this matter.

IV. SUMMARY OF OPINIONS

11. It is my opinion that the product described in Spitballs is a SAP under the Administrative Law Judge's ("ALJ") claim construction of "super absorbent polymer" in the ITC Case.

12. It is my opinion that it was well known prior to 2010 that the properties of hydrated SAP particles, such as size, shape, gel strength and absorbency, are the result of structure-property relationships. Prior to 2010, a Chemist would have been able to achieve different material properties and physical characteristics of SAP ammunition, including adjustments to desired size of the hydrated SAP and adjustments to the strength and durability of the hydrated SAP.

V. THE '255 PATENT

13. The '255 Patent indicates "[s]uper absorbent polymers (SAPs) were first invented… in the 1960s and are commonly used in personal disposable hygiene products such as diapers, protective underwear, and sanitary napkins" and "are

polymers that can absorb an extremely large amount of liquid relative to their own mass." *Id.,* 4:54-59.

VI. PERSON OF ORDINARY SKILL IN THE ART (POSITA)

14. In the ITC Case, I understand that the Petitioner and Mr. Delman proposed that a person of ordinary skill in the art at the time of the alleged invention of the Parent Patent ("POSITA") would be someone who (i) had a Bachelor's degree in Industrial Design or Mechanical Engineering or (ii) a toy designer with at least five years' experience designing toys (including launchers), with both of (i) and (ii) having access to a chemist knowledgeable regarding super absorbent polymers.

15. I understand that Patent Owner proposed, in the same related proceeding before the ITC, that a POSITA would (1) have had a Bachelor's degree in mechanical engineering, industrial design, or an equivalent, with at least one year of relevant experience designing projectile launching systems and (2) be a member of a team, which would include a person with a Bachelor's in materials science, chemistry, or equivalent, or has at least one year experience working with materials for use in consumer products.

16. My background is in material science and engineering and the chemistry of these polymeric materials. Therefore, I am providing my analysis from the perspective of the person that the POSITA in this matter would either be 1)

working with, 2) having access to, or 3) collaborating with under Petitioners/Mr. Delman's definition and Patent Owner's definition.

VII. CLAIM CONSTRUCTION

17. Claims 1 and 13 of the '255 Patent state ". . . soft-projectiles formed from hydrated super absorbent polymer." I understand that in the ITC Case, the ALJ construed "super absorbent polymer" in connection with the Parent Patent to mean a "polymer that can absorb an extremely large amount of liquid relative to its own mass."

VIII. Technology Background And State Of The Art

A. Polymers and Polymer Gels

18. Polymers are large molecules made from one or more repeat units. Both chemically and physically, polymer chains exist in many different configurations. Long polymer chains are akin to strings or fishing line – they can entangle with one another, held together by weak interactions between chains, or they can exist as an individual polymer chains.[1] Both the chemistry and the size of the polymer

[1] Callister, W. *Materials Science and Engineering, An Introduction.* John Wiley and Sons, Inc., **2009,** (Callister), pp. 544-545. Appendix Callister.

molecules impact the observed macroscopic properties of the material, including deformability and physical integrity.

19. Upon the application of stress to a polymer system, the polymer chains may slip past one another to uncoil, elongate, and align in response to a directional stress.[2] If, however, anchor points were to be introduced between the strings in the tangled mass, these would act to prevent chain alignment as stress is being applied, increasing the polymer network resistance to an applied stress, as demonstrated in Figure 1. These anchor points act to reduce the degrees of freedom within the entanglement, binding polymer chains together through permanent or transient bonds, depending on the nature of the bond. The higher the density of anchor points or crosslinks between polymer chains, the higher the material stiffness, tensile strength, and resistance to plastic deformation, as well as the lower the ability to absorb compatible fluids.[3] This is shown schematically in Figure 2. In the case of a covalently crosslinked polymer network, introducing additional crosslinks further reduces the degrees of freedom, leading to stronger networks and less fluid absorption capability.

[2] Callister, pp. 582, 588. Appendix Callister.

[3] Callister, pp. 589. Appendix Callister.

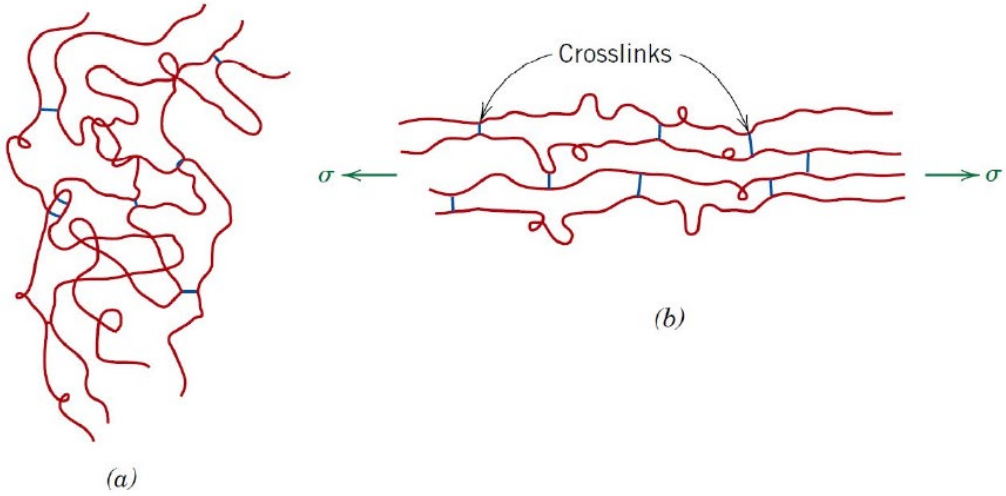


Figure 1. Visual representation of crosslinked polymer chains(*a)* in a relaxed state and (*b)* elastically deformed due to applied tensile stress.[4]

[4] Callister, p. 588. Appendix Callister.

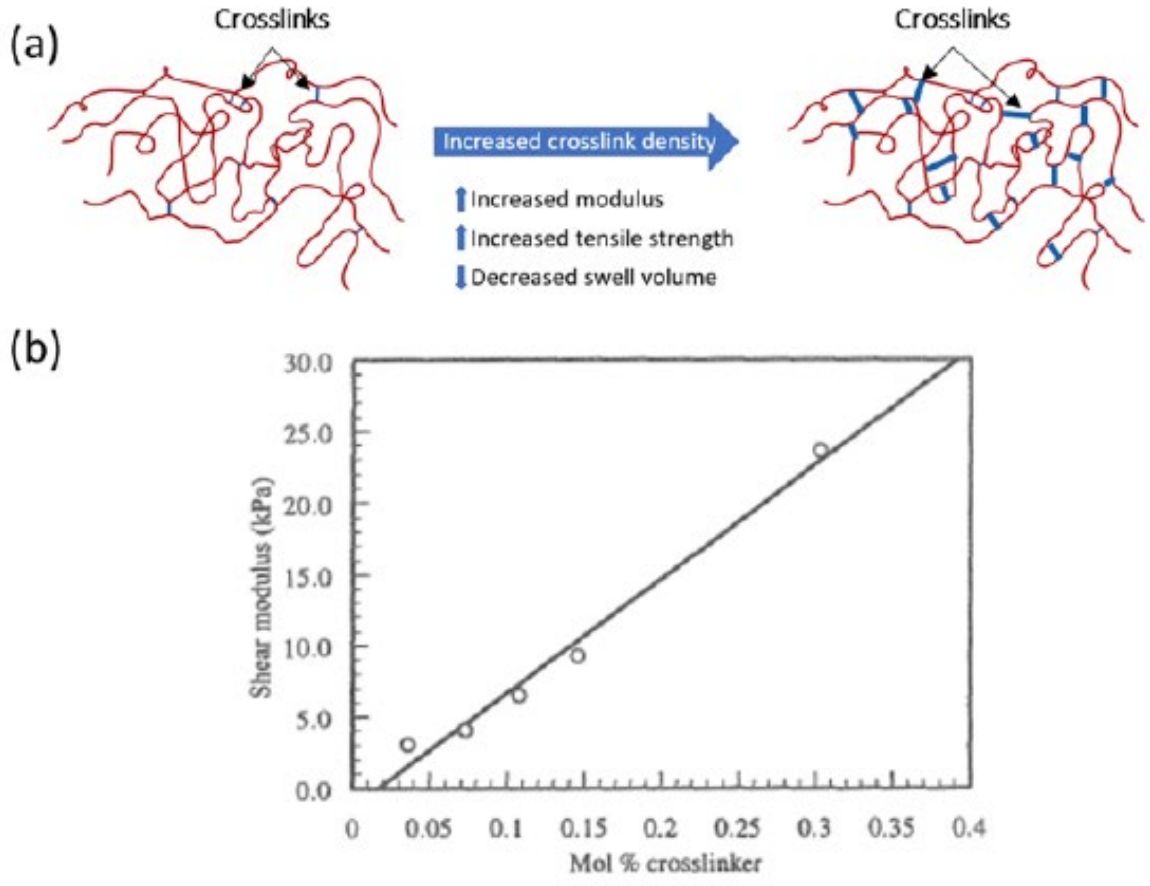


Figure 2. (a) Schematic representation of crosslinked polymer chain molecules with different crosslink densities. A crosslinked polymer network with an increased crosslink density would have an increased modulus, increased tensile strength, and decreased swell volume.[5] (b) Graphical representation of the

[5] Adapted from Callister, p. 589. Appendix Callister.

relationship between crosslink density and shear modulus in a specific polyacrylate.[6]

20. For polymeric materials, the introduction of small molecules between polymer chains (e.g., such as water in hydrophilic polymers) modifies the interaction between chains and results in the plasticization and softening of the polymer network. When polymers are exposed to compatible fluids, a chemical potential causes the fluid molecules to diffuse in to the polymer mass to occupy positions along the backbone of the polymer chain, resulting in swelling. The degree of swelling depends on the chemical interaction between the fluid and polymer as well as the physical connectivity of the molecules.[7] The absorption behavior of the polymers can also be sensitive to environmental factors such as time, temperature,

[6] Buchholz, F. L., Graham, A. T. *Modern Superabsorbent Polymer Technology.* John Wiley and Sons, **1998,** (Buchholz), p. 172. Appendix Buchholz.

[7] Callister, p. 707. Appendix Callister.

pH, and ions present.[8] When the polymer swells within the chosen medium under chosen conditions, this is because the polymer chains are forced apart by the small molecules along and between segments of the polymer chain, increasing the local separation. As the polymer chains separate, the secondary intermolecular bonding forces decrease, resulting in a softer more ductile material.[9] When a fluid swells a crosslinked material, the polymer chains can separate to a limit determined by the chemistry and physical attributes of the network but will not dissolve; instead, a gel is formed.[10]

B. Superabsorbent polymers (SAPs)

1. SAPs form gels by absorbing large amounts of a fluid

21. Polymers that are referred to as superabsorbent polymers (SAPs) are a large class developed to provide the ability to absorb and hold liquids. They are

[8] Zohuriaan-Mehr, M. J., Kabiti, K. *Superabsorbent Polymer Materials: A Review*. Iranian Polymer Journal, 17 (6), **2008** (Zohuriaan-Mehr), p. 460. Appendix Zohuriaan-Mehr.

[9] Callister, p. 707. Appendix Callister.

[10] Bucholz, p.10. Appendix Buchholz.

crosslinked networks of polymer chains, imparted with chemical functionality that allows them to hold liquid within their crosslinked network.[11]

22. One trait of SAPs is that they can take up large amounts of fluid relative to their dry mass but they do not dissolve in the fluid upon swelling. Instead, the polymer physically increases in size and exhibits modified mechanical properties that are the combined effect of the specific polymer chemistry, morphology and fluid characteristics. Due to the crosslinked nature of the material, SAPs can absorb fluids and change their volume and shape while becoming solvated without dissolving.[12]

23. While SAPs are well known in the polymer industry and have been widely used since the 1960s in a variety of products, SAPs are not rigidly defined by any technical specification, and are instead a classification of polymers that tend to have certain behaviors. These key behaviors include being a crosslinked network of flexible polymer chains,[13] absorbing a large amount of fluid relative to their dry mass (the definition of "large" can vary by source),[14] not dissolving upon swelling

[11] Buchholz, pp. 4-7. Appendix Buchholz.

[12] Buchholz, p. 10. Appendix Buchholz.

[13] Buchholz, p. 6. Appendix Buchholz.

[14] Buchholz, p. 1. Appendix Buchholz.

by the fluid,[15] and possessing a level of mechanical integrity in their swelled state to allow for retention of fluid and retained shape during use.[16]

24. An early embodiment of SAPs, mentioned in the specification of the '255 patent,[17] was described by the U.S. Department of Agriculture in the 1970's.[18] They describe water insoluble, starch-based materials that absorb in excess of 300 times their mass in water. Specifically, they describe hydrolyzed starch-g-poly(acrylonitrile) (HSPAN) and marketed them as "Super Slurpers" for applications in personal hygiene and agriculture.[19] This embodiment of a SAP represents one example of polymer and cross-linker chemistries that results in a superabsorbent material with a particular set of mechanical properties.[20]

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[15] Buchholz, p. 7. Appendix Buchholz.

[16] Zohuriaan-Mehr, pp. 452-453. Appendix Zohuriaan-Mehr.

[17] '255 Patent at 4:54-58. Appendix 255 patent.

[18] U.S. Patent 3,997,484A, Dec. 14, **1976**. Appendix US Patent 3,997,484A.

[19] U.S. Patent 3,997,484A, Dec. 14, **1976**, 1:40-50., Super Slurper: Compound with a Super Thirst. June **1975**, Agricultural Research. Appendix US Patent 3,997,484A.

[20] Zohuriaan-Mehr, pp. 455-459. Appendix Zohuriaan-Mehr.

25. Another example of a class of polymers commercially referred to as "SAPs" is the class containing crosslinked polyacrylamides, which offer different combinations of mechanical properties.[21] This class of SAPs is not described in the specification of the '255 patent, by chemical compound or structure.[22]

2. SAPs can have different chemical compositions

26. The overall genus of SAP chemistries is much larger than the HSPAN "Super Slurpers" and can be categorized generally as non-ionic (i.e., no discrete charges exist on the polymer backbone), ionic (i.e., either anionic or cationic charges exist on the polymer backbone), amphoteric (i.e., both acidic and basic groups capable of ionizing into anionic or cationic groups exist on the polymer backbone), or zwitterionic (i.e., both anionic and cationic charges on the backbone of the polymer). The nature and density of charges on the polymer will affect the interaction with fluids as well as observed macroscopic properties such as degree of swelling, degree of softening with fluid absorption, strength, and allowable deformation before fracture. Each of the charge-based categories of SAPs includes a range of polymers with differing structures and properties. Some examples known

[21] Buchholz, p. 11-12, 19, 252-259. Appendix Buchholz.

[22] Buchholz, p. 260. Appendix Buchholz.

prior to 2010 include certain polysaccharides (including starch and cellulose), proteins (including modified soy, fish protein, or collagen),[23] maleic anhydride copolymers (e.g. with hydrophobic olefins or vinyl ethers),[24] polyacrylamides, and copolymers with various ratios of, for example, acrylic acid, acrylamide and potassium acrylate.[25]

27. SAPs absorb fluid because a chemical potential related to the polymer chemistry and the fluid chemistry drives diffusion of the fluid into the crosslinked network.[26] The fluid is retained due to chemical interaction with the polymer chains.

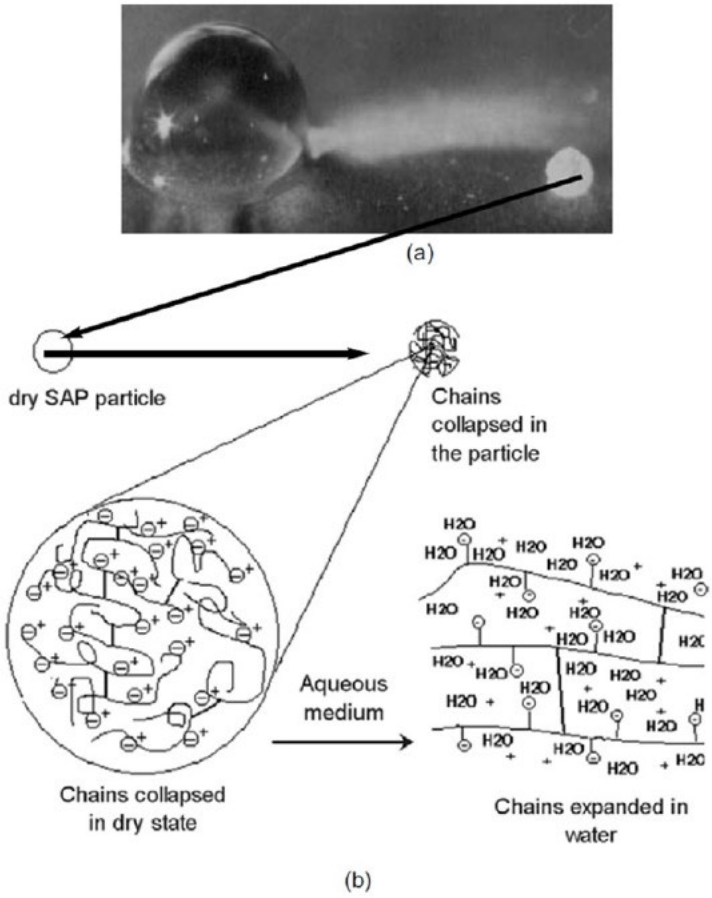
[23] Zohuriaan-Mehr, pp. 457-458. Appendix Zohuriaan-Mehr.

[24] Po, p. 638-642. The polymers remain hydrophobic until a base treatment, which ring-opens the anhydride monomers and renders the polymer hydrophilic and water-absorbent. Appendix Po.

[25] Zohuriaan-Mehr, pp. 455-457; Po, pp. 621-625. Appendix Zohuriaan-Mehr.

[26] The motion of fluids in superabsorbent materials is distinct from materials that wick to absorb fluids. In absorbent materials, fluid diffusion is governed by Darcy's law, with the flow rate proportional to a physical pressure gradient (e.g., from capillary forces or hydrostatic liquid pressure). In comparison, for

One example of this is depicted in Figure 3, where the anionic charge on the backbone of the polymer interacts with water, which is a polar molecule. Other types of interactions occur for nonionic, cationic, zwitterionic and other types of backbone characteristics, which are related to the composition of the network.



superabsorbent materials, the absorption is proportional to the gradient of chemical activity and is governed by Fick's law. (Buchholz p. 8). Appendix Buchholz.

Figure 3. Depiction of an anionic SAP material excerpted from a 2008 review paper: (a) SAP sphere prepared by inverse-suspension polymerization in both a dry (right) and swollen state (left). (b) Schematic illustration of swelling of an anionic SAP in an aqueous solution at a molecular level.[27]

3. SAPs can have different cross-link characteristics

28. The designation as a SAP is not specific to the chemistry of the material, and prior to 2010 it was known that in addition to the options of large number of different base polymer compositions, a crosslinked SAP network could be prepared using a wide variety of crosslink types and a wide range of crosslink densities in order to obtain desired properties.

29. The possible crosslink configurations in the genus of SAPs includes covalent crosslinks, wherein covalent chemical bonds are formed between chains; ionic crosslinks, wherein charged species on different polymer chains or between polymer chains and a crosslinking molecule are charge-paired with one another; or physical crosslinks, including linking together of polymer chains by hydrogen

[27] Zohuriaan-Mehr, p. 460. Appendix Zohuriaan-Mehr.

bonding.[28] While each type of crosslink creates a node in the polymer network, the behavior of the different types is not necessarily equivalent under certain types of loading or certain types of environmental conditions.

30. The type, number and density of crosslinks also will affect the interaction with fluids as well as observed macroscopic properties such as degree of swelling, degree of softening with fluid absorption, strength, and allowable deformation before fracture. For example, Figure 4 illustrates the effect of crosslinker type and amount on one mechanical property, the shear modulus, of a SAP.[29] The divergent curves indicate that one crosslinker will allow for a stiffness level not possible with the other, and that for a given stiffness, the tightness of the network (which relates to swelling behavior), will differ.

[28] Buchholz, pp. 10-11. Appendix Buchholz.

[29] Buchholz, pp. 174. Appendix Buchholz.

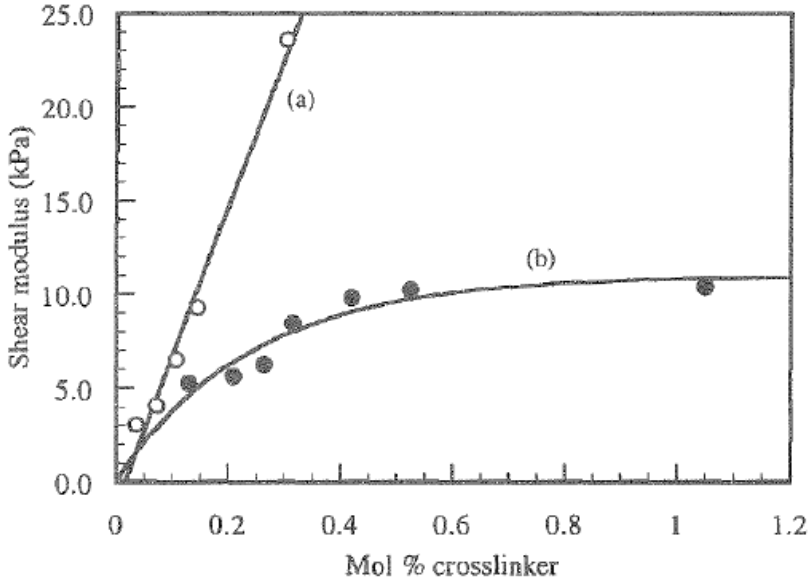


Figure 4. Impact of crosslinker loading per mole of monomer on the shear modulus of a SAP using (a) 1,3-butyleneglycol diacrylate and (b) triallylamine as crosslinking agents.[30]

4. SAP can have different network characteristics

31. Two potential descriptors of SAPs are the network topology (as defined by chain structure and crosslink density) and the chemical affinity for a target fluid (which is substantially related to the chemistry and associated charge density of the polymer networks). It was known prior to 2010 that several factors are associated with these two features, including the molecular weight of the polymer

[30] Buchholz, pp. 174. Appendix Buchholz.

chain between crosslinks, the amount of un-crosslinked polymer remaining, the entanglement of chains, the volume of polymer during preparation, the spacing of charge along the polymer chain, the solvent interaction, and the number of crosslink points. These network characteristics contribute to the inherent material properties such as gel strength and stiffness and swellability and can contribute differently depending on the conditions of end-use.[31]

32. It was known prior to 2010 that the observed mechanical properties of a gel, including a SAP, are closely related to the crosslink density of the SAP. In fact, one standard way to change the strength, fracture behavior, and elasticity (i.e., ability of the gel to be deformed and return to its original shape), of a polymeric material is to change the cross-link density of the material. Changing the cross-link density is also a standard means of changing the resistance of a gel to deformation, for example under the effect of gravity or applied shear forces.[32]

33. The swelling behavior and observed extent of swelling of a SAP are closely related to the cross-link density of the networks—a polymer network with

[31] Buchholz, pp. 168-171. Appendix Buchholz.

[32] Buchholz, pp. 9, 158-159. Appendix Buchholz.

higher crosslink density can swell less than a loosely crosslinked network.[33] Swelling is also related to other SAP characteristics such as charge density (e.g., from chemical makeup and ionization), the properties of the swelling fluid, and environmental conditions (e.g., pH, salt content, temperature).[34,35] Figure 5 provides an example of the dependence of the swelling capacity of a SAP on the crosslinker concentration (i.e., cross link density) for swelling solutions with varying salt concentrations. A number of relationships have been developed to describe the interactions of these factors for crosslinked polymers including SAPs (e.g., Flory Huggins theory, Flory Erman theory, Flory Rehner equation and the phantom network approximation).[36]

[33] Buchholz, pp. 168-169. Appendix Buchholz.

[34] Buchholz, pp. 147-49. Appendix Buchholz.

[35] Buchholz, p. 154. Appendix Buchholz.

[36] Buchholz, pp. 168-171. Appendix Buchholz.

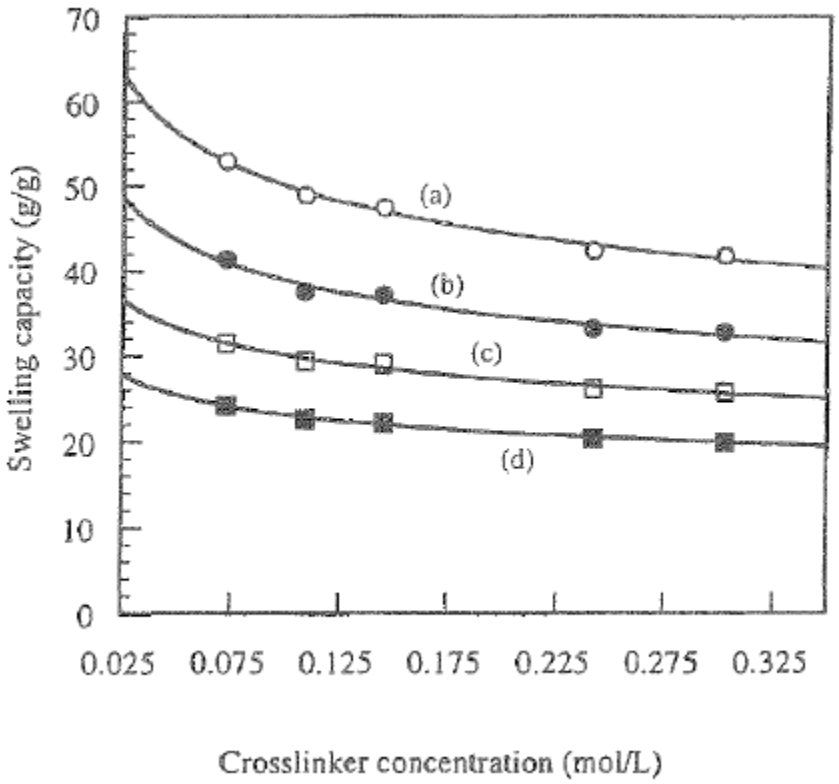


Figure 5. Swelling capacity as a function of crosslinker concentration when a SAP series is swollen in various salt solutions: (a) 0.225% NaCl, (b) 0.45% NaCl, (c) 0.9% NaCl, (d) 1.8% NaCl.[37]

34. The swollen modulus of the material, which is a measure of resistance to deformation, also depends on cross link density and is commonly engineered based on factors such as the molecular weight between crosslinks, the backbone molecular weight, the concentration of chains during crosslinking, and the extent of

[37] Buchholz, p. 183. Appendix Buchholz.

swelling associated with use conditions.[38] An example of the dependence of shear modulus on SAP swelling ratio is shown in Figure 6. Increasing the crosslink density of the gel particles results in higher modulus, high absorption under pressure, but lower free swelling capacity (meaning that it will absorb less water when not under pressure than a gel particle with a lower crosslink density). Prior to 2010 it was reported that in polyelectrolyte SAPs, the modulus decreases and then increases as swelling progresses, likely due to the extended chain configurations possible at high charge density and low ionic strength when swelling is high.[39] This is a slightly different relationship than was understood for non-ionic SAPs, where the modulus decreases as the swollen volume of the crosslinked polymer increases due to the decrease in concentration of the elastic chains.[40] The known relationship between cross-linking density and gel strength enables a Chemist or material scientist to make adjustments to the strength and resistance to deformation of a SAP simply by adjusting the cross-linking density.

[38] Buchholz, pp. 171-172, 184. Appendix Buchholz.

[39] Buchholz, p. 175. Appendix Buchholz.

[40] Buchholz, pp. 168-69, 175. Appendix Buchholz.

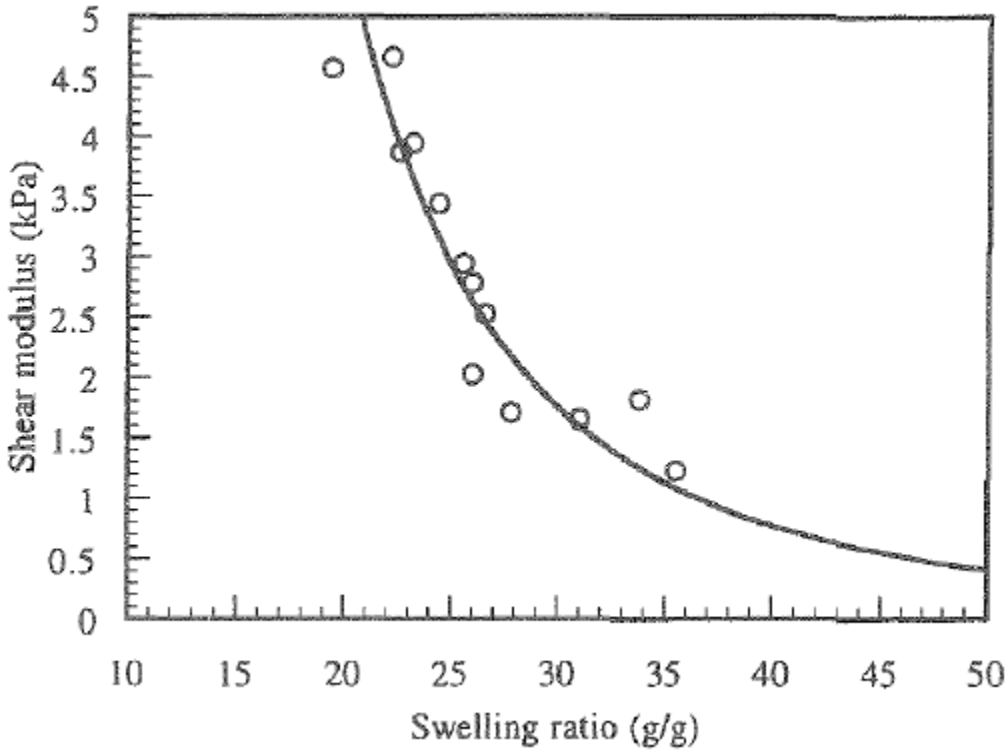


Figure 6. An example of shear modulus as a function of swelling ratio for SAP samples at equilibrium after swelling in a 0.9% NaCl solution.[41] Changes in gel strength relative to swelling ratio are specific to the analyzed SAPs.

35. It was known prior to 2010 that the size of the polymer particles prior to swelling also effects the absorption and swelling rate, as well as equilibrium

[41] Buchholz, p. 9. Appendix Buchholz.

size.[42,43] In other words, a smaller starting polymer will result in a smaller gel that has fully absorbed the liquid in which it is placed, and vice-versa. This is in part because the swelling process reflects the diffusion of water or another fluid into the polymer, which allows the polymer chains relax and expand outwardly into the liquid.[44] The diffusion process is influenced by the size and shape of the polymer particle because these help define the contacting areas and the chemical potential gradient.

C. SAPs can be manufactured to achieve desired sizes and shapes

36. The size, shape, and strength of a SAP material results from engineering choices based on generally recognized relationships between Chemistry, processing, and properties and can therefore be tuned through specific manufacturing conditions for a selected material. It was known prior to 2010 that these materials can be prepared by several polymerization methods (e.g., solution,

[42] Buchholz, p. 154. Appendix Buchholz.

[43] Buchholz, p. 194. Appendix Buchholz.

[44] Buchholz, p. 154. Appendix Buchholz.

inverse suspension, emulsion, and bulk methods)[45] and that the dominant commercial manufacturing process for partially neutralized, acrylic acid-based SAPs was solution polymerization.[46] Commercial scale production of SAPs via solution polymerization involves multiple steps, including raw material preparation, feeding of reactants, polymerization, drying, sizing (grinding), and other post-treatment.[47] Raw material design, such as the types and concentrations of selected monomers, crosslinkers, additives, and solution media (water), as well as other parameters such as degree of neutralization and the order in which the reactants are added to the reaction vessel are part of what govern the final properties of the SAPs.[48] Material size and shape can be controlled at the reactor level, or in post-reactor processes. Surface crosslinking is a known technique in SAP production that

[45] Kiatkamjornwong, S., Superabsobent Polymers and Superabsorbent Polymer Composites. ScienceAsia, 33 (1), **2007 (**Kiatkamjornwong), p. 40. Appendix Kiatkamjornwong.

[46] Buchholz, p. 71. Appendix Buchholz.

[47] Buchholz, p. 73-74. Appendix Buchholz.

[48] Buchholz, p. 74-77. Appendix Buchholz.

increases crosslinking at the surface of particles and subsequently improves absorbency under load.[49]

37. Commercial solution polymerizations to yield SAPs may be carried out in batch or continuous reactors and the size of the resultant SAPs will depend on reactor/impeller configuration details such as clearances between stationary and rotating members.[50] After the neutralized reactor, steps such as sizing (e.g., agitation, extrusion), mechanical shaping (e.g., grinding), and screening operations are performed to regulate final product particle size distribution.[51] One example of this type of manufacturing prior to 2010 produced a final "mass median" particle diameter between 0.4 mm and 0.700 mm.[52] In another example, post-reactor extrusion was utilized to create particles between 0.5 mm and 3 mm, depending on the die hole size.[53]

[49] Buchholz, p. 74, 97-101. Appendix Buchholz.

[50] Buchholz, p. 77-84. Appendix Buchholz.

[51] Buchholz, p. 74, 85-87, 93-94. Appendix Buchholz.

[52] Buchholz, p. 95. Appendix Buchholz.

[53] Buchholz, p. 87. Appendix Buchholz.

38. Bulk polymerization is the simplest polymerization technique, involving only monomer and monomer-soluble intiators. No suspension agents, solvents, or other additives are required.[54,55] This polymerization method is advantageous because the resulting polymer is highly pure, of high molecular weight, and produced at a high rate.[56] Bulk polymerization with appropriate heat management also yields particles that are spherical in shape with narrow particle-size distribution.[57,58,59] It is therefore easy to design SAPs to have a spherical shape.

[54] Kiatkamjornwong, p. 40. Appendix Kiatkamjornwong.

[55] Baranwal, K. and Stephens, H. *Basic Elastomer Technology.* Rubber Division, American Chemical Society, The University of Akron., **2001** (Baranwal), p. 422. Appendix Baranwal.

[56] Kiatkamjornwong, p. 40. Appendix Kiatkamjornwong.

[57] Baranwal, p. 422. Appendix Baranwal.

[58] Kiatkamjornwong, S., p. 40. Appendix Kiatkamjornwong.

[59] Odian, G., Principles of Polymerization, Wiley-Interscience, **2004,** p. 297. Appendix Odian.

39. Suspension polymerization[60] and reverse-phase suspension polymerization[61] are also methods used specifically for manufacturing spherical SAPs and were known prior to 2010 to yield spherical particles.[62] Several early commercial SAPs for diapers were reported to be manufactured using suspension polymerization in 1996.[63,64,65] The size of the particles made by this method depends on various factors including concentration and type of suspending agents, agitation

[60] Suspension polymerization is polymerization of droplets of monomer-containing solution dispersed in a continuous phase (e.g., solvent), under constant agitation. The continuous phase is chosen such that it is immiscible with the monomeric phase.

[61] Reverse-phase suspension polymerization employs a polymerization in which aqueous droplets of water-soluble monomers are suspended in a non-aqueous liquid in the presence of suspending agents (e.g., emulsifier and/or stabilizer)

[62] Buchholz, p. 109. Appendix Buchholz.

[63] Buchholz, pp. 70, 113-114. Appendix Buchholz.

[64] Buchholz, pp. 104-105. Appendix Buchholz.

[65] U.S. Patent 4,506,062 to Flesher issued on March 19, 1985 at 1:5-16. Appendix US Patent 4,506,062.

rates, viscosities, volume ratio, and interfacial tension between monomeric phase and continuous phase, and can be predicted from these factors.[66] Depending on the suspension aid, typical particle sizes of 200 to 1000 μm out of the reactor are possible.[67] Various sized spherical polymer particles with uniform particle size distribution have been reported using reverse-phase suspension polymerization of ionic monomers[68] and this can beneficially reduce the need for separate sizing process of dry product.[69] Generally, the shape of final product particles is determined by the shape of polymerizing droplets at the gel point.[70]

[66] Buchholz, pp. 104-105. Appendix Buchholz.

[67] Buchholz, p. 108. Appendix Buchholz.

[68] U.S. Patent 4,506,062 to Flesher issued on March 19, 1985 at 6:6-10, 6:18-21. Particle size is generally within the range of 50 to 1000 μm in diameter for large particles and 0.2 to 5 μm in diameter for small particles. Appendix US Patent 4,506,062.

[69] Buchholz, pp. 71, 113. Appendix Buchholz.

[70] Buchholz, p. 105. Appendix Buchholz.

D. Examples of Application-Specific SAP Property Profiles that can be Varied to Accomplish Different Objectives

40. It was understood prior to 2010 that the intended application for an SAP impacts the bulk characteristics that the material must exhibit, and that these characteristics can be adjusted to meet different end goals for the SAP. For example, as one potential application, SAPs have been used to absorb liquids in personal care sanitary products,[71] and this is consistent with the specification disclosure that they are commonly used in personal disposable hygiene products.[72] While there are shared requirements for SAPs in this application, there are also differences in the desired combination of properties and this was understood prior to 2010. The polymer properties that are of principal commercial importance in this application include the amount of liquid that can be absorbed, the rate at which a liquid is absorbed, and the amount of liquid that is retained in the gel under varied compressive forces.[73]

[71] Buchholz, p. 167. Appendix Buchholz.

[72] '255 Patent at 4:54-58. Appendix 255 patent.

[73] Buchholz, p. 167. Appendix Buchholz.

41. In early development of SAP-containing diapers, the absorption capacity for urine was maximized, resulting in a swollen gel that then limited the penetration of urine into the diaper structure and led to leaks.[74]

42. Later on, a means to prevent this leaking was achieved through increasing the gel strength or modulus of the SAPs by increasing the crosslink density of gel particles; the resulting SAPs had higher moduli and higher absorption under pressure, but lower free swelling capacity.[75] This resulted in an overall improvement in the diaper performance, even though the equilibrium swelling capacity was lowered.[76]

43. Sanitary products meant for adult usage, such as adult incontinence products, also utilize SAPs to absorb urine, but require different material characteristics.[77] Relevant and different product factors include thinness to allow for discrete use and disposal, as well as the ability to manage the larger adult-level

[74] Buchholz, p. 254. Appendix Buchholz.

[75] Buchholz, p. 254. Appendix Buchholz.

[76] Buchholz, p. 254. Appendix Buchholz.

[77] Buchholz, p. 257. Appendix Buchholz.

urination volume, urination rate, and exertion pressure.[78] Therefore, the SAP technology used for infants cannot be directly applied to adult incontinence products. Fast-swelling SAPs for adult usage typically utilize smaller particle sizes, for a higher surface to volume ratio, porous smaller particles, and highly wrinkled particles compared to SAPs for infant usage.[79]

44. Many feminine hygiene products also utilize SAPs that have been designed to address challenges associated with the fluid to be absorbed, including higher viscosity and increased chemical complexity compared to urine collection.[80] Cells cannot diffuse into the SAP network and instead they adsorb onto the surface of the SAP particles, resulting in a reduction in material efficiency due to the surface layer of de-watered cells depending on the osmotic pressure of the SAP.[81] As such,

[78] Buchholz, p. 257. Appendix Buchholz.

[79] Buchholz, p. 257-58. Appendix Buchholz.

[80] Buchholz, p. 258. In diapers, the absorbed fluid is a low viscosity aqueous solution generally consistent with salt and urea; whereas, for feminine hygiene, the fluid is a more complex mixture of water, salts, and cells with a higher viscosity. Appendix Buchholz.

[81] Buchholz, p. 258. Appendix Buchholz.

these SAPs must be chemically modified, like other polymers used for surgical tools or surgeries, to prevent undesired blood clotting.[82]

45. While the intended role of the SAP remains the same in these sanitary products, to absorb the liquid of interest, the specific usage application dictates the necessary SAP properties. Adjustments are often made, through changes to the size, shape, and chemical functionality of the SAP particles, to suit the necessary characteristics of different applications.

E. Adjustment of SAP Physical Characteristics Was Well-Known in the Art

46. It is my opinion that a Chemist prior to 2010 would have known how to adjust the physical characteristics of SAPs to control their shape, size (both initial and once fully hydrated in a given solution), strength, and absorbency. These SAP properties are the result of scientific concepts and structure-processing-property relationships that were well known at the time of the alleged invention in February 2010. A Chemist would have been able to achieve different material properties and physical characteristics for SAP ammunition, including adjustments to desired size of the hydrated SAP and adjustments to the strength and durability of the SAP,

[82] Buchholz, p. 258. Appendix Buchholz.

before 2010. These would all be routine adjustments that would not require extensive effort.

47. As discussed above, bulk polymerization and cross-linking followed by drying and grinding can yield spherical particles.[83] Additionally, suspension and reverse-phase suspension polymerizations yield spherical SAPs by their nature, with specific conditions of the polymerization able to prescribe the shape and size of the resultant particle more specifically.[84] Spherical particles can also be obtained by selection of manufacturing conditions (e.g. shear forces to cause droplet formation).[85] It was well-known in the art before 2010 that the strength and absorbency of an SAP can be tailored by adjusting the crosslink type and crosslink density of the material.[86] An increase in crosslink density of a SAP results in the higher modulus, high absorption under pressure, but lower free swelling capacity.[87]

[83] Buchholz, pp. 73-74, 85-87, 93-94, 109-113. Appendix Buchholz.

[84] Buchholz, pp. 74-77, 109-113. Appendix Buchholz.

[85] Buchholz, pp. 86-87. Appendix Buchholz.

[86] Buchholz, pp. 168-176. Appendix Buchholz.

[87] Buchholz, pp. 175. Appendix Buchholz.

48. Further, as discussed above, the final size obtained upon hydrating the SAP is dependent on the swelling conditions. A larger or smaller final diameter can be achieved by adjusting the starting size, swell time, and swelling fluid characteristics. Smaller initial diameters, shorter swell times, higher salt content, and reduced polymer-fluid interaction are all factors that would decrease the final diameter, while the opposite would increase the final diameter for a given SAP chemistry and crosslinker.[88]

49. Claims 1 and 13 of the ’255 patent requires that the plurality of soft-projectiles have the same shape. A Chemist would have known before 2010 that the strength and modulus, e.g., softness, of the hydrated SAP particle could be tailored by the chemistry and degree of hydration, which is achieved by selecting the primary polymer and adjusting the crosslinker and crosslink density of the material to produce a soft projectile.[89] The Chemist further would have known before 2010 that employing a gel formation technique such as bulk polymerization and cross-linking followed by drying and grinding to the desired shape and size; suspension or reverse-phase suspension polymerization; or, extrusion into droplets or pellets would be

[88] Buchholz, p. 150. Appendix Buchholz.

[89] Buchholz, 168-176. Appendix Buchholz.

expected to yield particles of the same shape.[90] By 2010, a Chemist would have known that these processes could be utilized to yield SAPs having the same shape.

50. Claim 16 of the '255 Patent specifies that "the soft-projectiles have a diameter of 10 millimeters or less." A Chemist would have known before 2010 that the size of the SAP can be prescribed by either processing conditions (e.g., cutting and grinding of dried gels or the pelletizing process) and/or the polymerization conditions, including the employed cross-link density of the material.[91] Further, a Chemist would have known before 2010 that the swelling conditions could also be tailored to achieve a desired final hydrated size of the SAP.[92] For example, it was well-known by 2010 that the final size of a hydrated SAP could be changed based on the chemical makeup of the SAP and/or the conditions of the hydrating fluid such as the pH, salt content, or temperature, as discussed in more detail above.

51. Therefore, for the reasons described above, a Chemist would have known before 2010 how to produce soft-projectiles made from SAP having the same shape, including a round or spherical shape, and with a diameter of 10 mm or less.

[90] Buchholz, pp. 73-77, 86-87, 109. Appendix Buchholz.

[91] Buchholz, pp. 109, 86-87. Appendix Buchholz.

[92] Buchholz, p. 150. Appendix Buchholz.

Adjustments to size, strength, and durability of the gel were all routine and easily accomplished by well-known methods.

IX. SPITBALLS WERE SAPs

52. Spitballs describes "Spitballs" as a toy projectile that can be launched using a launcher. I understand that Spitballs were listed for sale and described by toy retailer ThinkGeek by November 27, 2009. Ex. 1002.

53. The Spitballs product packaging shown in Ex. 1002 also states that the Spitballs balls "grow[] 200x their size," that they "slip, slide, bounce, and explode," and that they are "fun to throw." Ex. 1002

54. The description of Spitballs in Ex. 1002 (*see* p. 21) states that "Spitballs start out as tiny balls and expand 200 times when stuck in water." After hydration, "[t]hey are slimy and squishy." *Id.* Spitballs "[w]ill bounce and/or explode into mushy parts on impact (depending on the force you throw them)" and that the balls are "spherical polymers." *Id.* "Spitballs grow to about 0.6" in diameter (the longer they absorb water, the bigger they grow)." *Id.*

55. The description of Spitballs in Ex. 1002 (*id.*) also shows many Spitballs that are hydrated and resting in a hand. It also shows a bowl of what appear to be hydrated Spitballs. *Id.*, *see* the below images:



56. The Spitballs packaging also included a packet containing more than 150 dehydrated SAPs. *See* Ex. 1002, pp. 18, 21 (packet is located directly above "They Slip, Slide, Bounce & Explode"). The Spitballs packaging teaches to hydrate the dehydrated Spitballs by emptying them into a bowl or cup of water. *See* Ex. 1002, p. 21. The product listing teaches that the dehydrated Spitballs can "grow up to 200 times their original size" as they absorb water. Ex. 1002, p. 21.

57. As discussed below, it is my opinion that the Spitballs described in Ex. 1002 were "super absorbent polymer[s]" (SAPs) under the claim construction adopted by the ALJ in the ITC Case.

58. As a starting point, Ex. 1002 refers to Spitballs as "spherical **polymers.**" Ex. 1002, p. 21 ("What if instead of real expectorations, you flung awesome spherical **polymers**. We're here for you: get thyself some Spitballs!").

Because super absorbent **polymers** are by definition polymers, this language would have indicated to a Chemist at the time it was published that Spitballs could be SAPs.

59. I also considered additional language in Exhibit 1002 that would have indicated to a Chemist at the time it was published that Spitballs were SAPs. For example, Ex. 1002 states that Spitballs "grow up to 200 times their original size" and "expand 200 times when stuck in water" and will change from "small hard little spheres" to be "slimy and squishy" after hydration. Ex. 1002, p. 21. These are well known properties of hydrated SAPs. Buchholz, pp. 1, 10. Appendix Buchholz.

60. At the time that Ex. 1002 was published, a Chemist would have understood from the images in the publication, when viewed in conjunction with the text, that Spitballs were SAPs. The particles inside the packet look like tiny, dried out grains, as shown in the figure below, which was the typical appearance of dehydrated SAPs. Ex. 1002, p. 18, Buchholz, p. 1. Appendix Buchholz.



61. There are several images of hydrated Spitballs in Ex. 1002, including enlarged spherical Spitballs on the packaging itself, positioned in front of the

packing, resting in a hand, and sitting in a bowl. Ex. 1002, pp. 15, 18. These hydrated Spitballs are much larger than the unhydrated SAPs shown in the image of the packet. Ex. 1002, p. 18. The fact the hydrated Spitballs grew to sizes much larger that the dehydrated Spitballs without dissolving would have indicated to a Chemist at the time that the Spitballs are SAPs. Buchholz, pp. 1, 7, 10. Appendix Buchholz.

62. Ex. 1002 teaches that Spitballs should be soaked in water to swell the Spitballs. Ex. 1002, p. 21. The clear appearance of the hydrated SAPs in the images would have also suggested to a Chemist that the Spitballs were swelled with water (a clear liquid). The ability of a material to absorb a liquid and grow to a transparent sphere, much larger in size, without dissolving is unique to crosslinked hydrophilic polymers such as SAPs. Buchholz, pp. 1, 7, 10. Appendix Buchholz.

63. Finally, at the time it was published, a Chemist would have understood the following teaching in Ex. 1002 to mean that Spitballs were SAPs: "Spitballs start off as small hard little spheres. Soak Spitballs in water for about 4 hours … and they will absorb water and grow up to 200 times their original size." Ex. 1002, p. 21. This is the exact type of behavior that the peer reviewed literature (discussed above) describes as being characteristic of SAPs. Buchholz, pp. 1, 7, 10. Appendix Buchholz.

64. Changes in size of an SAP can be described by changes in mass, volume, or diameter, because these attributes are directly related in SAPs. A Chemist would know that an SAP grows when it absorbs water and recognizes that changes in mass and changes in size are directly related such that one does not occur without the other. As an SAP absorbs water, it swells. This growth in size is a result of the uptake of the water which has mass. Buchholz, pp. 1, 7, 10. Appendix Buchholz. This can be illustrated by considering that for water with a density of 1 g/ml, 1 gram of water occupies 1 cm^3 of volume, equivalent to a sphere with a diameter of 12.4 mm. This is calculated using the following equation and units conversion:

(a) Volume of a sphere =(4/3)*pi*r^3, where r is the radius

(b) Water has a known density of: 1 g/cm3 = 0.001 g/mm3

(c) 1 mm = 10 cm

65. Thus, a 200-fold increase in the mass would correspond to approximately a 6-fold increase in the diameter. The size change from water uptake by an SAP can be assessed by quantifying change in mass. If the statement, "grow up to 200 times their original size" (Ex. 1002 at 21) refers to the Spitballs' mass, a Chemist would have understood that Spitballs is a polymer that absorbs up to 200 times its own mass in water, and thus, meets the '255 Patent SAP limitation, using the construction found by the ALJ in the ITC Case.

66. Accordingly, if the statement "200 times their original size" were interpreted to refer to volume, a Chemist would still have understood Spitballs to be SAPs according to the definition of SAPs as constructed by the ALJ in the ITC Case. The size change from water uptake by an SAP can also be assessed by quantifying a change in volume, which for spherical SAPs can be observed in two dimensions (*e.g.*, in a photograph) by a change in diameter. Because a Chemist would understand that mass and size are directly related for SAPs, a Chemist would have understood the Spitballs meet the claimed SAP limitation based on its absorption capacity. The information provided in the Spitballs listing establishes the mass of water absorbed by Spitballs assuming a 200 times change in volume by applying the below well-known equations:

(a) mm = inch * 25.4

(b) Diameter = 2r, where r is the radius

(c) Volume of a sphere =(4/3)*pi*r^3, where r is the radius

(d) Water has a known density of: 1 g/cm^3 = 0.001 g/mm^3

67. Spitballs discloses that "Spitballs grow to about 0.6" in diameter." Ex. 1002, p. 21. Using equation (a), the maximum diameter of each Spitball when fully hydrated is 15.24 mm. Applying equation (b), the maximum radius of each fully hydrated Spitball is 7.62 mm radius. The maximum volume of each fully hydrated

Spitballs (per equation (c)) is 1,853 mm^3. Thus, to the extent that Patent Owners argue that "grows up to 200 times their original size" refers to volume and not mass, then dividing the 1,853 mm^3 final volume by 200 would mean the dry, unhydrated Spitballs have a starting volume of 9.3 mm^3, a radius of 1.3 mm (applying equation (c)) and a diameter of 2.6 mm (applying equation (b)). Although the water-polymer interactions do affect the final volume, the water absorbed can be estimated by subtracting the dry polymer volume from the final hydrated volume. In this case, the amount of water absorbed to get from 9.3 mm^3 (dry polymer volume) to 1,853 mm^3 (polymer + absorbed water volume) would be 1,844.06 mm^3 (absorbed water volume). The mass of 1,844 mm^3 of water would be known to be 1.844 g (based on above equation (d)).

68. A Chemist would also understand that the mass uptake by a Spitball can be calculated from the above relationship and the disclosure that there are "about 150 or so" in 2 grams of Spitballs. This would be calculated as:

$$\frac{150\ Spitballs}{2\ grams\ of\ polymer} \times \frac{1.84\ grams\ of\ water}{1\ Hydrated\ Spitball} = \frac{138.6\ grams\ water}{gram\ of\ polymer}$$

69. A Chemist would understand this absorption of 138.6 grams of water per gram of polymer meets the claimed SAP limitation according to the definition of SAPs as constructed by the ALJ in the ITC Case.

70. To summarize, to the extent that hydrated Spitballs are "200 times their original size" when they also exhibit a diameter of 0.6" (15.2 mm) when hydrated, then a Chemist would understand that volume and mass are related, and would understand that Spitballs have a starting dry diameter of about 2.6 mm and are able to absorb approximately 138 times their dry mass in water. On the other hand, if "200 times their original size" is a reference to mass uptake, then a Chemist would understand that Spitballs absorb 200 times the original mass in water. Under either interpretation of the phrase "200 times their original size," Spitballs would meet the claimed SAP limitation according to the definition of SAPs as constructed by the ALJ in the ITC Case.

I hereby declare under penalty of perjury under the laws of the United States of America that the foregoing is true and correct, and that all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true.



Maureen T.F. Reitman, Ph.D.

Dated: October 2, 2023



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Professional Profile

Dr. Reitman leverages her understanding of the fundamental principles of materials science and the technology of macromolecules to assess risk and performance for end users, distributors, manufacturers, product designers and raw material suppliers across a wide range of industries. Her expertise includes polymer and composite technology, mechanics of materials, adhesion science, fiber mechanics, history and technology of plastics, and material failure analysis. She is skilled in the development and use of testing tools and methods and has applied them to plastics, rubber, textile, metal, glass, ceramic, and composite materials and systems. She is experienced in major aspects of product development, including materials selection, formulation, scale-up, end-use testing, failure analysis, certification procedures and issues related to intellectual property.

Dr. Reitman has conducted research in the areas of medical plastics and devices including implants, diagnostic components, and transdermal drug delivery systems; plastic packaging and barrier materials; paints and coatings; plastic pipes; spray foam insulation; adhesives, sealants, and encapsulants; additive manufacturing / 3D printing; molding compounds; composite materials; high temperature resins; rubber gaskets and seals; nanoparticles; fibers and textiles; polymer chemical resistance; wire and cable insulation; connectors and splices; environmental effects on durability; and product aging. She has used her expertise to address problems and opportunities related to coatings, fibers, films, and extruded and molded products, and their use in the telecom, electronics, electrical, energy, transportation, construction, fire protection, medical, and consumer products markets. Dr. Reitman also assists clients with matters related to intellectual property, including support related to patent filings, technical due diligence, and technical aspects of trade secret, patent infringement, and patent validity disputes.

Dr. Reitman is active in technical and business advisory roles. She has served on technical advisory boards for materials and manufacturing companies as well as in several Board of Directors positions for the Medical Plastics Division and the Failure Analysis and Prevention Special Interest Group of the Society of Plastics Engineers. Dr. Reitman is also a voting member of two Underwriters Laboratories Standard Technical Panels, addressing Polymeric Materials (UL 94, UL 746, UL 1694) and Appliance Wiring (UL758).

Prior to joining Exponent, Dr. Reitman worked for the 3M Company in both research and management roles. Her activities included technology identification, materials selection and qualification, product development, customer support, program management, acquisition integration, staff and organizational development, intellectual property analysis, and patent litigation support.

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American Association of Textile Chemists and Colorists — AATCC (senior member)

American Chemical Society (member)

ASTM International (member)

Society for the Advancement of Material and Process Engineering (member)

Society of Plastics Engineers (Fellow)

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Underwriter's Laboratory Standards Technical Panel STP 746 (Polymeric Materials, includes UL94, UL 746 and UL1694)

Underwriter's Laboratory Standards Technical Panel STP 758 (Appliance Wires/ UL758)

Medical Plastics Division Board of Directors, Society of Plastics Engineers

Failure Analysis and Prevention Special Interest Group Board of Directors, Society of Plastics Engineers

Patents

Patent 6,311,524: Accelerated Method for Increasing the Photosensitivity of a Glassy Material, issued November 6, 2001.

European Patent EP0830428: Tackified Polydiorganosiloxane Polyurea Segmented Copolymers and a Process for Making Same, published March 25, 1998.

Patent 5,731,051: Fiber Optic Fusion Splice Protector Sleeve, issued March 24, 1998.

Publications

Wade, RJ, Pittelli S, Reitman MTF. Stability of polypropylene mesh to acid, base, and peroxide chemical challenge. Singh Center for Nanotechnology 2021 Annual User Meeting. Philadelphia, PA, 2021.

Dimitriou, M., Moll, J., and Reitman, M. Polymer Materials in Architectural Applications: Building on Traditional Knowledge and Innovative Technologies in Materials Selection for Long-Term Success. In Susan E. Schur (Ed.) Architectural Plastics & Polymer Composites in the 21st Century Conference Proceedings Plus (Vol I). The Technology Organization, Inc., Somerville, MA, 2021.

White, C., Dimitriou, M., Moll, J., and Reitman, M. Traditional Polymer Materials in Innovative Architectural Applications: Understanding How Advances in Design Affects the Materials Selection Process. In Susan E. Schur (Ed.) Architectural Plastics & Polymer Composites in the 21st Century Conference Proceedings Plus (Vol I). The Technology Organization, Inc., Somerville, MA, 2021.

Garcia-Leiner, M., Reitman, M. T.F., El-Hibri, M. J. and Roeder, R. K. (2016), Structure-property relationships in commercial polyetheretherketone resins. Polym Eng Sci. doi:10.1002/pen.24472.

Farina, R., Reitman M. The effect of localized heating on polyethylene tubing. Proceedings, ANTEC 2015, Society of Plastic Engineers, Orlando, FL, March 2015.

Moalli P, Brown B, Reitman MTF, Nager C. Polypropylene mesh: Evidence for lack of carcinogenicity. International Urogynecology Journal 2014; 25(5):573-576.

Hoffman JM, Ralston B, Chakravartula A, Reitman M. ESC of polycarbonate exposed to hospital disinfectants. Proceedings, ANTEC 2013, Society of Plastic Engineers, Cincinnati, OH, April 2013.

Ralston B, Hoffman JM, Reitman M. Fractographic examination of failures in polycarbonate and polyxymethylene due to impact, tensile, fatigue, and creep mechanisms. Proceedings, ANTEC 2013, Society of Plastic Engineers, Cincinnati, OH, April 2013.

Kurtz S, Siskey R, Reitman M. Accelerated aging, natural aging, and small punch testing of gamma-air sterilized polycarbonate urethane acetabular components. Journal of Biomedical Materials Research Part B: Applied Biomaterials 2010 May; 93B(2):422-447.

Hoffman JM, Reitman M, Donthu S, Ledwith P. Complimentary failure analysis methods and their application to CPVC pipe. Proceedings, ANTEC 2010, Society of Plastics Engineers, Orlando, FL, May 2010.

Hoffman JM, Reitman M, Donthu S, Ledwith P, Wills D. Microscopic characterization of CPVC failure modes. Proceedings, ANTEC 2009, Society of Plastics Engineers, Chicago, IL, June 2009. Best Paper Award in Failure Analysis & Prevention.

Kurtz SM, Ebert M, Siskey R, Ciccarelli L, Reitman M, Harper ML, Chan FW. Natural and accelerated aging of polyurethanes in the Bryan cervical disc. Poster No. P158. Transactions of Spineweek 2008, Geneva, Switzerland, May 26-31, 2008.

Reitman M, Ledwith P, Hoffman M, Moalli J, Xu T. Environmentally driven changes in nylon. Proceedings, ANTEC 2008, Milwaukee, WI, Society of Plastics Engineers, May 2008.

Hoffman JM, Reitman M, Ledwith P. Characterization of manufacturing defects in medical balloons. Proceedings, ANTEC 2008, Milwaukee, WI, Society of Plastics Engineers, May 2008.

Moalli JE, Moore CD, Robertson C, Reitman MTF. Failure analysis of nitrile radiant heating tubing. Proceedings, ANTEC 2006, Society of Plastic Engineers, Charlotte, NC, May 2006.

Reitman M, McPeak J. Protective coatings for implantable medical devices. Proceedings, ANTEC 2005, Society of Plastic Engineers, Boston MA, May 2005.

McPeak J, Reitman M, Moalli J. Determination of in-service exposure temperature of thermoformed PVC via TMA. Proceedings, 31st Annual North American Thermal Analysis Society Conference, Williamsburg, VA, 2004.

Reitman MTF, Moalli JE. Product development and standards organizations: Listings and certifications for plastic products. 8th Annual International Conference on Industrial Engineering Theory, Applications and Practice, Las Vegas, NV, 2003.

Potdar YK, Reitman MTF. The role of engineering consultants in failure analysis and product development. 8th Annual International Conference on Industrial Engineering Theory, Applications and Practice, Las Vegas, NV, 2003.

Ezekoye OA, Lowman CD, Hulme-Lowe AG, Fahey MT. Polymer weld strength predictions using a thermal and polymer chain diffusion analysis. Polymer Engineering and Science 1998; 38(6):976-991, June.

Fahey MT. Nonlinear and anisotropic properties of high performance fibers. MIT Thesis, 1993.

Fahey MT. Mechanical property characterization and enhancement of rigid rod polymer fibers. MIT Thesis, 1990.

Book Contributions

Kreuzer, S.M. and Reitman, T.F. (2022). Design-Related Failures of Plastic Parts. In Todd J. Menna (Ed.) ASM Handbook, Volume 11B: Characterization and Failure Analysis of Plastics (pp. 589-598). ASM International. https://doi.org/10.31399/asm.hb.v11B.a0006938.

Reitman, M. T. F., Dimitriou, M. D., Vargas, J. R., & Madden, S. B. (2020). Why is service life prediction of polymers and plastics exposed to outdoor weathering important? An industrial perspective. In C. C. White, M. E. Nichols, & J. E. Pickett (Eds.), Service Life Prediction of Polymers and Coatings (pp. 19-32). William Andrew Publishing. https://doi.org/10.1016/B978-0-12-818367-0.00002-3

Reitman M, Jaekel D, Siskey R, Kurtz S. (2019) Morphology and crystalline architecture of polyarylketones, In: PEEK Biomaterials Handbook, Second Edition. Kurtz SM (ed), Elsevier William Andrews, Kidlington, Oxford, UK, 2019. ISBN 978-0-12-812524-3

Reitman M, Liu D, Rehkopf J. Chapter 38. Mechanical properties of polymers. In: Handbook of Measurement in Science and Engineering. Volume 2. Kutz, M (ed), John Wiley & Sons, Hoboken NJ, 2013. ISBN- 978-1-118-38464-0.

Reitman M, Jaekel D, Siskey R, Kurtz S. Morphology and crystalline architecture of polyarylketones, pp. 49-60. In: PEEK Biomaterials Handbook. Kurtz SM (ed), Elsevier William Andrews, Kidlington, Oxford, UK, 2012. ISBN 13:978-1-4377-4463-7

Tsuji JS, Mowat FS, Donthu S, Reitman M. Application of toxicology studies in assessing the health risks of nanomaterials in consumer products, pp. 543-580. In: Nanotoxicity: From In Vivo and In Vitro Models to

Health Risks. Sahu S, and Casciano D. (eds), John Wiley & Sons, Chicester, West Sussex, UK, 2009. ISBN 978-0-470-74137-5.

Reitman MTF. The Plastics Revolution. In: Research and Discovery: Landmarks and Pioneers in American Science. Lawson RM (ed), Armonk NY: Sharpe Reference 2008. ISBN 978-0-7656-8073-0.

Klein SM. Mid-century plastic jewelry. Schiffer Publishing, Atglen, PA, 2005. (Technical advisor to author).

Trade Articles

Comerford PJ, Reitman MTF, Cooner, DJ. The legal issues of the 3DP/AM revolution. RX for the Defense 2014 Jan; 22(1).

Comerford PJ, Vernon DV, Reitman, MTF. 3DP/AM revolution is also a legal revolution. (http://www.manufacturing.net/articles/) December 2013.

Comerford, PJ and Reitman, MTF. The 3DP/ AM revolution . Today's Medical Developments (cover story) (www.onlinetmd.com), October 2013.

Reitman, MTF, Moalli JE. Polymeric coatings for medical device. Medical Device and Manufacturing Technology, Touch Briefings 2006; pp. 28-30.

Selected Presentations

Reitman, M. Improving Outcomes for Patients and Societies. Keynote Speaker, Medical Plastics Minitec, Society of Plastic Engineers, Anaheim, CA February 2020.

Wade, RJ, Kiel J, Reitman MTF. Oxidative stability of polypropylene for biomedical applications. 257th American Chemical Society Meeting. Orlando April 2019.

Reitman MTF. Service Life and Practical Risk: Incorporating failure modes and predictive tools in product development. NIST/ UL Conference on Service Life Prediction of Polymeric Materials: Reaching New Heights. Boulder, CO March 2018.

Reitman MTF. Innovate from what you know: Tips and tricks for medical device development. Teel Medical Plastics Summit, Minneapolis MN, November 2017.

Reitman MTF. Characteristics and Stability of Implantable Polypropylene Fibers. Medical Plastics Minitec, Society of Plastics Engineers, Durham, NC, April 2016.

Reitman MTF. 3D Printing technology viewed from the inside: Recognizing opportunity and managing risk. Presenter and panelist, Product Liability Advisory Council Spring Meeting, Miami, FL, March 2016.

Reitman MTF. To Your Health: Polymers in Biology and Medicine. Medical Plastics Keynote. ANTEC 2015 Conference, Orlando, FL, March 2015.

Reitman MTF. Turning failure into success: tools, techniques and practical examples for product development engineer. ANTEC FAPSIG Tutorial, Las Vegas, NV, April 2014.

Reitman MTF. Materials science of surgical meshes: Polypropylene for soft tissue repair. AATCC International Conference, Materials Track-Medical Textiles, Ashville, NC, April 2014.

Reitman MTF. PEEK: A structure-property-performance overview for medical device designers. AAOS/Solvay Education Summit: Healthcare Industry Perspective to Support Innovation and Product Development in a Challenging Global Environment, New Orleans, LA, March 2014.

Reitman MTF. Assessment of proposed division by type for F2026 in light of material, manufacturing and testing variability. ASTM F04 Committee meeting, Jacksonville, FL, November 2013.

Reitman MTF. Materials science of surgical meshes: Polypropylene for soft tissue repair. American Urogynecology Society (AUGS) 34th Annual Scientific Meeting, Mesh Special Interest Group, Las Vegas, NV October 16, 2013.

Reitman MTF. Structure-property overview of medical polymers. 4th China International Medical Device Regulatory Forum (CIMDR), Xi'an, China, September 2013.

Reitman MTF. Failure analysis of polymeric materials in medical applications: Lessons for successful material selection. Polymers and Plastics in Medical Devices San Francisco, CA, June 2013.

Reitman MTF. Failure analysis tools. Workshop on Future Needs for Service Life Prediction of Polymeric Materials. NIST and Underwriters Laboratories, Gaithersburg, MD, October 2012.

Hoffman J, MacLean S, Ralston B, Reitman M, Ledwith P. Fractography of unfilled thermoplastic materials experiencing common mechanical failure modes. Materials Science & Technology 2012 Conference, Pittsburgh PA, October 2012.

Hoffman J, Reitman M, Ledwith P. Microscopic characterization of CPVC failure. Materials Science & Technology 2012 Conference, Pittsburgh PA, October 2012.

Reitman MTF. Polymer material properties for next generation medical devices. Invited Speaker: MedTech Polymers, UBM Canon, Chicago, IL, September 2012.

Reitman MTF. Polymers for medical applications. Fundamentals and Fellows Forum, ANTEC 2012, Orlando FL, April 2012.

Reitman MTF. Plastic and composite product failures. Invited lecture in Failure Analysis of Emerging Technologies. Stanford University Department of Materials Science and Engineering, Menlo Park, CA October 2009.

Reitman MTF. Factors for success: Plastics in injection molded medical devices. Part of Injection Molding Works for Medical Design, Design News Webcast, October 2008.

Reitman MTF. Plastic and composite product failures. Keynote Speaker: Third International Conference on Engineering Failure Analysis (ICEFA III), Elsevier, Sitges Spain, July 2008.

Reitman MTF. Multiphase materials for medical device applications, an overview. Medical Device and Manufacturing (MDM), Canon Communications, various locations, Jan-June 2008.

Reitman MTF. Nanotechnology and plastics for medical devices. Capitalizing on Nanoplastics, Intertek PIRA San Antonio TX, February 2008.

Reitman MTF. Nano additives in composites and coatings for medical device applications. Medical Device and Manufacturing Minneapolis, Canon Communications, Minneapolis MN, October 2007.

Reitman MTF, Swanger LA. Practical tips on how to manage your technical expert in patent disputes. Ropes & Gray IP Master Class, Live Teleconference, June 2007.

Reitman MTF, Kennedy E. Root cause failure analysis and accident investigation. Lorman Educational Services, Live Teleconference, November 2007.

Reitman MTF. Plastics failure analysis: Case studies. Baltimore/ Washington Chapter of SAMPE, October 2006.

Reitman MTF. Plastics failure analysis. Baxter Global Plastics Processing Conference 2005, Schaumburg IL, 2005.

Fahey MT. Fiber mechanics, corrosion, sealants: Tales of a 3M materials scientist. Class of 1960's Scholars Program, Williams College, 1999.

Fahey MT. Adhesives and sealants for the telecommunications industry. Riverwood V Conference, St. Paul MN, 1998.

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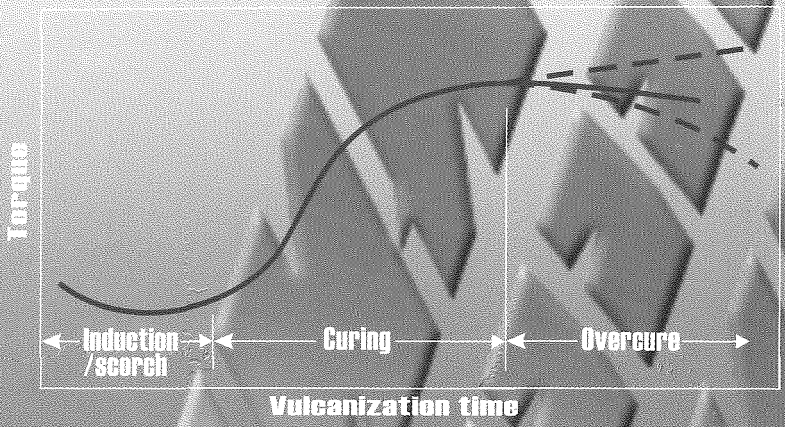
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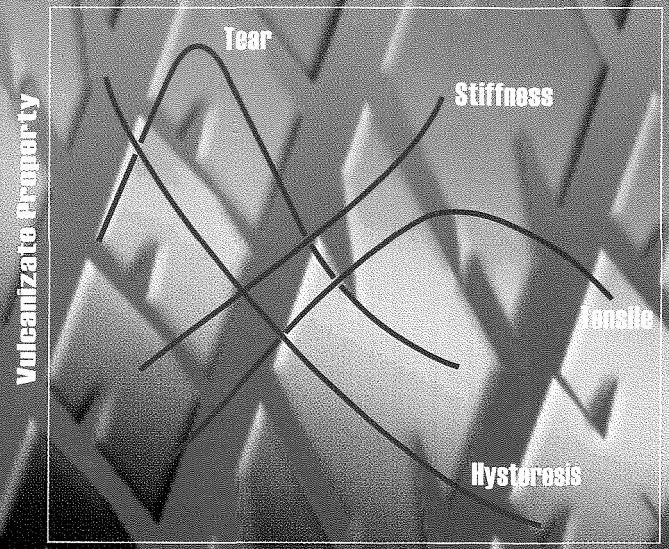
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1 of 8

Basic Elastomer Technology

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BASIC ELASTOMER TECHNOLOGY

FIRST EDITION

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PREFACE

Since its inception, the Education Committee of the Rubber Division of the American Chemical Society (ACS) has been the driving force in the establishment of the various Rubber Technology Courses that the Division offers to its members and others interested in the rubber industry.

The three correspondence courses—Basic, Intermediate and Advanced—were all developed from the Division's Educational Symposia given at meetings over the period of years starting in 1977, or by the use of several text books that were related to elastomers, their processes and uses.

This book is an update of the first complete text used by many of the Rubber Groups for their in-house courses at various locations throughout the United States and Canada. This original text, edited by Harry Long in 1985, was entitled "Basic Compounding and Processing of Rubber." Since that time many changes have occured both in the types of elastomers as well as the other materials used in rubber products.

Over the years since the introduction of the first correspondence course in 1963, as many as one thousand individuals per year have taken the three courses plus the two-day and one-week workshops that are offered by the Division each year.

It is with this background that this text was developed to better serve the Division's members and other individuals and interested groups. It updates the available elastomers, compounding materials and methods used to produce rubber products, thus providing a better understanding of the rubber industry as it exists today.

The editors wish to thank all the contributors who made this project possible. Also we thank Mrs. Joan Long, the Rubber Division Librarian, for her assistance in locating literature and confirming references cited in several chapters. Mrs. Marilyn Custer of Flexsys America L.P. is acknowledged for her excellent help in the preparation of the index for this text.

The invaluable assistance of Al Sullivan, The Managing Editor, is acknowledged. He provided the knowledge and skills necessary to edit and format the manuscripts into "print ready copy" giving this text a unique presentation for each of the chapters.

Krishna C. Baranwal
Howard L. Stephens

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4. Bulk polymerization.— Bulk or mass polymerization of PVC converts monomer to polymer without water or suspending agents, eliminating the need to remove water after polymerization. This provides a distinct cost advantage for such a process. In addition the resultant polymer does not contain any surfactant or suspending agent residues. Polymerization initiators are usually peroxydicarbonates or peroxyesters.

Commercial bulk polymerization was developed as a single step process by the French company, Saint Gobain, in the 1940s. This process was later refined to a two step process that has been licensed to other firms by Saint Gobain and its successor, AtoChem. The first step in this process is carried out in a vertical reactor fitted with a flat blade turbine. Given percentages of the vinyl chloride and initiator (partial batch) is introduced to the reactor and polymerization is carried out to around 10% conversion. The resultant 'seed' prepolymer is then transferred to the second stage reactor along with additional monomer. The second stage reactor is usually a horizontal, heated type fitted with curved, sweep agitator blades that slowly rotate and a cooling jacket. The remaining percentages of monomer and initiator are added and the reaction proceeds to 70–85% conversion. The heat of reaction is removed by the cooling jacket, the agitator shaft of the reactor and a reflux condenser.

Upon completion of the desired reaction (termination is accomplished by evacuation of remaining monomer), the resultant resin is discharged and conveyed to finishing operations (cooling, screening, and storage). Resin produced by this process is free of polymerization residues and is very porous. The product is very pure and displays excellent clarity. The resin has a narrow particle-size distribution being somewhat smaller than suspension polymerized PVC, and the polymer particles are spherical in shape.

5. Solution polymerization.— The solution polymerization of vinyl chloride to PVC is actually bulk polymerization in a solvent. The solvent of choice is usually one in which the monomer is soluble but the polymer, upon reaching a given molecular weight, is not. The process is not truly a solution process because the polymer does not remain in solution. Solvents such as benzene, *n*-butane, cyclohexane, and chlorinated aliphatics are often used. Monomer soluble initiators are used. Upon completion of polymerization, the slurry is filtered to remove the polymer and the filtrate is returned to the reactor. Solution polymerization is used to produce high quality copolymers, such as vinyl chloride–vinyl acetate. The resultant resins are of good clarity and high purity, free of polymerization residues. The major disadvantages of the solution process are the expense of solvent and the solvent recovery equipment required.

6. Copolymerization.— Copolymers of vinyl chloride can be made by any of the above processes, but suspension and solution polymerization are the methods most commonly used. Important comonomers that are used with vinyl chloride are vinyl acetate, vinylidene chloride, maleic esters, vinyl ethers, and propylene. Although copolymers of vinyl chloride are usually more costly than PVC homopolymer, their importance and usage continue to grow due to property enhancements that comonomers impart to vinyl chloride.

horough, up-to-date examination the science and practical application superabsorbent polymers

n Superabsorbent Polymer Technology takes a comprehensive look at the ure, properties, and uses of superabsorbent polymers. Prepared by s with over 20 years of experience in the field, it offers a unified ach to polymer science technologies and examines the key interrela- ips between structure, properties, behavior, and applications.

ook draws on the best and most relevant scientific papers from acad- nd industry, as well as numerous patents and patent applications. The is a compact, centralized source of information on superabsorbent ers that no polymer or chemical engineer will want to be without.

- cusses synthetic chemistry and the effects of synthesis on the ucture of superabsorbent polymers
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Modern Superabsorbent Polymer Technology

edited by
Fredric L. Buchholz
Andrew T. Graham

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1

ABSORBENCY AND SUPERABSORBENCY

Fredric L. Buchholz

Superabsorbent polymers are fascinating substances. The most commonly available superabsorbent polymers are hard, dry, granular powders that look much like clean, white sand or granular table sugar. Other shapes, such as microspherical powders and fine fibers, are also known. Any similarity to sand or sugar is immediately forgotten when the superabsorbent polymer is put into contact with water or water solutions. At first, the slurry of water and the particles of the hard, dry granules seems unremarkable, but gradually the superabsorbent polymer absorbs the water, turning into a soft, rubbery gel. Pads of fluffed cellulose pulp fibers will absorb about 12 g of water or other aqueous solutions per gram of dry fiber,[1] whereas superabsorbent polymers will absorb up to 1,000 g of water per gram of polymer and up to about 100 g of dilute salt solution per gram of polymer. Unlike the behavior of a soaked pad of cotton or a sponge, the superabsorbent polymer gel will not release the water when squeezed with the fingers.

The advent of superabsorbent polymers is a classic case of the substitution of materials. The principal use of superabsorbent polymers is as an absorbent for water and aqueous solutions, primarily in diapers, adult incontinence products, and feminine hygiene applications. In these applications superabsorbent materials are inexorably replacing traditional absorbent materials such as cloth, cotton, paper wadding, and batts of cellulose fiber. The substitution of superabsorbent polymers for fibrous wood pulp in disposable sanitary products has taken place gradually over a time span of about 20 years and is probably not yet complete. To explain better this process of substitution, and superabsorbents generally, the essential characteristics of the tradition-

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1.1.2. Physics of Absorbent Materials

The open space in absorbents can act as a reservoir for fluid storage only if a means for transporting the fluid into the open space is available. When the open space forms a connected path throughout the material, it becomes possible to transport liquid into and through the material. The transport of liquid into and through a porous medium requires, additionally, that a force or pressure of some kind be applied to the liquid.

The principal factors affecting the flow through absorbent materials may be related by means of Darcy's law, which is a general, empirical relationship describing the flow through a porous medium. For steady, slow flow in one direction, Darcy's law is given by

$$\frac{dv}{dt} = -\frac{\kappa_D A \Delta P}{\mu L} \tag{1.1}$$

where the volumetric flow rate dv/dt is given in terms of the cross-sectional area A of the sample, the length L of the sample, the viscosity μ of the fluid, the specific permeability κ_D of the sample, and the pressure difference ΔP driving the flow process. The specific permeability is a measure of the effective connectedness of the porous structure, be it a mat of fiber or a slab of foam, and may be specified in terms of the void fraction and extent of connectedness of the absorbent material. Numerous models of absorbent and porous media have been constructed that connect the specific permeability to the structure.[4] The structural factors are usually limited to an effective diameter of the pore, based on the diameters of the fibers or particles that make up the absorbent medium, and the porosity of the medium.

Many different forces may act on the liquid to move it into and through the open spaces, including gravity, hydrostatic pressure, and capillary pressure. The latter is of great importance in absorbent materials because it is responsible for the wicking action of the absorbent medium that acts to initially transport the liquid into the dry absorbent material. Consider for a moment a simple, cylindrical capillary tube, containing a liquid that perfectly wets the walls of the capillary and air. The contact angle of the liquid with the wall is zero, and the meniscus is spherical, for which the radius of curvature is equal to the radius of the capillary tube. In this case, the capillary pressure p_c is given by

$$p_c = \rho g h = \frac{2\sigma}{R} \tag{1.2}$$

where ρ is the density of the liquid, h is the height of rise of the liquid, g is the acceleration of gravity, σ is the surface tension of the liquid, and R is the radius of the capillary. Therefore, the height or distance of rise in a capillary tube is greatest in tubes of small radius. However, in applications of absorbent materials, the rate of absorption is also critically important.

The rate of wicking of liquid in capillaries is stated by the Lucas–Washburn equation:

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$$\frac{dh}{dt} = \frac{R^2}{8\mu h}\left[\frac{2\sigma\cos\theta}{r} - \rho g h\right] \tag{1.3}$$

In Eq. 1.3, dh/dt is the change in height h of liquid of viscosity μ versus time t (wicking rate) in a vertical tube of radius R under the influence of the capillary pressure and gravity. The capillary pressure is represented by the first term inside the brackets and is given by the surface tension σ of the liquid, the radius of curvature r of the meniscus of the air–liquid interface in the pore, and the cosine of the contact angle θ of the liquid with the substance forming the walls of the pore. The effect of gravity on the wicking rate in the pore (capillary) is given by the second term in the brackets and consists of the density ρ of the liquid, the gravitational acceleration g, and the height of the liquid column. Liquid will rise in the capillary until the interfacial tension is balanced by the weight of liquid in the column. The contact angle is a measure of the wettability of the solid surface by the liquid and ranges from 0° (perfect wetting) to 90° (nonwetting). Wicking is driven, therefore, by the spreading of a liquid of high interfacial tension (with air) along the surface of the solid absorbent material. The maximum height of wicking in a capillary is achieved with liquids that perfectly wet the solid surface of the walls of the pore or capillary and with small capillary radius (as in Eq. 1.2). Maximum rate of wicking requires a large capillary radius and a liquid with low viscosity. To complicate matters, most absorbent materials have extremely irregular pores, with many different radii, and with the radius changing size along the flow path. This irregular structure contributes to poor wicking in absorbents. Liquid also may be transported by other mechanisms, and these are also important in practical absorbents.

Another force that can drive fluid flow is an externally supplied hydrostatic pressure difference between the faces or ends of the absorbent material. In contrast to wicking, liquid flow under an imposed hydrostatic pressure can be maintained in a saturated pore or capillary if a pressure difference is maintained across the pore or across the ends of a capillary. Whereas the capillary pressure "pulls" fluid into the pore, an applied hydrostatic pressure "pushes" liquid into the pore. When the entire capillary is wet, the meniscus at the wet–dry interface disappears and the capillary pressure vanishes, but any imposed hydrostatic pressure remains.

The structure of the absorbent also governs its mechanical rigidity or modulus, which in turn determines the propensity of the wetted structure to be dewatered by application of external forces such as mechanical compression. Mechanical dewatering is usually quite easy for most traditional absorbents, and this feature is a principal deficiency in applications where liquid retention is important, for example, in diapers or paper towels. The compressibility of the materials is determined by the modulus of the porous structure. The Young's modulus E_f of the porous structure is determined by the modulus E_0 of the solid, structural substance and its volume fraction ϕ in the absorbent material. For example, the apparent modulus of foams may be calculated as follows[5–7]:

$$\frac{E_f}{E_0} = \phi(2 + 7\phi + 3\phi^2)/12 \tag{1.4}$$

Even with sufficient structural rigidity to prevent compressional collapse, tradition-

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al absorbents may be dewatered by application of additional gravitational force. In a centrifuge, for example, dewatering may take place by overcoming the capillary pressure of the material. Resistance toward extra gravitational force requires very small capillaries, which have a large capillary pressure. However, for a fully saturated absorbent, any application of an accelerational force will cause some dewatering (see Eq. 1.1).

In summary, the absorbency of traditional materials is a function of the relative volume of open space in the sample (the porosity), the extent of connectedness of that volume, the size of the individual pores, and the mechanical strength of the porous structure, especially when wet. These factors are controlled by the choice of the structural material or fiber type, by the radius and length of the fibers and the pores, and by the method used to manufacture the absorbent structure.

1.2. SUPERABSORBENTS

1.2.1. Physics of Superabsorbents

Superabsorbent polymers are crosslinked networks of flexible polymer chains. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. A schematic drawing of such a network is shown in Figure 1.2. Except for the molecular-sized chains that make up the network, this picture of a network is remarkably similar looking to the mass of cotton fibers shown in Figure 1.1d. However, whereas traditional absorbents, like cotton, take up liquids by a flow

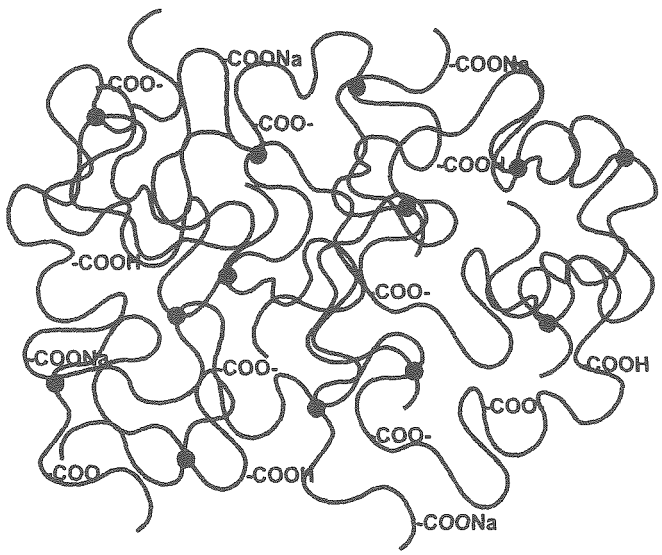
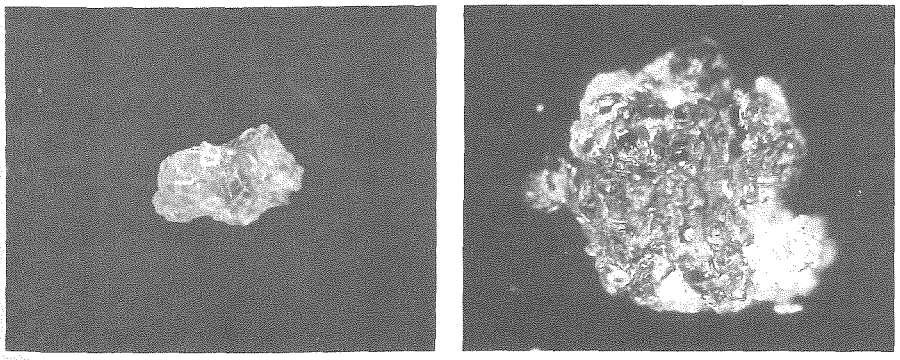


Figure 1.2. Schematic representation of a crosslinked polymer network. The dots represent the crosslinks between the coiled polymer chains, which have ionic carboxylate functional groups spaced along their length.

or convective mechanism, superabsorbents function by means of a diffusive mechanism. Diffusion is a molecular phenomenon wherein molecules move in a random, nonorganized manner as a result of their thermal energy. Increasing the temperature makes the molecules move faster, and the diffusive processes occur therefore at a faster rate. The molecules are in constant motion and will move from their average position in space toward regions of lower activity by purely statistical means.

Water moves into a particle of superabsorbent polymer because the activity of water is initially lower in the interior of the particle. As water diffuses into the particle, the particle volume increases and the polymer chains that form the superabsorbent polymer network must also move, generally in a direction opposite to that of the water molecules, in order to accommodate the volume of the additional molecules of water. The change in volume is apparent in Figure 1.3, which shows a particle of superabsorbent polymer before and after swelling in a dilute salt solution. Because polymer molecules are much larger than water molecules, they diffuse much more slowly. Not only are the polymer molecules larger, but they are also connected one to the other by the crosslinks, so that the polymer does not eventually dissolve in the water and become useless as a superabsorbent. Therefore, to move in a certain direction, the polymer chains must move cooperatively, requiring more time than if each polymer chain, or each monomer segment, moved individually. The slow polymer motion is a principal rate-limiting phenomenon in polymer swelling. This slow motion and the factors that affect it are discussed more fully in Chapter 5.

The polymer chains each have a preferred size and orientation in space that depends on their environment and their own thermal motion, which keeps them in constant, random motion about an average location. When water diffuses into the superabsorbent polymer, the favored, random configuration is disturbed, because the chain elongates as a necessary consequence of the change in volume of the particle. At first the disturbance is not very large, but as more water diffuses into the particle, the magnitude of the disturbance increases. Eventually, the force resulting from the elongation of the polymer chains balances the force that results from the



(*a*) (*b*)

Figure 1.3. Water absorption by superabsorbent polymer: **(a)** dry granule and **(b)** swollen gel particle. Magnifications ×25.

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difference of water concentration between the inside and the outside of the particle, and water stops moving into the particle. The position of the resulting equilibrium depends on the interconnected structure of the polymer in the particle and on the nature of the liquid that diffuses into the particle.

The process of diffusion is described by Fick's law (Eq. 1.5), which relates the diffusional flow rate f to the concentration gradient dc/dx of the diffusing substance in the sample

$$\frac{f}{A} = -D\frac{dc}{dx} \tag{1.5}$$

where f is the flow rate in the x direction, A is the cross-sectional area of the sample, and D is the diffusion coefficient (proportionality constant).

It is important to recognize that different mechanisms control the motion of fluids in absorbent and superabsorbent materials, even though the flow phenomena may be described mathematically in similar ways.[8] For absorbents, the flow rate is proportional to the pressure gradient according to Darcy's law (Eq. 1.1). The gradient may be a result of a positive, hydrostatic liquid pressure head or a negative, capillary suction pressure. Therefore, the flow depends on the leveling of water at two different heights by gravitational force, or the surface tension of a liquid pulling water along a wetting surface. For superabsorbents, the absorption is proportional to the gradient of chemical activity, according to Fick's law. The flow depends therefore on the random motion of individual molecules and on their size and thermal energy. This is not to say that physical phenomena such as liquid leveling and surface tension of the liquid are not important in the functioning of superabsorbents. In any practical application of superabsorbent polymers, liquid must flow to the surface of the superabsorbent polymer before the diffusive process can begin, and the ability of the liquid to spread on the surface of the superabsorbent polymer, and flow between the particles, will affect the process. A simplified approach to convective flow in particulate masses of deformable gels is described in Chapter 5. Because the absorption process in superabsorbents depends on the size and thermal energy of the molecules, the resulting changes in the state of the molecules after absorption are of principal interest.

When superabsorbent polymers absorb liquids, an elastic gel forms. The gel is a soft, deformable solid composed of water and the expanded polymer chains. The expansion of the polymer chains is limited by the crosslinks. The behavior of the gel at equilibrium may be described by an equation of state, which is analogous to the equations of states of gases, for example, the ideal gas law

$$PV = nRT \tag{1.6}$$

where P is the pressure in the gas, V is its volume, n is the number of gas molecules, R is the gas constant, and T is the temperature of the gas. Similarly, the state of the gel may be given in terms of the pressure, which is manifested as the rigidity (modulus) of the gel and which derives from the elasticity of the polymer chains in the

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gel, the volume, which depends on the amount of liquid absorbed, the number of polymer chains that forms the gel, and the temperature of the gel. The interrelationships of these factors are described more fully in Chapter 5. The principal features of interest in the technology of superabsorbents are the volume of the gel and how to optimize the volume in light of the other properties and the methods used to synthesize the polymer. These factors are described more fully in Chapters 2 and 3. The fundamental relation, however, is that the volume is inversely proportional to the elastic modulus of the gel, just as the volume of an ideal gas is inversely proportional to the pressure of the gas. This relationship is demonstrated in Figure 1.4, which shows the relationship of the equilibrium swollen volume of a superabsorbent polymer gel to its shear modulus G. Both quantities are controlled by the extent of crosslinking in the sample.

1.2.2. Superabsorbent Polymer Types

1.2.2.1. Polyelectrolyte Vs. Nonpolyelectrolyte Hydrogels. Absorbent polymers may be divided into two classes: nonionic and ionic polymers. The ionic polymers may be further classified into anionic and cationic polymers. Nonionic polymers absorb water and aqueous fluids by means of the energetic and entropic interactions made possible by mixing the aqueous fluids with the hydrophilic groups that are present along the polymer chain. The hydrophilic groups are solvated by the water molecules through hydrogen bonds. In addition, the entropy of the system may be increased during mixing by a decrease in the partially ordered struc-

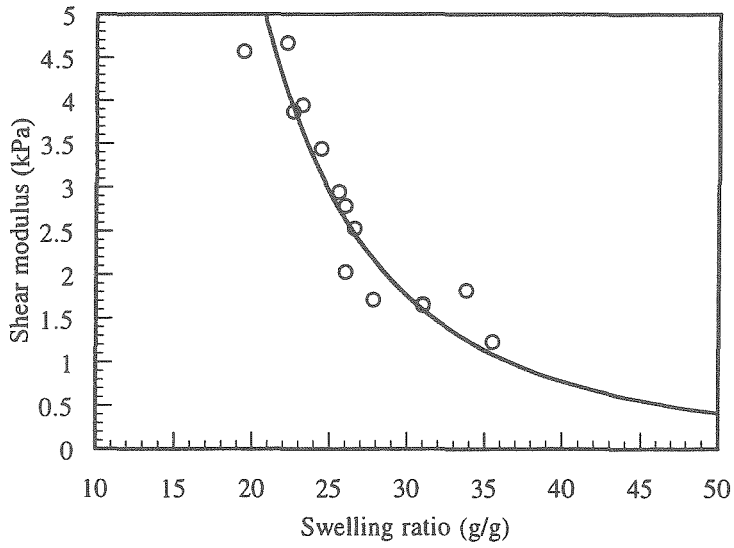


Figure 1.4. The correlation of shear modulus to the swelling ratio for superabsorbent polymers swollen to equilibrium in 0.9% NaCl solution. The samples vary in crosslink density. The shear modulus scales as the −2.83 power of the swelling ratio in this figure.

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ture of pure, liquid water. These are the same phenomena that lead to the dissolution of water-soluble polymers. The principal distinction of absorbent polymers over water-soluble polymers is the presence of crosslinks within the molecular structure of the absorbent polymers. The crosslinks connect the various polymer chains into a huge, insoluble molecule that nevertheless can change its shape and volume as it becomes solvated by water. The result of the absorption of solvent is a swollen, soft gel.

Superabsorbent polymers are in distinct contrast to the nonionic absorbent polymers. The energetic and entropic mechanisms present with nonionic polymers are still operative, but are largely overshadowed in magnitude by the presence of the ionic charges that are spaced along the polymer chains of superabsorbent polymers, as shown above in Figure 1.2. The presence of the polymeric ions results in increased absorption because the ions are more strongly solvated than nonionic functional groups, as a result of strong ion–dipole interactions. The ions that are fixed to the polymer chains (negative carboxylate groups or sulfonate groups, or positively charged quaternary ammonium groups, for example) also repel each other (coulombic interaction) and tend to stiffen the polymer chain. As a result, the stiffened chain occupies a greater solvated volume. Because electrical neutrality is required for the polymer, each of the charges along the polymer chain must be matched with an ion of opposite charge. These counterions also are solvated strongly. As a result of their large number in the polymer system, a large driving force for swelling (osmotic pressure) is present. From a thermodynamic perspective, there is no difference in the effects of positively charged polymer chains compared with negatively charged chains, but there is a difference in the mass efficiency of the absorption process, as described below.

1.2.2.2. Covalent Vs. Ionic Vs. Physical Gels. The nature of the crosslinks plays a significant role in the properties of superabsorbent polymers. There are three principal bonding types that are used to bind the polymer chains together: covalent, ionic, and hydrogen bonds. Two basic methods are used to introduce covalent crosslinks. Covalent crosslinks are formed when the major monomer (e.g., acrylic acid) is copolymerized with a di-, tri-, or tetra-vinyl monomer such as *N,N′*-methylenebis(acrylamide), 1,1,1-trimethylolpropanetriacrylate, or tetraallyloxyethane, in a free-radical initiated addition polymerization.[9] The structures of some of these crosslinkers are shown in Chapter 2 (see Fig. 2.2). Covalent crosslinks are also introduced by reacting the preformed polymer chains with a di- or tri-functional reagent that reacts with (for example) the carboxylic acid groups by means of a condensation or addition reaction. This type of crosslinking is analogous to the vulcanization of rubber. An example of a condensation reaction used with superabsorbent polymer is a simple esterification of the carboxylic acid groups with ethylene glycol or glycerol. Such an esterification of poly(acrylic acid) and poly(vinyl alcohol) was used to make one of the early examples of a chemomechanical, polyelectrolyte gel[10] that may be induced to change its state by the application of an electrical potential across the sample. An example of an addition reaction is the addition of the carboxylic acid function to the oxirane rings of ethyleneglycol

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diglycidyl ether,[11] as shown in Chapter 2 (see section 2.7.3). One benefit of covalent crosslinks is that they are permanent and stable with time, so that the properties are maintained during use. By proper choice of the crosslinker and the synthetic conditions, some control over the placement of crosslinks is achieved.

Ionic crosslinks are formed by reacting a polyvalent ion of opposite charge with the charged polymer chains. The crosslink forms as a result of charge association of the unlike charges. Examples are crosslinking of carboxylic acid with aluminum [12] or chromium ion or with an organic polycation such as a diquaternary ammonium compound. Because the bond is formed by ion association (charge neutralization), the chemical structure of the crosslinker is less important in determining the placement of the crosslinks compared with covalent crosslinks. If ionic components are present in the liquid to be absorbed, ion exchange may occur with the ionic crosslinks, which may alter the nature of the crosslinks and the behavior of the polymer in ways that may be unforeseen. Also because the interionic reaction is very fast, the incorporation of the crosslink and the resulting structure of the crosslinked polymer can be difficult to control.

A third type of crosslink is the physical crosslink, which is usually formed by means of hydrogen bonding of segments of one chain with the segments of another chain. A classic example is the gelling of gelatin solutions, wherein the regular structure of the polypeptide chains allows strong hydrogen bonding between chains and the formation of associated regions of polymer segments that act as crosslinks. A principal drawback of such crosslinks is that they can be destroyed by merely heating the polymer. The crosslink region typically extends over many segments of the polymer chains, leading to poor mass efficiency of crosslinker.[13]

1.2.2.3. Survey of Polymers. A number of nonionic water-soluble polymer types are known, and these may be used as absorbent polymers when crosslinked in a suitable fashion. As before, a distinction is made between nonionic and ionic polymers. Outside of the large contribution of ions to swelling, several other characteristics of the polymer system are important for making absorbent polymers. For example, the molecular weight of the polymer chains should be large for optimum absorbency (see Chapter 5). But the maximum size of polymer chains that it is possible to make depends on the structure and reactivity of the monomers and the synthetic conditions (see Chapter 2). Also, the absorbency depends on the mass of the monomer unit and its solvating character. A high-molecular-weight, hydrophobic monomer will not yield an absorbent polymer optimized for water absorption on a weight basis. In addition, the relative cost of the monomers affects the cost-effectiveness of absorption, as does the relative complexity of the processing steps necessary to synthesize the polymer. The following brief survey of absorbent polymer types is given with these characteristics in mind.

Polyacrylamide is a well-known water-soluble polymer and has been crosslinked by numerous methods to form an absorbent polymer.[14] Unless some of the amide functions are hydrolyzed to anionic carboxylates, the polymer is nonionic. Acrylamide is one of the very few monomers that can be easily polymerized to extremely high molecular weight (~10 million g/mol), which is an advantage for making ab-

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sorbent polymers. A principal drawback is the practical difficulty of reducing the quantity of residual acrylamide in the final product to extremely low levels. This is desirable because of the well-documented toxicology of acrylamide monomer. The monomer is relatively inexpensive.

Poly(ethylene oxide) has rarely been used as an absorbent polymer, even though the monomer is relatively low in cost. Processing of the gaseous, highly reactive ethylene oxide adds to the cost of the polymer, and preparing stable, very-high-molecular-weight polymers is difficult. The molecular weight is limited to about 600,000 g/mol. Crosslinking may occur either by endlinking the hydroxyl end groups with an appropriate reagent (e.g., polyisocyanates) or by means of radiation treatment. Efficient endlinking is quite difficult for very-high-molecular-weight prepolymers as a consequence of the low concentration of end groups. Radiation crosslinking typically involves some chain scission events, which lower the molecular weight and the resulting effectiveness of the absorbent polymer. In addition, poly(ethylene oxide) is highly crystalline (T_m = 66°C), and water absorption is significantly suppressed as a result.

Poly(vinyl alcohol) gels have been extensively studied as absorbent polymers. They are prepared by reacting vinyl acetate to form poly(vinyl acetate), transesterifying the poly(vinyl acetate) to poly(vinyl alcohol), and finally reacting with a crosslinker such as a polycarboxylic acid (forming ester crosslinks), sodium borate (forming borate complexes), or glyoxal. Poly(vinyl alcohol) is limited to practical molecular weights of about 700,000 g/mol as a result of significant chain transfer reactions to the monomer and can be highly crystalline (depending on the mole fraction of hydroxyl groups), both features that limit the swelling. The monomer is moderately expensive when considered on a "vinyl alcohol" basis.

The primary example of a commercially available polypeptide is gelatin, which is a common food additive. This is a relatively expensive polymer, which must subsequently be crosslinked. The extensive hydrogen-bonded structure, which leads to the well-known physical gelation of a cooled gelatin solution, also results in less mass-efficient water absorption.

The principal superabsorbent polymer used commercially is crosslinked, partially neutralized poly(acrylic acid).[15] Some graft copolymers are also employed, such as partially neutralized starch-g-poly(acrylic acid) and partially neutralized poly(vinyl alcohol)-g-poly(acrylic acid). The polymer is made from acrylic acid and sodium hydroxide or sodium carbonate (and the grafting agent if desired), which are relatively inexpensive reagents. The polymer is most often made by co-polymerizing the partially neutralized acrylic acid in aqueous solution with a di- or tri-vinyl crosslinking monomer. There are many acceptable crosslinkers available commercially (see Chapter 2), and one commonly used crosslinker is 1,1,1-trimethylolpropane triacrylate. Acrylic acid forms relatively high-molecular-weight polymers, with molecular weights typically in the range of 1–3 million g/mol. Acrylic acid is not usually co-polymerized with monomers other than the crosslinkers, because most other monomers are more expensive than acrylic acid and usually provide no performance advantage to offset the higher cost.

Another well-known superabsorbent polymer is the "super slurper," which was

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2

CHEMISTRY OF SUPERABSORBENT POLYACRYLATES

Thomas L. Staples, David E. Henton, Fredric L. Buchholz

Among the absorbent and superabsorbent polymer types described in Chapter 1, the crosslinked, partially neutralized poly(acrylic acids) are the principal superabsorbent polymer of commerce. Numerous other polymers have been crosslinked to form water-swellable gels, but no other polymer can provide the high charge-to-mass ratio as economically as poly(sodium acrylate). For this reason, this chapter on the chemistry of superabsorbent polymers is restricted to the formation of crosslinked networks of poly(acrylic acid) and its salts.

General descriptions of other absorbent and superabsorbent polymer types are available in the literature. Gels of some of the cellulose-based, water-swellable polymers, such as sodium carboxymethylcellulose, are described by Doelker.[1] Alginate gels are described by Segeren et al.[2] and Aslani and Kennedy[3] and in the numerous references therein. Other biopolymer gels have been described by Clark and Ross-Murphy[4] and Clark.[5] Hydrogels of poly(vinyl alcohol) are reviewed by Peppas,[6] and those of poly(ethylene oxide) are reviewed by Graham[7] and Apicella et al.[8] More extensive discussions of these and other alternatives to polyacrylate absorbents may be found in Chapter 6.

To introduce the descriptive chemistry of superabsorbent polymers, we first present two example polymerizations. Polymerization kinetics are then discussed in some detail, illustrating how process conditions affect the structure of the polymer

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Table 3.1. Worldwide production capacity for producers of superabsorbent polymer (thousand metric tons [t])

Producer	1986	1989	1992	1995	1996	1998[g]
Allied Colloids	2.0	2.0	11.4	15.5	15.5	30.9
AMCOL Int. (Chemdal)	—	20.0	20.0	110.0	120.0	120.0
Arakawa	4.0	4.0	6.0	6.0	6.0	6.0
Atochem	—	5.0	8.0	9.0	12.0	12.0
Dow Chemical	22.7	46.4	60.0	90.0	90.0	120.0
U.S.	22.7	36.4	50.0	50.0	50.0	80.0[a]
Europe	—	10.0	10.0	40.0	40.0	40.0
Formosa Plastics	—	0	6.0	12.0	12.0	12.0
Hoechst	—	29.0	55.0	97.0	97.0	97.0
U.S. (Hoechst Celanese)	—	24.0	40.0	69.0	69.0	69.0
Europe (Casella)	—	5.0	15.0	28.0	28.0	28.0
Kao Soap	—	5.0	10.0	10.0	10.0	10.0
Kolon	—	—	—	12.0	12.0	24.0
Mitsubishi	—	0	10.0	10.0	10.0	10.0
Nalco[b]	—	20.0	40.0	45.5	45.5	45.5
Nippon Shokubai	15.0	37.9	84.0	131.0	141.0	141.0
U.S. (NA Industries)	—	6.0	12.0	30.0	36.0	36.0
Europe (BASF)	—	0.4	12.0	20.0	24.0	24.0
Japan	15.0	31.5	60.0	81.0	81.0	81.0
Nippon Synthetic[c]	—	3.0	4.5	6.8	10.0	10.0
Sanyo	8.0	17.0	20.0	50.0	55.0	55.0
Sekisui	—	0	3.0	6.0	6.0	6.0
SNF	—	0	0	2.0	7.0	22.0[d]
Stockhausen	—	50.0	79.5	110.9	110.9	110.9
U.S.	—	20.0	29.5	55.5	55.5	55.5
Europe	—	30.0	50.0	55.5	55.5	55.5
Sumitomo	3.1	5.6	8.0	22.0	32.0[e]	59.0[f]
Toa Gosei	—	0	10.0	10.0	10.0	10.0
Total	54.8	245.9	435.5	755.6	801.8	901.3

Data for 1992–1998 are from TranTech Consultants Inc. (TranTech began compiling their ChemPlan database for SAP in 1991.) Data for 1986 and 1989 are from The Dow Chemical Co. internal market studies.

[a]Includes 30,000 t potential capacity at low additional cost.

[b]Acquired by Stockhausen in 1996.

[c]Transferred technology and marketing rights to Mitsubishi in April 1996.

[d]Has capability to produce 15,000 t in Riceboro poly(acylamide) line.

[e]10,000 t of this capacity is suspension polymer.

[f]10,000 t of this capacity is suspension polymer. Total capacity includes 27,000 t/yr for Singapore for 1998.

[g]Estimated.

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small in the major populated countries of Asia. Current manufacturers of acrylate-based superabsorbents in the United States include The Dow Chemical Co., Hoechst Celanese Corp., under a license from Sanyo Chemical Industries,[7] NA Industries (a subsidiary of Nippon Shokubai Co., Ltd.), AMCOL International (Chemdal), and Stockhausen GMBH. AMCOL has recently added significant manufacturing capacity both in Europe and in the United States. European superabsorbent manufacturers include AMCOL, Stockhausen GMBH, Dow, Hoechst Casella, Allied Colloids, Ltd., and BASF Aktiengesellschaft in partnership with Nippon Shokubai.[8] Japanese producers include Nippon Shokubai, Sanyo, Mitsubishi Petrochemical Co., Ltd., Kao Soap, and Sumitomo Seika. There are also a number of smaller producers in the United States, Europe, and the Far East. Elf Atochem S.A., Sumitomo Seika, and Kao Soap have been the three most prominent users of a suspension process to make superabsorbent polymers.

The synthesis and use of crosslinked, partially neutralized, polyacrylate superabsorbents have been the subject of several reviews[1,2,9–11]; however, very little information about manufacturing processes has been given. Perhaps the most unique, and arguably the first, commercial process is the polymerization technology patented by Sanyo[12] and licensed[7] to the Hoechst companies. Acrylic acid, in aqueous solution, was simultaneously polymerized, crosslinked and grafted to starch, and then neutralized and dried. Over the last 10 years, the dominant commercial technology for manufacturing superabsorbents has been solution polymerization of partially neutralized acrylic acid in the presence of a crosslinker using free-radical initiators, typically without a graft substrate. The resultant hydrogel is dried and ground to the desired particle size. Reverse-phase suspension polymerization is also practiced, but volumes produced are small relative to those from solution polymerization.

In this chapter, aspects of polymerization technology are reviewed, emphasizing commercial practice. While the review of the patent documents is intended to be thorough, it is not exhaustive. Our hope is to provide some insight into the interaction of engineering and chemistry in the design and implementation of commercial processes for the manufacture of superabsorbent polymers.

3.2. SOLUTION POLYMERIZATION: UNIT OPERATIONS AND THEIR EFFECT ON PRODUCT QUALITY

3.2.1. Introduction to Solution Polymerization Processes

3.2.1.1. Scale-Up Considerations. The initial development of a new superabsorbent polymer typically takes place at the laboratory scale, employing from a few grams up to several hundred grams of reactants. As with other polymeric products, it is convenient to think about the chemistry of the superabsorbent polymerization process as chemistry at the parts per thousand or parts per million scale (ppm). Polymerization initiators and crosslinkers are used at levels ranging from a few tens of ppm to several thousand ppm. Impurities in the monomer can have a strong effect on both the polymerization process and product quality. For example, the inhibitor methyl ether of hydroquinone (MEHQ), acrylic acid dimer discussed in Chapter 2,

or iron as an (unwanted, variable) catalyst for an initiator system each affects the process when present in very small quantities.

Early patents cite examples involving small-scale experiments, while later patents focus on problems associated with commercial scale processes. Typically, as the size or volume of the equipment or process increases, the impact on the final product properties of variables or processes (unit operations), taken for granted in small-scale laboratory work, becomes significantly more important. The larger quantities of raw materials and product handled at a commercial scale require greater and more detailed knowledge of the chemistry and engineering variables.

At the laboratory scale, reactants are typically weighed to several significant figures and then mixed in open beakers either on a bench top or in a fume hood. At the manufacturing scale, liquid reactants are handled in closed containers of up to several thousand gallons and moved from one container to another in piping made of appropriate materials of construction. Quantitation of reactants may be accomplished by load cells attached to a vessel, by a level measurement in a vessel, or by integrated flow measurements. In each of these cases, process considerations affect the ability to hit the desired target quantity. For instance, the time needed to open or close a valve in a large-scale manufacturing facility affects the amount of material that is transferred through that valve and must be accounted for in the plant operations. Small-quantity additives may be weighed with great accuracy using an analytical balance in the laboratory. However, at a commercial scale they are added either continuously and quantitated using in-line flow meters, weigh-cells mounted on one of the vessels, or batch-wise using a small closed vessel ("shot pot") that may weigh 10–10,000 times more than the quantity of reagent being added from or to that container. Other variables affecting scale-up of most processes include mixing and heat transfer. Also of concern in a commercial process are releases of small amounts of vapors or liquids to the environment, which, on a laboratory scale, would be handled, for example, in a fume hood. The need to process large quantities of raw material, in-process intermediates, and product, and the manner in which the process actually functions, are affected by these considerations. These factors should be considered in the discussion that follows.

Typically chemists and engineers are most familiar with chemical reactions that take place in the liquid state because liquid-state reactions are the most easily managed at any scale. Applying the principle that research effort should be focused on the most obvious issues first, typically, at least initially, the primary reaction step is considered most fully. As the development of superabsorbents has proceeded, the problems associated with the polymerization reaction have been solved, and the importance of process steps (unit operations) beyond the polymerization reaction has become more evident. These other process steps include preparation of the wet hydrogel for drying, drying of the wet hydrogel, sizing of the dried particles to a size useful for the diapers, and the addition of additives for property enhancement.

3.2.1.2. Overview of Unit Operations. Figure 3.1 is a block flow diagram of a generic solution polymerization process. This diagram represents laboratory practice as well as commercial processes of the major superabsorbent polymer manufac-

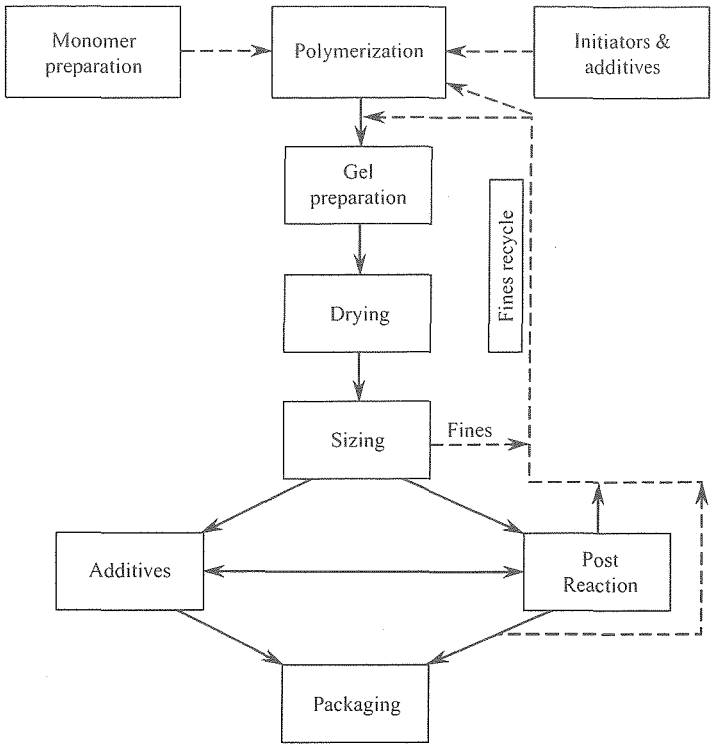


Figure 3.1. A block flow diagram of a generic solution polymerization process.

turers. A monomer mix is first prepared (see section 3.2.2) from acrylic acid, water, a crosslinking monomer, and, in many cases, a base, and then transferred to a reaction vessel. Contacting the monomer mix with an inert gas, either in-line during the transfer or in a batch process, for example, by bubbling with nitrogen, removes oxygen from the liquid. Addition of free-radical initiators, for example, sodium persulfate, or redox couples, for example, ascorbic acid and hydrogen peroxide, causes the monomer mix to polymerize (see section 3.3.3) with the evolution of heat (~77.4 kJ/mol acrylic acid).[13] The reaction mix begins to gel at just a few percent conversion as a result of crosslinking and the high backbone molecular weight. During the polymerization process, the gel may be broken up to produce a rubbery particle that is either dried directly or further reduced in size to facilitate drying. High monomer conversions (90%–95%) are attained in reaction times as short as 30 min. However, the polymer intermediate is held for an extended period of time at elevated temperature, in the reactor or in a separate hold tank, to achieve the ultrahigh conversion required in the dried commercial products.

Various types of dryers, including through-circulation conveyor dryers, fluidized-bed dryers, and rotating drum dryers (see section 3.2.5), are used to dry the polymer. A combination of grinding and screening the dried gel gives the final

product particle size distribution. The presence of extremely fine particles ("fines"), typically less than 140 μm in diameter, has been unacceptable in the commercial product for diapers. Several means of converting the fine material to other saleable products, or recycling it in the current process, are described in section 3.2.7.

Technology for preparing products with a higher degree of crosslinking on the surface has long been known and is useful as a means of increasing absorption rate. More recently, superabsorbent products with an improved combination of swelling capacity and absorption under a compressive load (see Chapter 5) have been realized using such structured particle technology. Often, a crosslinker is added to the desired particle size distribution and is reacted to yield the structured product. Patents describing the chemistry indicate that a variety of blenders and heating devices are suitable.

Most unit operations in a commercial superabsorbent polymer plant have the potential to release small quantities of acrylic acid, other organics, or particulates to the environment. For example, as the polymerization reactor is filled with liquid, the vapor in the vessel is displaced and must be treated to remove any acrylic acid vapor before being released to the environment. The hot, moist gel fed to a dryer may release small quantities of unreacted acrylic acid into the surrounding air, creating an industrial hygiene problem for plant personnel. Also, in addition to containing unreacted acrylic acid, the air used in a through-circulation dryer to transfer heat to the polymer may contain fine particles of dry polymer product. These would need to be removed before the air from the dryer is returned to the environment. Enclosing the operations allows the air to be treated to remove contaminants. All major U.S. and European manufacturers treat their air streams to reduce emissions.

3.2.2. Raw Material Preparation

In this step, the ingredients to be added to the reactor, acrylic acid, water, an optional graft substrate, for example, starch[12] or poly(vinyl alcohol) solution, and a base, are prepared,[14–18] usually in a batch-wise fashion. The decisions taken in this step affect how the rest of the process operates, particularly the polymerization reaction, and are the primary determinants of the network structure of the dried particle. Monomer concentration (polymerization solids), the degree of primary crosslinking, and percent neutralization of the final product are typically set in this step. The degree of crosslinking affects the final product performance properties, swelling, and modulus (see Chapter 5). The degree of neutralization also affects the swelling behavior of the final product. However, when the pH of the product is to be maintained in a range safe for contact with human skin,[18] the most desirable percent neutralization is from 60 to 90 mol%. The monomer concentration in the reaction step determines, throughout the reaction, the demands on the heat removal system and the rheology of the partially polymerized hydrogel. The modulus, swelling capacity, and amount of extractable polymer of the polymer gel, determined in the polymerization step, affect its subsequent handling.

The primary monomer is high purity acrylic acid alone or in combination with its partial sodium or potassium salt. Typical impurities in acrylic acid include the

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dimer of acrylic acid, the polymerization inhibitor MEHQ, and small amounts (ppm) of several other materials. In at least one case, purification by distillation, just prior to use, of the acrylic acid monomer removes the inhibitor MEHQ and removes acrylic acid dimer to prevent the formation of β-hydroxypropionic acid.[19]

The formation of diacrylic acid (acrylic acid dimer) from acrylic acid during storage has long been known. The rate of formation is temperature dependent and dependent on the amount of moisture present as an impurity in the acrylic acid; this has been thoroughly documented.[20] The dimer of acrylic acid can be decomposed by heating[21] at temperatures from 120° to 220°C, yielding 2 mol of acrylic acid.[22,23] Acrylic acid dimer, because it contains a double bond, may also be incorporated into the polymer backbone.[20] A portion of the incorporated dimer may be cleaved during the drying of the polymer and apparently leads to 1 mer of polymer backbone and 1 mer of acrylic acid. The percentage of dimer cleaved depends on the heating temperature.[24] The unreacted acrylic acid is detectable as residual monomer. To minimize the amount of acrylic acid detectable in the product, the quantity of dimer in the acrylic acid feed is generally minimized.

Acrylic acid containing dimer may be treated with strong aqueous base prior to polymerization.[20,24,25] The reaction product of dimer hydrolysis is 1 mol of acrylate ion and 1 mol of β-hydroxypropionic acid. The β-hydroxypropionic acid may be trapped in the polymer matrix (although not polymerized) and will not be detected as residual acrylic acid by standard techniques (see Chapter 4, section 4.4.1). The β-hydroxypropionic acid may also be dehydrated to acrylic acid during a heating step.[26] However, it is our experience that higher temperatures are required to dehydrate β-hydroxypropionic acid than are required to thermally cleave acrylic acid dimer incorporated in the polymer backbone.

MEHQ is added to acrylic acid during its manufacture and acts in combination with oxygen as a polymerization inhibitor during storage and handling. It is normally present in acrylic acid at 200 ± 20 ppm. MEHQ, in combination with the thermal initiator persulfate ion can contribute to color formation in the final product.

A primary crosslinker is used at concentrations of about 500 ppm to 1 wt% (0.01–0.2 mol%), based on acrylic acid, so that the reaction product will be a crosslinked gel of the desired swelling capacity. Suitable divinyl crosslinkers include trimethylolpropane triacrylate, methylenebisacrylamide, diethyleneglycol diacrylate, triallylamine, allyl methacrylate, tetraallyloxyethane, and the like.[17,18,27–29] The choice of crosslinker,[30] through the crosslinker reactivity ratio, in combination with other polymerization parameters, will affect the amount of soluble polymer produced. Additional minor components in the reaction mix include chelants and dispersants,[28] or surfactants,[18] to aid in the solubilization of the hydrophobic crosslinkers.

Lower monomer concentrations have been chosen to improve end-use properties[18,31] or to facilitate handling. However, operating at the highest monomer concentration possible improves reactor throughput, in mass of product per unit time, and economics. However, as monomer concentration increases, a higher adiabatic temperature rise is possible (Fig. 3.2). Thus, higher monomer concentrations, in combination with temperature-sensitive initiator systems, lead to higher tempera-

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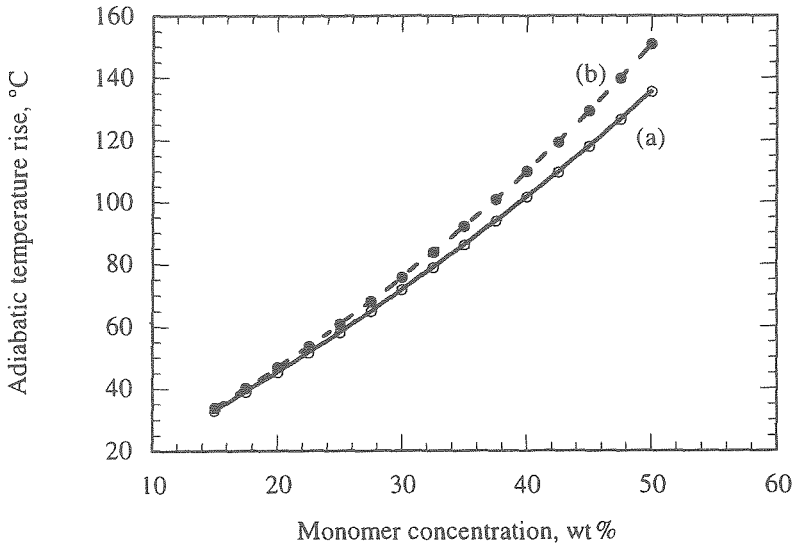


Figure 3.2. Adiabatic temperature rise for polymerizations of crosslinked partially neutralized acrylic acid as a function of monomer concentration. The heat of polymerization of acrylic acid was taken as 77.4 kJ/mol, and the heat capacity of the polymer was taken as either 0.50 **(a)** or 0.35 cal/g°C **(b)**.

tures and higher initiation rates near the end of the polymerization when monomer concentration decreases. As a net result, lower molecular weight chains are produced near the end of the polymerization. If the crosslinker concentration is constant or decreasing, which depends on the relative reactivity of the crosslinker and the monomer, the shorter chains are less likely to be crosslinked into the network structure. Therefore, larger quantities of undesirable[31] extractable polymer (lower molecular weight polymer, not crosslinked into the network structure) are produced toward the end of the polymerization. Commercially useful monomer concentrations range from about 15% to 30% for the polymerization of acrylic acid[12] and from 30%–43% for the polymerization of partially neutralized monomer.[16,17,25,28,29,32,33]

The degree of neutralization (mole basis) used for polymerization ranges from 0% (unneutralized)[31,34,35] to 80%. When acrylic acid is polymerized, the polymer is subsequently neutralized to an extent of 50%–80%, most typically from 60% to 75%, by adding a solution of sodium hydroxide or sodium carbonate to the acidic gel polymer. At the commercial scale, neutralization of the monomer may be accomplished either by simply adding the aqueous base to the acid monomer or by more involved processes. In one specific process[25] the monomer is neutralized to greater than 100.1 mol% and held at that composition for up to 2 hours to hydrolyze acrylic acid dimer to β-hydroxypropionic acid.[19,25] The pH of the monomer mix must be greater than about a pH of 12 to effectively hydrolyze the acrylic acid

dimer.[24] This process results in a reduction in the residual monomer content of the final product.

Several orders of addition of reactants are possible, including the order specifically described earlier in discussing the neutralization process. The order of addition of ingredients may also be adjusted to accommodate factors such as crosslinker solubility or crosslinker sensitivity to hydrolysis. The crosslinker may be added to the acrylic acid prior to neutralization or to the fully neutralized monomer mix. If desired, the oily crosslinker may be dissolved in a portion of the acrylic acid prior to addition of the mixture to the balance of the neutralized monomer mix. Other orders of addition are described in the examples of the references of this section. After preparation, the monomer mix is moved to the polymerization step.

3.2.3. Polymerization Vessels and Systems

In the polymerization process, the monomer mix prepared in the previous process step is converted to a hydrated gelatinous rubbery polymer (hydrogel) with the evolution of heat. The polymerization vessel used for this process has substantially different requirements placed on it compared with a vessel for a liquid system because of the rubbery, semisolid nature of the crosslinked polymer hydrogel. In liquid systems, mixing in a reaction vessel is often of primary concern as a means of both uniformly mixing reactive ingredients and improving heat transfer required to maintain a uniform temperature in a vessel. However, essentially no mixing can take place after gelation, which occurs at only a few percent conversion, because of the high monomer concentrations, the high molecular weights achieved, and the presence of crosslinker.

The temperature increases in a reaction system if the rate of heat generation (rate of reaction) is faster than the rate of heat removal. Adiabatic or nearly adiabatic polymerizations of acrylic acid or partially neutralized acrylic acid can be very rapid, taking only 10–30 min to go from a few percent conversion to over 90% conversion (Fig. 3.3). This situation is favorable economically because it permits a high space–time yield for the capital dollars invested in reaction equipment. The kinetics of adiabatic polymerizations of acrylamide[36] and methyl methacrylate[37] have been reported and are similar in many features to those observed for acrylic acid or partially neutralized acrylic acid (see Chapter 2). Smaller molecular weight at high conversion (and higher temperature) results from lower monomer concentration, increased probability of chain transfer reactions, and increased initiation rate from the thermally activated initiators used for the polymerization. Therefore, to control the temperature of polymerizations with relatively large adiabatic temperature rises, and to avoid polymer degradation at high temperatures,[18,31] an efficient means of heat removal is required. However, the ability to remove heat is also affected by gelation at low percent conversion. When the surface-to-volume ratio is low, efficient mixing is required to transfer heat to a cooling surface such as a reactor wall.

Several polymerization systems have solved these problems. In one case, polymerization of acrylic acid is conducted at only about 20 wt% acrylic acid, thereby reducing the need for heat removal by limiting the total heat released. Also, the

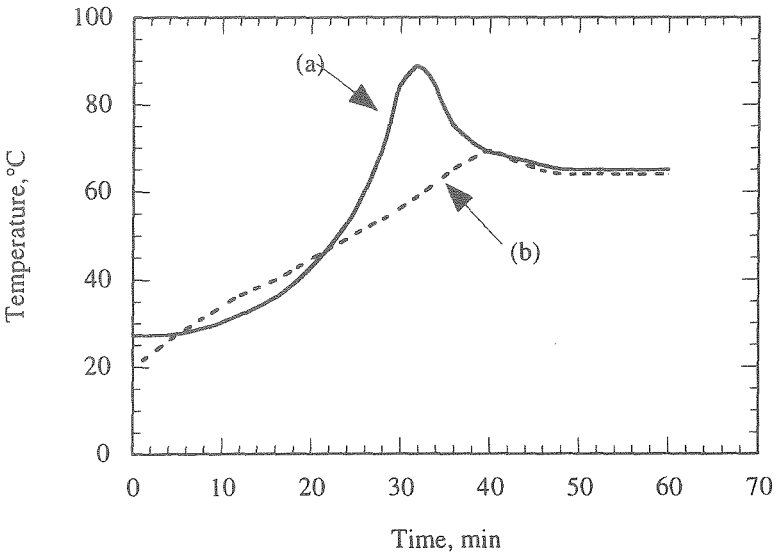


Figure 3.3. Temperature versus time for polymerizations in a 2-L laboratory reactor with no cooling except through heat losses to the atmosphere. Monomer solution 1,200 g was loaded to the reactor: **(a)** 32 wt%, 65% neutralized acrylic acid[28]; **(b)** 20 wt% acrylic acid.[35]

acidic hydrogel is more easily broken up than is the product that is neutralized prior to polymerization. In a second case, batch or continuous reaction systems have been designed that will grind the hydrogel into smaller particles, which may be easily removed from the reactor and which will permit heat removal from the rubbery polymer hydrogel. This system can be used for the polymerization of either acrylic acid or its partially neutralized salt. However, commercially, it is used for the polymerization of partially neutralized acrylic acid. In a third case, a continuous polymerization process has been developed in which the monomer is polymerized on a continuous belt. The thickness of the polymer layer is about 6–12 cm and may be several meters in width. The rate of heat loss from the relatively thin strand to the surroundings (or to the cooled belt) is apparently great enough to avoid problems with elevated temperatures in the reacting gel. The resulting strand may be successfully fed to a gel grinding device. This process is used commercially to polymerize partially neutralized acrylic acid.

In the first case above,[35,38] in which the concentration of acrylic acid and the need for heat removal are limited, solutions of acrylic acid at concentrations of 17–25 wt% have been polymerized to yield a high viscosity gel that can subsequently be extruded into strands. At these lower monomer concentrations, the adiabatic temperature rise is about 50°C (Fig. 3.2) so that a polymerization initiated at 20°C reaches high conversion by about 70°C. The patents specifically describe a batch polymerization process in which an "adiabatic reaction" is initiated at between 5° and 20°C, with a peak temperature of not greater than 90°C. "The peak temperature is controlled, if necessary, so as not to exceed 90°C," and is preferably about 70°C;

however, no information is given as to how the temperature control is accomplished.[35]

A reactor for the solution polymerization of acrylamide has been described in which the high-molecular-weight and high-viscosity, soluble, linear polymer is pushed or extruded from the reactor by a piston.[39,40] In the patent examples for crosslinked poly(acrylic acid) superabsorbents the polymerization vessel is only described as a stirred vessel, but a high-viscosity, gel-like product is pumped from the reactor and extruded (through a die) into strands. The patent descriptions seem to suggest a process that is an extension of the technology cited above for aqueous solution polymerization of uncrosslinked acrylamide or acrylic acid. The strands are chopped into small pieces so that subsequent gel handling and drying steps may take place satisfactorily.

The use of the crosslinker tetraallyloxyethane, the initiator system consisting of the redox pair ascorbic acid and hydrogen peroxide, and the thermal initiator 2,2′-bisamidinopropane dihydrochloride are specifically claimed for polymerizations of acrylic acid.[35] In another example, acrylic acid was polymerized at a concentration of about 25% and initiated with either a sodium sulfite or, preferably, sodium thiosulfate redox pair with *tert*-butyl hydroperoxide. The thermal initiators sodium persulfate and 2,2′-bisamidinopropane dihydrochloride were also used.[41]

In the second case, the need for improved heat removal led to several different reactor designs in which the rubbery, semisolid hydrogel could be broken into small pieces. The design of these vessels addresses, first, the need to control the peak polymerization temperature[18,31,35] and therefore removal of the heat of polymerization and, second, the need to size the polymer gel prior to drying.[18] These problems have been solved for reaction vessels mounted either vertically or horizontally (see below), and at least some designs may be used for either a continuous or a batch process. A common feature of these vessels is an agitation system designed to knead or tear the polymerizing rubbery mass into small pieces. As conversion (polymer concentration) increases, the modulus and strength of the partially converted rubbery gel increases. Under the stress of the agitation system, in a manner similar to that of taffy as it is being pulled, the rubbery hydrogel fractures to finally produce a collection of rubbery gel particles, each of which has a consistency somewhere between that of gelatin and an automobile tire.

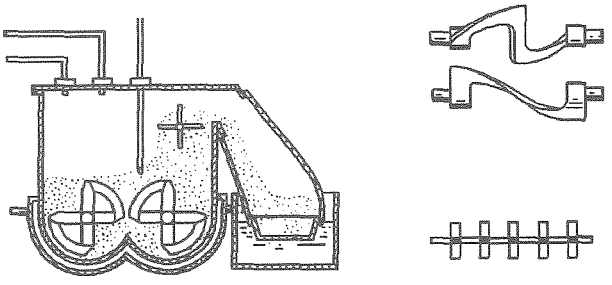
The size of the resulting pieces depends on the agitator configuration, especially on clearances between stationary and rotating members, and is characterized as a few millimeters to several centimeters. These smaller pieces have several advantages. First, smaller pieces are easier to handle than chunks the size of a commercial reactor (3–40 m^3). A reactor agitation system can move smaller pieces around within a reactor so that, over time, more hot polymer surface area will be able to contact a cold, jacketed, reactor wall and improve cooling. Also, the larger ratio of surface area to volume of small polymer pieces improves any cooling as a result of vaporization of water under an applied vacuum using a vacuum/condenser system.[28,32] Drying of the wet hydrogel is also more rapid using the smaller sized gel particles.[18]

A number of polymerization vessel types have been described in some detail: vertical agitated vessels[17,28,42] and several types of horizontal vessels.[32,43–45] The

horizontal vessels may have either a single shaft or several mutually parallel rotary stirring shafts[32,33] (Fig. 3.4). The agitators on both vertical and horizontal vessels have high torque agitation systems. The shear forces between the rotors and stators of the agitation system provide the energy to tear the polymerizing hydrogel into small pieces. Careful design of clearances between the agitator members and the reactor walls is required to produce the desired small hydrogel pieces and to avoid mechanical problems (for example, contact of rotor members with the vessel wall) that could lead to eventual vessel damage. Polymerizations at lower monomer concentrations require less shear energy to tear the hydrogel and, consequently, a less-robust agitation system, because, as monomer concentration is reduced, fewer carbon–carbon bonds must be broken to produce a unit of surface area in the polymerizing hydrogel. In all cases, the agitator members are designed to resist the mechanical stress of moving and tearing the semisolid rubbery hydrogel, and both vertical and horizontal vessels deliver a finely divided gel product.

In addition to careful design of agitator clearances for particle sizing, suitable agitation systems are all designed so that the combination of rotors and stators "scrape" all the surfaces of the vessel and the rotating members. The scraping action minimizes deposition of polymer on the vessel walls and on the agitator itself. A surface coating for the reactor walls such as tetrafluoroethylene resin helps prevent or minimize build-up of polymer.[32] A combination of very smooth reactor surfaces and vessel jacket temperature less than 70°C is also used to minimize fouling of the reactor wall and agitator.[46]

Either vessel configuration is suitable for the polymerization of either unneutralized[32,33] or neutralized[33] acrylic acid and may be used in a continuous[32] or a batch[33] polymerization process. Single shaft, two-arm, and three-arm "kneaders" are described. Where multiple agitator shafts are used, the shafts are rotated in opposite directions and may be rotated at unequal rates. Rotary stirring shafts may use blades of various types, including S-type, sigma, fish tail, and Banbury type blades. Efficient use of the capital invested in the polymerization vessels requires that the majority of the vessel contents are emptied from the reactor after each batch polymer-



(a) Reactor

(b) Two alternate stirring shafts

Figure 3.4. Dual-shaft jacketed kneader reactor and two other possible rotary stirring shafts. (Drawn from Tsubakimoto and Shimomura[32]).

ization. In one case, a "self-purging effect of more than 80%" is required.[43] Appropriate dimensions and blade arrangements have been briefly described.[43] In practice, either horizontally or vertically mounted reaction vessels can be used to polymerize superabsorbent polymers.

Polymerization vessels may be provided with a jacket through which hot or cold water may be circulated either to heat or to cool the reactor and contents. The polymerization vessel may also be connected to a condenser that provides heat removal during the polymerization.[28,32] Typically, condenser systems are used in which the condensate is drained back to the reaction vessel. In the early stages of polymerization,[43,47] reduced pressures may be used to fix the temperature and to remove heat by vaporization of water. In a second stage the temperature and pressure may be increased to 100°–170°C and 1–8 bar, respectively, to complete the polymerization.

Advantages of the kneader reactors in continuous service are those that would be expected. These include an improvement in operational efficiency in that once the reaction has reached steady state virtually no manual work is required to maintain the reaction and a more constant generation of heat of polymerization. Another advantage claimed for a kneader reactor, either in a continuous process or in a batch process, is that the reaction product is broken up into small pieces of a few millimeters in diameter with essentially no large chunks.[32]

Commercially, batch processes are used with polymerization vessels of the above types. A batch monomer mix, prepared as described above, is about 55%–80% neutralized and has a monomer concentration of about 30%–43%.[16,17,25,28,29,32,33] Recycling of dry ground fine particles to the polymerization by addition of the fines to the monomer mix is described in more detail in section 3.2.7.

To prevent excessively long reaction times, oxygen, required as part of the inhibitor system for storage of acrylic acid monomer, must be removed from the monomer solution prior to polymerization. Oxygen removal may be accomplished by the in-line addition of nitrogen as the monomer mix is transferred to the reactor[48] or by addition of inert gas (typically nitrogen or carbon dioxide) to the monomer either in the polymerization vessel or in a monomer storage vessel prior to the polymerization.[27] Possible mixing devices for in-line deoxygenation include static mixers of various types, aspirators, or perforated plates.[48] After addition to the reaction vessel and deoxygenation of the monomer mix, the free-radical polymerization of the monomer mix is initiated with redox pairs such as bisulfate/persulfate or ascorbic acid/persulfate.[16,25,49,50] Redox initiators are used so that the polymerization may begin at temperatures lower than those that are accessible using thermal initiators alone. Low initial temperatures, for example, 20°–25°C, are preferred for at least two reasons. First, low temperature initiation reduces the amount of heat that must be removed toward the end of the polymerization, and, second, polymerization at lower temperatures avoids some chain transfer reactions (see Chapter 2, section 2.4.4), which can reduce the average backbone molecular weight of the polymer. Thermal initiators such as sodium persulfate or 2,2′-bisamidinopropane dihydrochloride, are also required for optimum reduction of residual monomers toward the end of the polymerization.[51]

A belt reactor for the polymerization of water-soluble monomers, such as acry-

lamide and acrylic acid, was described in 1973.[52] An improved belt polymerization apparatus[53] and process[27] for using that apparatus were subsequently patented. The improved apparatus (Fig. 3.5) consists of a continuous belt whose shape can be changed by strategically placed rollers. The belt first provides a trough for the containment of liquid monomers that are added to the belt. As the polymerization proceeds, the monomer solution thickens and gels; the belt is caused to flatten and pull away from the polymerized gel mass. When the polymerization is complete, the gel strand is pulled over a guide roller, onto a spiked roller, and carried forward for further processing. Strand thicknesses of 6–12 cm and belt speeds of 5–12.5 cm/min are cited. A continuous, high monomer concentration process using two belts in series has also been described.[54] Although the claims of the patent are specifically limited to a high solids process,[54] this latter process is also expected to be adaptable to lower solids polymerizations and their consequent lower polymerization temperatures and higher product quality.

A comparison of patent examples shows that the chemistry used with the continuous single-belt process[27,53] is not significantly different from that described above for batch polymerizations. A batch monomer mix is first made up, as described above. The acrylic acid is about 55%–80% neutralized, and the monomer concentration ranges from 30%–43%.[27,29] Recycling of fine particles to the polymerization by addition of fines to the monomer mix, is also employed with this process. Catalysts can be redox pairs, photochemical initiators, thermal initiators, or combinations and are contained in the monomer mix as it is added to the belt. The catalysts are mixed "in a mixing tube" prior to adding the monomer mix to the belt. The

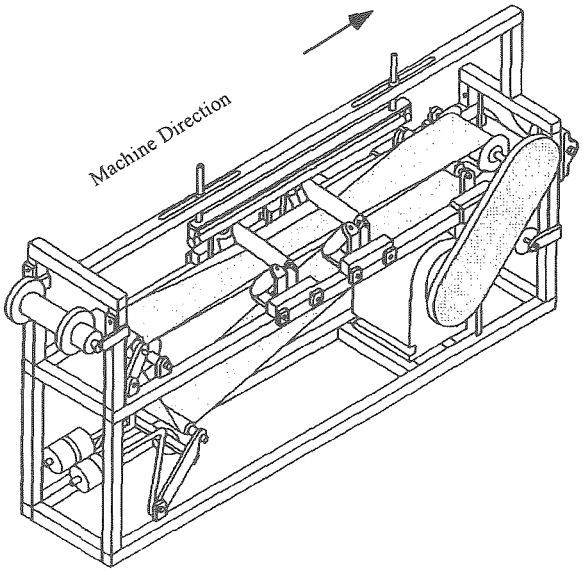


Figure 3.5. Continuous belt reactor with trough to contain liquid monomer. (Drawn from Chmelir and Paven[27]).

monomers have been deoxygenated prior to the addition of the catalyst. The monomer mix is then fed to the belt polymerizer.[27]

It is not clear whether the atmosphere above the belt is maintained oxygen free, as would be normally required to avoid inhibition of typical monomer systems. However, enclosing the belt in a hood might serve to minimize the volume that would need to be maintained oxygen free.

Polymerization temperatures above about 80°C adversely impact the product properties.[18,31] Higher adiabatic temperature rises are associated with higher monomer concentration combined with limitations on heat removal. Therefore, limitations on heat removal with increased strand thicknesses would constrain the combination of monomer concentration and strand thickness that could be used to obtain the desired product properties. Cooling and heating devices are referred to, but no details are given. In a subsequent patent, temperature control in a continuous process[55] is obtained by polymerizing the monomer mix between two continuous thermally conducting belts that are adjustable to provide a thickness of 1–30 mm. The belt surfaces are heated or cooled to maintain the desired temperature. Similar, modified, continuous processes may also be used to polymerize poly(acrylic acid) onto a substrate, for example, a fabric.[56] Deoxygenated monomer mix containing initiators is applied to a porous substrate. The monomer-impregnated substrate, sandwiched between two polymerization-inert surfaces, is polymerized by heating to 100°C.

In 1985, polymerization technology for a batch reactor without agitation or conventional heat removal was disclosed.[57] Monomer concentrations greater than 70% by weight are taught. Potassium hydroxide alone or in combination with ammonium hydroxide is used to neutralize the monomer. These bases are used instead of sodium hydroxide or sodium carbonate because of the higher solubility in water of potassium and ammonium acrylate than sodium acrylate. Initiation is provided by the redox system sodium bisulfite/sodium persulfate. As the heat of polymerization is liberated, water contained in the monomer mix boils, providing some temperature control to the polymerization. An advantage cited for this process is that a substantially dry (<15% by weight of water) product may be obtained without any special drying equipment.

A continuous process based on the previous batch process was also developed.[58] Monomer mix is pumped into the bottom of an inverted conical vessel, simultaneously with initiator solution. As the material polymerizes, it is forced out of the narrow top of the cone onto a moving belt. In one example, employing a 70% neutralized, 73% monomer concentration reaction mixture,[58] the maximum reaction temperature was 130°–135°C. Some cooling can be provided by circulating water in the jacket of the conical reactor. Additional cooling can be obtained by including 1%–10% of an organic solvent with a boiling point range of 55°–120°C. The polymerization is completed on the belt to yield a substantially dry (<15% by weight of water) product. As with the earlier batch process, cooling is provided by the evaporation of water and organic solvent as the heat of polymerization is liberated. The very high temperatures reached during the polymerization and their negative effects on the desired combination of product properties (low extractables, high modu-

lus)[18,31] are disadvantages of this process. Advantages include the substantially dry product (<15% by weight of water) and the fast absorption rate of the rather foamy product commercially produced by this process.

3.2.4. Gel Handling

3.2.4.1. Post-Reactor Chemistry. After the polymerization in the primary reactor has been substantially completed, as determined by the presence of a measurable exotherm, the conversion is expected to be in the range of 93%–97%. Additional time must be allowed for the reaction to proceed to higher conversion, typically about 98.5%–99.9%, prior to drying. This higher conversion is reached by holding the polymer at an elevated temperature for an extended period of time. In one case, after reaching the peak reaction temperature of about 70°C, the polymer is kept in an insulated vessel for 2–12 h so that the residual monomer is reduced below about 1,000 ppm.[35] In another process, "the reactor is maintained at a desired hold temperature for a period of time necessary for high monomer conversion to be achieved."[17] In another example, a two-stage reaction process is described. The first stage is used to set temperature and to remove heat by vaporization of water. The polymerization is completed in a second stage at a higher temperature and pressure.[43,47] These references imply that all of the reaction chemistry is accomplished in the polymerization vessel. However, for optimum capital utilization a second, separate vessel might be used while the reaction proceeds to very high conversions.

The time and temperature needed to reach high conversion was not specified by the examples cited above. The temperature of the product and the amount of time ("hold time") the product must spend in this step to obtain the desired properties are defined by the reaction kinetics (see Chapter 2) and the desired process throughput. The rate of monomer reaction at conversions greater than 90% is independent of the concentration of persulfate. However, we would expect any chain scission process to be dependent on the concentration of any persulfate or azo-initiator. Thus a lower temperature (Table 3.2) or a reduced initiator concentration would tend to reduce the rate of formation of extractable polymer. This, in turn, through the reaction kinetics, affects the operator's selection of vessel temperature and the amount of thermal initiator, for instance, sodium persulfate, that is actually added in the primary reaction step. At this stage, it is still desirable to maintain the process under nitrogen because of the negative impact of oxygen on free-radical processes. These considerations, with the desired process throughput rate, allow the process engineer to determine the required vessel volume for this process step.

The kinetics described in Chapter 2 describe the rate at which unreacted monomer will decrease in this step. However, the effects of chain scission on swelling capacity and extractables are not described and can only be inferred from the material presented. To better illustrate these effects, a series of samples was made in the laboratory using 2,000 ppm of trimethylolpropane triacrylate as the crosslinker. The recipe, reactor, and process were as described in Comparative Example A of Graham and Gartner[17] except that the reactor contents were held after the peak reaction temperature for 3 h at the indicated hold temperature. The gel was

dried at 100°C in a circulating air oven and the properties measured using the methods described in Chapter 4. As hold temperature increased, extractables and swelling capacity increased as shown in Table 3.2. (Tables II and III of Graham and Gartner[17] show similar data, but also include data on modulus and unreacted acrylic acid.) Increasing hold time and increasing amounts of sodium persulfate, as can be inferred from the kinetic results presented in Chapter 2, also increase the swelling capacity and extractables (data not shown).

3.2.4.2. Post-Reactor Gel Preparation. The next logical unit operation in the flow sheet might be viewed as drying. However, preparation of the hydrogel prior to drying is essential for economical operation. The desire to optimize drying (reduce dryer size and cost) is often mentioned in patents that disclose polymerization process technology. One means of increasing drying rate is by reducing the particle size of the gel. This takes advantage of Fick's second law of diffusion[59] that relates diffusion-controlled drying time to the square of the particle radius.

Two methods of sizing absorbent hydrogels prior to drying are discussed in the literature. They are gel sizing in the reactor and gel sizing in a separate unit operation. When sizing in the reactor, the agitator must also be designed as an effective shearing device (section 3.2.3). The descriptions of some of the preferred polymerization vessels,[32,33] teach the need to produce a finely ground material suitable for drying. The action of the vessel agitator produces a ground gel material with 98% of the product finer than 3 cm and the majority of particles between 0.5–1 cm. Improved grinding of gel may be obtained if a hydraulic pressure head is maintained on the reactor during the gel grinding process.[60] Attempting to use an agitator in this fashion no doubt increases the power and torque requirements of the agitation system and may make it excessively costly and prone to maintenance problems. Therefore, a separate unit operation is usually chosen to make the particle size of the dryer feed as uniform as possible.

Preparing dryer feed for through-circulation belt dryers, a type of dryer commonly used for superabsorbents, is well-known technology.[61] Some types of materials can be dried without any special shaping or sizing. However, pasty materials are often extruded to form spaghetti-like pieces, about 6.3 mm in diameter. Gel grind-

Table 3.2. The effect of hold temperature on swelling capacity and extractable polymer

Hold Temperature (°C)	Swelling Capacity[a] (g/g)	% Extractables[b] (4-h swelling time)
60	34.3	7.3
70	36.0	11.8
78	35.9	12.2
90	39.3	18.9

[a]Method of Chapter 4, Section 4.6.1.2.
[b]Titration method of Chapter 4, Section 4.3.4.

ing and extrusion have also been used to prepare dryer feed when the product is dried on drum dryers.[35]

An extruder[18,35,62] can reduce the particle size of the rubbery gel in a cost-effective manner because the shear developed between the stationary extruder wall and the moving screw grinds the rubbery particles. The efficiency of the extruder allows particle sizing at lower cost than with a reactor agitator.[63] Standard references discuss the principles of operation.[64,65] In summary,[63] the extruder's screw speed, screw design, and die design and the polymer's temperature, crosslink density, and water content all affect the degree of particle size reduction. The majority of the size reduction occurs in the screw as a result of back pressure from the die rather than of the rubbery hydrogel being reduced in size as it is squeezed through the holes of the die. Following this logic, either a single screw extruder or a double screw extruder could be made to grind the rubbery superabsorbent gel. Also, the exact geometry of the die holes is not as important to effective grinding as is the back pressure generated by the screw design and the combination of hole geometry and percent open area chosen for a given die design.

The reaction kinetics previously described also influence the selected operating parameters for the gel grinding equipment. The hydrogel, prior to grinding, is at the temperature of the holding vessel, and reactions are still proceeding in the gel as they would have in this vessel. Then, mechanical energy, as power supplied to the extruder screw, is added to the sticky, rubbery hydrogel in order to effect the grinding process. The result will be an increase in polymer temperature. The magnitude of the temperature increase depends on the amount of energy input per mass of hydrogel and affects the reaction processes taking place in the gel. Thus, some designs of this system can increase swelling capacity and extractables of the resulting polymer while decreasing absorbency under load (Table 3.3).[63]

The discussion of the desirability of hydrogel grinding, the parameters affecting the grinding process, and the chemistry occurring in the gel during the grinding step may serve as a starting point for understanding the development of grinding technology for superabsorbent hydrogels. Initial descriptions of hydrogel sizing de-

Table 3.3. Properties of the dried product after extrusion of the gel through a die with circular die holes of the indicated diameter. Data reproduced from reference 63.

Die Hole Size (mm)	Absorption Capacity[a] (g/g)	Absorbency Under 2.0 kPa Load[b] (g/g)	Extractable Polymer[c] (%)
2	34	23	11.6
4	29	25	9.3
6	29	25	8.8
8	29	25	9.2
10	29	25	8.7

[a]Method of Chapter 4, Section 4.6.1.2.
[b]Method of Chapter 4, Section 4.6.4.2.
[c]Method of Chapter 4, Section 4.3.4.

scribed cutting or extruding the wet hydrogel such that the surface area per unit volume was at least 9 cm^2/cm^3 (a sphere of 3.3 mm diameter would have this ratio of surface to volume).[18] In the patent examples, a small single-screw extruder having a die with 1.5 mm holes was used. If the information is taken at face value, the particle diameter was twice the hole size so that substantial energy input into the gel must have been required to force it through the holes. In later patents assigned to the same company, the descriptions of preferred polymerization vessels[32,33] teach the need to produce a finely ground material. It is preferred that 98% of the product is finer than 3 cm in diameter and the majority of particles be 0.5–1 cm in diameter. In a subsequent optimization, a polymer gel in the temperature range of 45°–90°C is extruded through a perforated plate containing holes in the range of 6.5–18 mm. The most preferred final gel particle size is 0.5–3 mm, the same final particle size range as first described.[18] Now, the particle size is smaller than the hole size, suggesting lowered energy input into the gel and reduced property degradation. Thus, extrusion through a die is used[14] so that the gel is formed into "shapes having sufficient surface area for drying." At least for one manufacturer of superabsorbents,[62] the hot hydrogel (50°–70°C) is extruded through a die with holes whose size may range from 8 to 15 mm. The acceptable percent open area of the die covers a broad range, 30%–90%. This set of conditions yields a ground hydrogel of highly uniform particle size, with an average particle diameter of 0.5–3 mm with a high swelling capacity and low extractable polymer content.

An additional benefit of a separate unit operation for gel is that mixing of additives may be accomplished in the equipment during chopping/grinding.[35] When acrylic acid is polymerized, the polymerized and ground hydrogel may be neutralized in a gel grinding step using sodium hydroxide solution, typically at 50 wt% concentration.[35] If an ester crosslinker such as trimethylolpropane triacrylate is chosen for the polymerization, the neutralization would preferably be accomplished with a sodium carbonate solution to avoid hydrolysis of the crosslinker. Other additives may be added in this step with, if needed, additional gel mixing and grinding. Additives include recycled fines,[15] an additional crosslinking reagent such as ethylene glycol diglycidyl ether,[35] sodium bisulfite for reduction of residual monomer,[66] or an inhibitor to suppress the formation of unwanted soluble polymer that may be produced during later processing steps.[66]

3.2.5. Drying

The water present in the hydrogel intermediate (added during the preparation of the monomer) is removed by evaporation using convective or conductive heating devices. Because the monomer concentration ranges commercially from about 16% to about 43% on a weight basis, about 2–5 kg of water must be removed for 1 kg of polymer produced. The moisture concentration at the end of the drying step will be from about 1 to 5 wt% as measured by the 105°C oven test described in Chapter 4, section 4.5.3.1. Fundamentals of the drying process are discussed in a number of chemical engineering references. Drying rate is controlled by the dryer design, chemical properties of the hydrogel, such as the diffusion coefficient of water

drum rolls, the hydrogel is limited to a thickness on the drum that can be dried in about three-fourths of a revolution of the drum roll. Air flow is across the surface of the drying gel rather than through it. Where steam provides heat to the dryer rolls, the drying temperature may be regulated by the steam pressure supplied to the rolls. The hydrogel throughput rate depends primarily on the surface area of the rolls, the thickness of the hydrogel layer (controlled by the gap, or nip, between the rolls), the speed at which the rolls are turned, and the desired final product moisture. Some means of evenly spreading the granular gel across the width of the rolls would be required for efficient drying.[35] To have a thin enough gel layer to dry efficiently, the hydrogel must be of low enough modulus to be deformable in the dryer nip. Patent examples use concentrations of polymer in the gel feed to the drum dryers of 22–30 wt%, although we have successfully drum-dried polymer concentrations as high as 36 wt%. Drying temperatures from 100° to 200°C are taught. However, the drying temperature was 105°C in one example.[35]

The product is removed from the rolls with flaking knives, yielding a flaked product rather than the granular product resulting from the through-circulation dryer. Our experience suggests that drum drying leads to a product of higher surface area and faster liquid absorption rate than that achieved with oven drying or through-circulation belt drying.

3.2.6. Handling of the Dried Material: Particle Sizing

After drying, the superabsorbent product would not usually be in the correct particle size for a particular application. The product from the dryer may range in character from individual particles to a porous sheet of dried polymer, the dimensions of which may be the width of the dryer and the depth of the wet cake added to the dryer (reduced by the drying process). A two-stage dryer may yield chunks of dried sheet at the end of the drying process. If a two-stage dryer is not used, some means of breaking up the sheet of material exiting the dryer must be provided before attempting to feed the product to the particle sizing step. Dryer manufacturers often supply this equipment as part of the dryer. In all cases, the particle size distribution of the final product may be obtained by a combination of comminuting (milling) and screening to give a particle size distribution ranging from about 200 to 800 μm. The reader is referred to standard references[61,77] for descriptions of suitable process equipment.

To achieve the rather narrow particle size distribution advocated for use in diapers,[78] two-stage milling is used in combination with product screening and recycling of the oversize stream back to the grinding step. This process may consist of two dissimilar or two identical milling stages, typically selected for a gentle grinding action. Knife mills, attrition mills, roll crushers, and the like are suitable for use in the first stage. The first stage of sizing prepares the polymer for the second stage and narrows the overall distribution of particle sizes fed to the second sizing step.

The requirements on particle sizing in the second stage are more stringent because of the desirability of producing a narrow particle size distribution with minimum fines generation. Roll crushers (Fig. 3.8) are commonly used for this portion

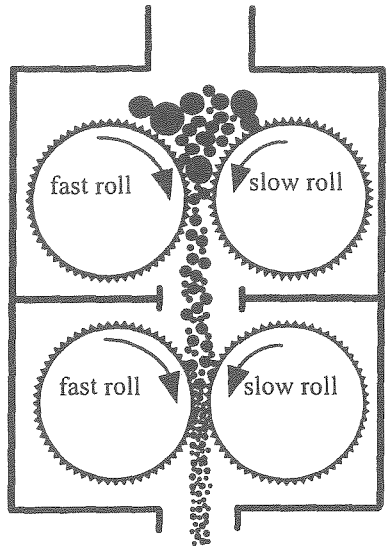


Figure 3.8. Schematic diagram of a two-pair high roll crusher.

of the particle sizing process. A particle classification step, usually screening, is used in combination with the grinding step. The polymer granules pass through a series of screens of decreasing opening size. The fraction of particles that is larger than the desired particle size is recirculated to the grinding step, while the on-size fraction is forwarded to the next unit operation. A screening operation may be used in combination with one or both of the grinding steps. Undersize or fine material may be separated from the desired particle size fraction at this step.

Figure 3.8 is a schematic of a two-pair-high roll crusher. The rolls are typically corrugated, with the corrugation pattern strongly affecting the particle size distribution of the ground product. The corrugation design includes the groove size and spacing between grooves. The angles associated with the shape of the grooves may also be varied and have been optimized by the equipment manufacturers. In combination with the selection of equipment for the first stage of the grinding process, roll groove design, roll operational parameters (rpm of the rolls and differential rpm between the rolls), and gap between pairs of rolls are chosen to give the desired particle size distribution. The primary variable in setting the particle size distribution for a given set of rolls, however, is the gap between the rolls. Increasing the gap reduces the amount of grinding that is performed, to produce larger particles. The gap between the rolls also acts as an internal classifier in the mill, allowing only particle sizes larger than the gap setting to be crushed. Particles that are smaller than the desired size pass through the mill without further size reduction, thus minimizing the quantity of undesirable fine particles. However, feeding the mill at too fast a rate may result in a broader particle size distribution as a result of particle–particle grinding. Guidance is available on choice of equipment for comminuting and screening[61] and for minimizing the width of a particle size distribution.[79]

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The desired product particle size cut is then transported to the next operation in the process. This may be merely dropping the product vertically through a pipe, or it might require specialized solids transporting equipment. Choices include belt conveyors, bucket conveyors, screw conveyors, vibratory conveyors, and dilute or dense-phase pneumatic conveyors.[80,81]

The choice and design of a solid transport system depends on plant layout and the results expected of the transport process. Commercial processes are designed to minimize particle attrition for at least two reasons. First, it is desirable to minimize the generation of quantities of particles smaller than about 140 mesh (100 μm), as noted below. Second, degradation of the product properties may result from attrition of the particle surface (see section 3.2.8.1).[82] For short transport distances, low-attrition mechanical conveyers are desirable. For longer transport distances, pneumatic conveyor systems are preferred. Since particle attrition depends on the velocity at which the product is transported, lower velocity systems are advantageous.

Only limited information is available concerning particle size distributions for the final product. One reference specifies a final "mass median" particle diameter between 400 and 700 μm, with the amounts of very small and very large particles kept below a minimum concentration.[78] The presence of fine particles (fines), typically below about 100 to 150 μm in diameter, is unacceptable in the product sold to the customer.[14,78,83] Several means of converting the fine material to a saleable product or reusing it in the current process are described in section 3.2.7.

The choice of sizing and handling equipment, including gel grinding, also affects the bulk density and flowability of the product (for measurement of these characteristics, see Chapter 4, section 4.5.6). Microscopic examination of particles led to the conclusion that generation of fines can occur as rough edges of the product particles are rounded off in milling or transporting of the product. A higher product bulk density results from the elimination of void volume arising from irregular particle shape. The presence of amounts of fine particles also alters product flow characteristics. Product flow characteristics, in turn, affect particle segregation in storage hoppers (and, therefore, the design of the storage hoppers) and product flow in feeding and metering equipment associated with diaper manufacturing. For further information in this area, the reader is referred to standard materials on the handling of solids.[61]

3.2.7. Fines Recycle

The production of particles over a range of sizes is an inevitable result of the grinding, screening, and solids handling operations used to handle dried superabsorbent polymers. Fine fractions in superabsorbent polymers or, indeed, any solid water-soluble or water-swellable product are undesirable to the extent that "gel-blocking" occurs when the product contacts an aqueous fluid. Gel-blocking occurs when the outer surface of a tightly packed mass of fine particles swells too quickly, preventing penetration of the liquid into the interior particles, whether by diffusion or by capillary action. It is primarily this effect that leads to reduced product performance in superabsorbent products containing too great a fraction of fine particles.

3.2.8. Addition of Post-Treatments

3.2.8.1. Advanced Products. The processes described above produce a particle with crosslinking that may be assumed to be essentially uniform throughout the particle. As such, the swelling and modulus behavior of the product particles can be described by theories of network swelling and elasticity (see Chapter 5). One problem associated with these superabsorbent polymers was also recognized in a variety of water soluble polymers, e.g., poly(acrylamide), cellulose ethers,[95] or soluble poly(acrylic acid).[96] This problem is the tendency of the granular polymers to clump, "gel block," or form fish-eyes when aqueous liquids are added to them or they are added to aqueous liquids. The surfaces of the massed particles swell rapidly to form a soft, deformable layer. The resulting particle deformation and interparticle adhesion reduces interparticle porosity and limits the swelling rate of the polymer mass to the diffusion rate of liquid through the partially swollen mass.

The first attempts to solve this problem in highly absorbent anionic polyelectrolytes used multivalent cations to form a crosslinked surface layer that was more rigid than the original core polymer.[97] Subsequently, to give products with improved dispersibility and absorption rate, the surface of crosslinked polyacrylate particles was reacted with a variety of multifunctional organic compounds.[49,50,98,99] This structural improvement is shown schematically in Figure 3.9. Swelling capacity data as a function of particle size readily demonstrate that a shell of real, as opposed to infinitesimal, thickness is formed by surface crosslinking processes. The shell of higher crosslink density provides a more rigid surface layer during swelling and prevents the gel-blocking that would otherwise occur early in the swelling process (Chapter 5). As a result, liquid can flow through the bed of particles to each particle, increasing the effective surface area available for swelling and the apparent swelling rate. The swelling and modulus behavior of structured particles are discussed in Chapter 5.

Because a surface layer is formed on each individual particle, the crosslinking reaction, but not necessarily the reagent addition, must occur after achieving the desired particle size distribution. Any compound that can react with two or more functional groups on the polymer backbone can function as a surface crosslinking reagent. For superabsorbents, this requires reagents that can react with the car-

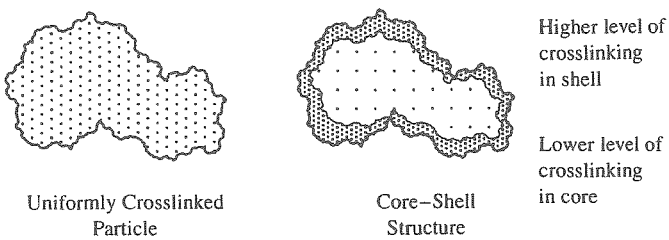


Figure 3.9. Schematic representation of a uniformly crosslinked superabsorbent particle and a structured particle with a surface layer of higher crosslink density.

boxylic acid or carboxylate moieties on separate, adjacent polymer chains. Quaternary amines have been used,[100] but the most common reagents add surface crosslink density as a result of formation of ester crosslinks. These surface crosslinking agents include polyhydric alcohols,[49,50] glycidyl compounds,[101–103] and alkylene carbonates.[104]

Blenders suitable for the addition of surface crosslinking agents include screw mixers, ribbon mixers, fluidized beds,[49] high-speed rotating paddle mixers,[50,90] vortex mixers, rolling mixers, or double screw mixers.[104] Spraying the surface crosslinking reagent into the blender, using small droplet sizes, preferably less than 300 μm, helps reduce the amount of liquid required to disperse the surface crosslinking reagent.[50] A high-speed paddle mixer used for this process operates at greater than about 600 m/min of a lead-end peripheral speed.[90] In one example, a Turbulizer, produced by Hoskawa Micron K. K., was operated at 3,000 rpm. The inner surface of the mixer is preferably coated with a material that minimizes adhesion of the wetted polymer to the walls of the mixer, for example, polypropylene or a poly(tetrafluoroethylene) resin. When a high-speed mixer is used, the amount of organic solvent used to help disperse the surface crosslinking reagent may be minimized or even completely eliminated.

A heating step is normally necessary for the reaction of surface crosslinking agents with the partially neutralized poly(acrylic acid) backbone. The time and temperature of heat treatment are chosen, considering the reactivity of the crosslinking reagent, to give the desired end-use properties. Naturally, longer reaction times and higher temperatures increase, for a reagent of any reactivity, the extent of reaction. Tsubakimoto et al.,[50] claim temperatures of 90°–300°C while Dahmen and Mertens[104] teach 150°–300°C. However, at temperatures greater than about 250°C, degradation of the polyacrylate by oxidation or decarboxylation may become significant (see Chapter 2, Section 2.5.4.2). More specifically, the reactive epoxy groups in ethylene glycol diglycidyl ether react in 30 min at 140°C.[105] The less reactive ethylene carbonate requires 1 h at 180°C or 15 min at 215°C.[104]

Suitable heating devices include fluidized-bed dryers, infrared dryers, agitated-trough dryers,[49] paddle dryers,[50] vortex dryers, or rotating-disc dryers.[104] Comparative data that would allow the selection of the most suitable device are not given. Both direct-contact dryers (rotating-disc dryers, paddle dryers) and fluidized-bed dryers are used commercially to provide heat for the reaction step. Direct-contact dryers deliver heat to the polymer particles by contact of the particles with a hot surface, while fluidized-bed dryers deliver heat to the particles with a stream of hot air of high enough velocity to suspend the particles in the airstream. Direct-contact dryers, for this application, must be designed keeping in mind the possibility of attrition of the particle surface (from the mechanical action of the paddles or other movable surfaces on the particles) and consequent degradation in product properties. The air-handling equipment associated with fluidized-bed dryers may make them expensive to operate.

Initially, structured particle technology was viewed as solving the problem of gel-blocking, as measured by a fish-eye test[49] or a similar test conducted without a compressive load. These early tests were only able to qualitatively distinguish be-

tween structured polymers made under different sets of process conditions. For example, Tsubakimoto et al.[50] showed that a water/alcohol carrier for the surface crosslinking reagent yields a structured polymer with less fish-eye formation than when the reagent is added undiluted. Later, more sophisticated tests (see Chapter 4, section 4.6.4) that measure swelling under a compressive load (absorbency under load) were able to quantitatively distinguish between structured polymers made under different sets of process conditions. Results of these tests suggest that penetration of the reagent into the particles and control of the dispersion of the crosslinking agent over the surface of the particles are critical process considerations for achieving success in the absorbency under load test.

Optimization of the surface crosslinking process to reduce gel-blocking in an absorbency under load test has been addressed in a number of ways. Surface crosslinking reagents have been added in aqueous solutions and other diluents such as alcohol or aqueous salt solutions.[102,103] However, there are several difficulties with these approaches.[106] Water swells the particle surface and lowers the glass transition temperature of the polymer at the surface, increasing penetration of the surface crosslinking agent into the polymer particle. However, excessive amounts of water cause the polymer to swell and can make handling difficult. Inorganic particulates, such as silicates, in addition to controlling the hydrophilic/hydrophobic balance of the treatment reagent, are used, in combination with high-speed blending of the reagents with the polymer, to control agglomeration during the reagent addition process.[50,90] The alcohol or salt solution helps disperse the surface crosslinking agents over the powder by diluting the crosslinker (larger volume) and helps control or prevent agglomeration of the powder by reducing the activity of water in the solution. The use of an organic solvent has the obvious disadvantage of requiring recovery and recycle. Also, for example with the lower alcohols, the low flash points require extra equipment and more safeguards to maintain safe operation.

Adding 0.2 wt% glycerol, in combinations of water and *n*-propanol, to a 65% neutralized polyacrylate made by the process of Siddall and Johnson[28] shows the effect of reagent penetration. One gram of liquid was added to 100 g of polymer powder. Twenty-five grams of the reagent treated polymers was heated in an aluminum dish for 15 min at 200°C in a preheated circulating-air oven equipped with a steel plate as a heat sink. Table 3.5 shows the swelling capacity (method described in Chapter 4, section 4.6.1.2) and absorbency under load (described in Chapter 4, section 4.6.4.2) data. Swelling capacity decreases as the amount of water in the reagent solution increases. Similar results have been obtained by using aluminum acetate, ethyleneglycol diglycidyl ether, or ethylene carbonate as the surface crosslinking reagent. This has been interpreted as resulting from increased penetration of the reagent into the particle and increased crosslinking throughout the particle rather than just on the surface.

Other process choices also affect the resulting properties. Table 3.5 suggests that for glycerol the optimum weight ratio of water to *n*-propanol is about 30:70 (based on the values of swelling capacity and absorbency under load). The amount of water may be reduced by choosing a more hydrophilic organic solvent such as methanol. Increasing the salt concentration of the crosslinker solution also decreases the hy-

Table 3.5. The effect of solvent hydrophilicity on the properties resulting from surface crosslinking of a polyacrylate treated with 0.2 wt% glycerol and then heated at 200°C for 15 min

Solvent Composition Water/*n*-propanol (w/w)	Swelling Capacity (g/g)	Absorbency Under 2.0 kPa Load (g/g)
Starting material	39.0	9.0
0/100	36.4	23.2
10/90	35.0	21.6
20/80	34.7	29.0
30/70	28.8	29.3
40/60	30.5	29.3
50/50	29.3	28.6

drophilicity of the solution (reduced particle surface swelling) and has the expected effect on product quality. The amount of crosslinker solution and the concentration of crosslinker in the solution also impact the results. When too little crosslinker solution is used, for example to avoid agglomeration, the particle surface coverage can be incomplete, leading to increased gel-blocking in the swelling under load tests. When the concentration of crosslinker is too low, or an insufficient quantity of reagent is applied, the amount of additional crosslinking at the surface does not make the surface sufficiently rigid to give the required resistance to gel-blocking.

More recently, the desire for products with an improved combination of swelling capacity and absorption under load[107,108] has led to more complex surface crosslinking sytems.[100,106,109] In one case,[100] a shell structure is achieved by using two surface crosslinking reagents with different solubility parameters, one greater than 12.5 $(cal/g^3)^{1/2}$ and the other less than 12.5 $(cal/g^3)^{1/2}$. The combination of solubility parameter and low molecular weight of the crosslinking reagents (less than 350 g/mol) is said to optimize the penetration of the surface crosslinking reagent into the particle (compare row 4 to rows 2 and 3 of Table 3.6). In a second case, surface crosslinking with a specific class of high-molecular-weight (greater than 1,000 g/mol) azetidinium compounds leads to polymer particles with more ideal shell thicknesses (less than 10% of the particle radius).[109] The high molecular weight of the reagent limits the penetration of the crosslinking agent into the particle so that the swelling capacity is not reduced too greatly. A range of surface tension, about 40–50 dynes/cm, of the applied crosslinker solution promotes spreading of the crosslinker solution over the surface of the particles.[110] A two-step addition of surface crosslinking agent also leads to improved properties.[111] Another two-part process, in which a first crosslinker (hydrophilic polymer or metallic compound) is reacted with a second additive on the surface of a wet polymer (10–100 parts), has also been described. The extent of hydration of the polymer and crosslinker are chosen to give the desired penetration of the surface crosslinking reagents into the particle and the desired combination of properties. The process seems most suitable for suspension-made polymers, but its inventors claim its utility is for polymers made by solution polymerization. In one example, a coating of poly(ethyleneimine)

Table 3.6. A comparison of properties resulting from "optimum" process conditions for making structured particles

Reagent	Swelling Capacity[b] Before Treatment (g/g)	Swelling Capacity (g/g)	Absorbency Under Load[c] (g/g)		
			2.0 kPa	3.9 kPa	6.2 kPa
Aluminum acetate	39	35	25	18	—
Glycerol	39	35	33	21	12
EGDGE[a]	40	35	35	31	24
Glycerol/EGDGE (process of Date et al.[109])	45	35	35	31	26
Ethylene carbonate	50	36	30	25	21
Example 1 of Brehm and Hartan[111]	40	36	33	25	21
Process of Burgert et al.[112]	39	36	32	26	22

[a]Ethyleneglycol diglycidyl ether.
[b]Method of Chapter 4 Section 4.6.1.2.
[c]Method of Chapter 4 Section 4.6.4.2.

crosslinked with a polyglycerol polyglycidyl ether resulted in a superabsorbent resin with "excellent" stability (by which the inventors seem to mean gel modulus). This process is said to require less stringent temperature control to achieve adequate reaction.

Despite the differences in the various surface crosslinking reagents and the resulting differences in reaction conditions, products with very similar properties may be produced with a variety of surface crosslinking processes. Table 3.6 shows swelling capacity and absorbency under load results when a variety of surface crosslinking reagents were applied in a methanol/water solvent system to a 65% neutralized poly(acrylic acid). The reaction conditions (temperature and time) were chosen to give the highest values of absorbency under load at the target swelling capacity (35 g/g). The choices were based on our experience with these processes and on data in the indicated references.

The surface crosslinking process of Brehm and Hartan[111] and the alternate structured particle technology of Burgert et al.[112] (discussed in more detail below) also produce similar results (last two rows of Table 3.6). In each case, the absorbency under load was substantially improved compared with the material before surface crosslinking. Even so, property differences remain that depend on the individual surface crosslinking reagents or process, despite our attempts to optimize the process. Some of these may result from insufficient optimization of the process conditions, such as spreading of the reagent, or chemistry, as discussed in Chapter 2, section 2.7. However, a consideration of the several reagents leads to the speculation that the crosslinker structure might also be a factor in the performance of the structured particle. The distance between functional groups in the crosslinker might be such a factor. This is a question that needs to be resolved by future study.

3.3. SUSPENSION POLYMERIZATION

3.3.1. General Terminology

The phrase *suspension polymerization* as used here is compatible with the terminology described by Arshady[120] to mean a polymerization in which droplets of monomer or monomer-containing solution are dispersed in a continuous phase that is immiscible with the monomer-containing solution. The polymerization is carried out in the dispersed phase, and the monomer droplets polymerize independently of one another. There is no transfer of monomer to, or polymerization in, the continuous phase as is the case for a latex polymerization. The size of the resulting particles is typically greater than 1 μm. If the particles are smaller than this, the term *emulsion polymerization* is typically used. In principle, there is no upper limit on the product particle size. In practice, it becomes difficult to maintain the suspension if the monomer droplets are much larger than a few millimeters. Another feature of a suspension polymerization is that if the dispersed phase is a solution, the monomer and polymer are both soluble in the solvent. If the polymer precipitates as it forms, the term *dispersion polymerization* is used. The products described here are sodium polyacrylate gels, and the term *solvent* is used in the sense that the solvent is a good solvent for the uncrosslinked polymer. Uncrosslinked sodium polyacrylates have been made for many years by solution polymerization. Because the products are ultimately used in dilute aqueous solution as thickeners, and rapid dilution of the as-purchased polymer is desired, the products have been produced and sold as water-in-oil emulsions.

The essential features of a suspension polymerization are a continuous phase, a dispersed monomer-containing phase, and a suspension aid for stabilizing the dispersed-phase particles against recombination (agglomeration) during collisions. Sufficient agitation is supplied to initially break up the dispersed phase into droplets and then keep the droplets from accumulating at the bottom or top of the reactor as a result of any density difference between the two phases. Equation 3.4 has found utility in predicting the particle size[120]:

$$d = \frac{kD_v\eta_m\gamma R}{D_a\eta_c C_s N} \tag{3.4}$$

where d is the average particle size; k is a constant dependent on apparatus; D_v and D_a are the diameters of the vessel and agitator, respectively; η_m and η_c are the viscosities of the monomer phase and the continuous phase, respectively; γ is the interfacial tension between the two phases; R is the volume ratio of the monomer phase to the continuous phase; C_s is the concentration of the suspension aid; and N is the agitator speed. The droplet size and the final particle size are determined by the amount and type of suspending agent used and the intensity of agitation. Larger amounts of suspending aid or more vigorous agitation promotes smaller particle size. Conversely, if larger particles are desired, less suspending aid and less agitation are required. However, these factors are detrimental to maintaining a good suspension and preventing agglomeration. Reduced agitation is less efficient in pre-

venting settling of the dispersed phase in the reactor, and the lower particle velocity causes collisions to be longer in duration. This promotes coagulation and ultimately suspension failure (the whole dispersed phase has fused into a more or less polymerized mass of coagulated beads at the bottom or top of the reactor). Typical agitation rates in laboratory-scale reactors are 200–400 rpm.

With this brief description of a generic suspension polymerization process, the next section covers, in more detail, the suspension process as it has been applied to the production of superabsorbents. As for bulk-polymerized superabsorbents, most of the published literature is in the form of patents and patent applications. Much of the chemistry of the process is identical to that covered in other sections of this book. Those features that are truly unique to the suspension process are discussed in sections 3.3.3 and 3.3.4. Scale-up of agitation and the nature of the suspending aid and its effect on particle size are covered in section 3.3.3. In section 3.3.4 the discussion focuses on particle shape. One may say, "but a bead is a bead." Quite true, but even though the droplets begin as spheres, they need not maintain that shape during the polymerization. Crosslinked gels are being made, and whatever shape the polymerizing droplet has at the gel point determines the shape of the final product particle. As is described in section 3.3.4, a variety of shapes have been made. In section 3.3.5 some advantages and disadvantages of a suspension process are discussed and the status of this technology in the commercial sector is briefly reviewed.

3.3.2. Suspension Polymerization of Poly(Sodium Acrylate-Co-Acrylic Acid) Gels

The monomer-containing phase is essentially the same as that used for a bulk polymerization. Acrylic acid in water is neutralized with base, typically sodium hydroxide, to the desired degree of neutralization and total monomer concentration. To help with heat dissipation, the neutralization can be accomplished in a vessel that already contains the continuous phase. However, to ensure that even mixing of the two aqueous phases is achieved, the suspending aid should not yet be present. A crosslinker and, optionally, a chelating agent to prevent metal ion interference with the initiator system are added. If the initiator has poor solubility in the continuous phase it should be added to the monomer solution prior to suspension formation to ensure even distribution in the monomer phase. The crosslinker and initiators used are typically the same as are used in bulk polymerization. One advantage of a suspension system over a bulk system is that a much higher monomer concentration can be used in the polymerizing phase because the intimate contact of the continuous phase with the polymerizing particles facilitates heat transfer from the polymerizing particle. A disadvantage is that suspension stability limits the useful phase ratio (ratio of monomer to continuous phase) to 1:1 or less. Thus, the advantage of higher monomer concentration in the polymerizing phase is essentially negated by the volume dilution caused by the continuous phase.

The continuous phase can be nearly any liquid that, when compared to water, is a poor solvent for the monomer. This solubility requirement limits the degree of neutralization to a minimum of about 50%. Because any hydrocarbon is a good solvent

There are several ways to obtain larger particle size. Higher molecular weight, that is, polymeric, suspension aids may be used, including ethylene-co-maleic anhydride,[125] poly(α-olefin-co-maleic anhydride),[126] ethyl cellulose,[127] poly(laurylmethacrylate-co-acrylic acid),[128] and cellulose esters such as acetates, propionates, and butyrates.[122] Particle sizes in the 200–350 μm range can be obtained with these suspension aids. These polymeric suspension aids are soluble in hydrocarbons, although in some instances (ethyl cellulose in toluene, for example) heat is required to enhance solubility, and the polymerization process is run by slowly adding the monomer mix to the hot oil phase. These suspending aids work by forming a polymeric film around the monomer droplets that protects the individual particles during particle–particle collisions.

Even larger particle sizes (400–1,000 μm) can be made by using particulate suspension aids, such as hydrophobic fumed silica or cationic bentonite clays.[129] These materials are not truly in solution, but are merely dispersed. They function by accumulating at the surface and forming a protective sheath around the droplets. Anyone who has observed the film of dust encasing the first few drops of a rainfall has observed this phenomenon. Figure 3.12 shows the layer of fumed silica surrounding a dried polyacrylate bead.[129]

Both the type of suspending aid and the rate of agitation affect the particle size of the suspended products. In addition to the particle-sizing role, the agitation system must be capable of keeping the particles suspended through all phases of the process. These roles can easily conflict. The energy required to suspend the dense monomer phase (density of monomer phase neutralized to about 80% is about 1.2 g/cm^3) in the less dense organic continuous phase (0.75–0.85 g/cm^3) can easily shear the monomer droplets into too fine a particle size. Scale-up of a suspension process may worsen this conflict. Suspension of the disperse phase is dependent on bulk fluid motion while sizing, in combination with the suspending aid, is dependent on shear forces and microscale turbulence.

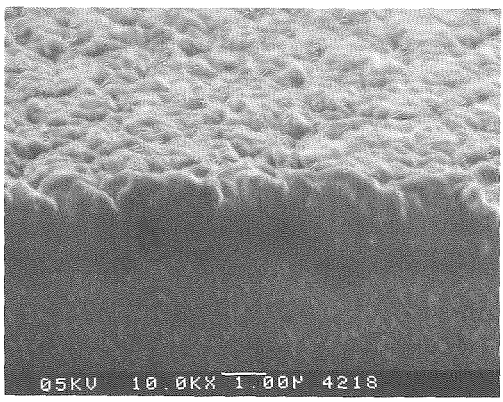


Figure 3.12. Cross section of a superabsorbent polymer bead showing the surface layer of hydrophobic fumed silica suspension aid.

The average droplet size of the dispersed phase obtained in a stirred vessel depends on the mechanism by which the droplets form. Droplet formation may be dominated by dispersive forces so that the droplet size decreases uniformly with agitation intensity. For systems of this type, mean droplet size is often found to be proportional to impeller tip speed (Eq. 3.4). This mechanism of droplet formation is common, and the theory is treated in standard works.[130] The nonparticulate suspending aids cited above would all be expected to exhibit this behavior.

When polymeric suspending aids are used in combination with particulate suspending aids, droplet coalescence at high agitation rates may lead to particle sizes larger than expected based on the results at lower agitation rates.[131] In a system of this type, mixing intensity must only provide small enough droplets so that the droplets may coalesce back to the desired larger size. Then the final droplet size is only weakly dependent on the agitation rate. Gregory et al.,[132] while determining the scale-up rules for a system of this type, found that particle size depended only on agitator speed N to the 0.3 power. As a result, once the droplets are sized, the agitation system need only keep the disperse phase suspended. It may then be possible to independently vary agitation rate and colloid concentration to achieve a desired particle size and thereby reduce the conflict between suspending and sizing droplets.

3.3.4. Particle Shape

Superabsorbents can be prepared in a variety of particle shapes by the suspension polymerization technique. Typically, suspension polymerizations yield spherical particles because this shape yields the minimum single-particle surface energy. The motivation to produce nonspherical shapes is related to certain shortcomings of spherical particles in the diaper application. First, spheres are susceptible to redistribution in the diaper, that is, they roll around.[133] Second, the minimal surface area leads to slow absorption rate when compared with particles of the same sieve cut prepared by grinding the product from a bulk polymerization.

One way to increase the surface area is to create porosity in the particle. One method of doing this is to carry out the polymerization by continuously adding the monomer solution to the preheated continuous phase.[134] The temperature, initiator concentration and identity, monomer concentration, and continuous-phase composition are chosen such that the water from the monomer phase and the oil in the continuous phase azeotropically boil and form vapor bubbles in the monomer beads at the precise moment of gelation. In this way the bubbles leave behind pores in the product, which lead to a faster absorption rate.

An alternate route to porosity is to polymerize an oil-in-water-in-oil (o/w/o) suspension wherein the monomer droplets themselves contain a second water-immiscible dispersed phase, which can be removed after the polymerization is complete.[135] Typical oil phases are hexane and cyclohexane for either or both the inner and outer oil phases. The oil-in-water phase is stabilized with poly(vinyl alcohol) and the o/w phase is stabilized in the outer oil phase by ethyl cellulose. The product is dried under vacuum to remove the inner oil phase. Void volumes up to 0.2 cm^3/g can be pro-

duced. Increases in absorption rate by up to fivefold are reported. Figure 3.13 shows the morphology of this product.

Another route to porous particles is described in those patents in which small particles are agglomerated to form larger aggregates. Such a reaction is conveniently carried out in an inert carrier, so a suspension process is ideal. The starting small particles can be prepared *in situ* prior to the aggregation step, or they can be prepared in a separate bulk polymerization. The primary polymerization can be carried out in concert with the aggregation as well in what amounts to controlled suspension failure. In one example the seed particles are slurried in the continuous phase, and more monomer mix is then added and polymerized.[127] In a second example, the agglomeration is carried out by simply adding a solution of a water-soluble polymer to a partially dried suspension polymer still dispersed in the continuous phase and then azeotropically drying the mixture.[136] As the last of the water is removed, the surfaces of the gel particles become sticky due to adsorbed polymer, and agglomeration occurs.

A process that not only results in a greater ratio of surface area to volume, but also produces a nonspherical product, has been described.[133] To understand how this process works it is necessary to consider the details of agitation. The monomer droplets are continually undergoing elongation as they move in and out of shear fields set up by the agitator. Typically, upon leaving areas of high shear, the particles immediately relax to spherical geometry. However, if the viscosity of the particles is high enough, the relaxation is slow enough that the particles enter another region of

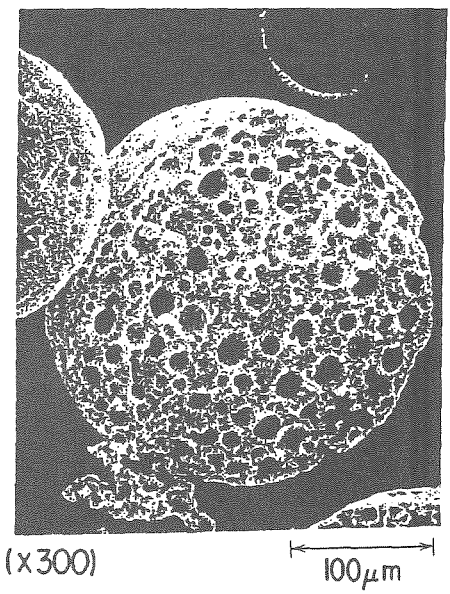


Figure 3.13. Cross-sectional view of porous beads prepared by o/w/o suspension polymerization.

high shear before the spherical shape is restored. In this way the particles can be made to have an elongated "Vienna sausage" shape. If the monomer phase has a viscosity of 15–5,000 mPas, spheres with a diameter of 100–600 μm are produced. If the viscosity is 5,000–1 million mPas, particles with a length of 1,000–10,000 μm and aspect ratios of 1.5–20 are produced. Hydroxyethyl cellulose or methyl cellulose can be used as the thickener for the monomer phase. Examples are shown in Figure 3.14.

As a final variation on the theme of morphology control, highly convoluted particles of superabsorbent polymer can be made by suspension polymerization.[137] These particles are so convoluted as to be almost all surface (Fig. 3.15). The important feature of the process used to produce these shapes is that the polymerization is caused to occur only near the surface of the particles. The initiation is by a redox system of sulfur dioxide and organic hydroperoxide. The sulfur dioxide is continuously added as a gaseous or liquid solution to the oil phase, and the hydroperoxide, typically *tert*-butylhydroperoxide, is homogeneously distributed throughout the monomer phase. The sulfur dioxide reacts with the water to produce bisulfite ion, which is the actual reducing agent of the redox couple. Initiation occurs at the surface of the droplets where the sulfur dioxide first contacts the aqueous phase. Gelation occurs almost immediately, as a gel layer forms on the surface of the droplets while the particle interior has not yet begun to polymerize. Details of the mechanism are not known. However, either hydrostatic pressure induced by the slight shrinkage that accompanies polymerization or simple solubilization of the gel by unreacted monomer solution could cause monomer to move from the interior of the droplet to the surface of the droplet. This monomer then polymerizes to form new surface. The rate of polymerization versus the rate of monomer movement causes the locus of polymerization to remain at the particle surface throughout the entire polymerization.

New surface is continuously produced by the transport of monomer from the interior of the particle to the surface. This results in a continual increase in the ratio of surface to volume as the surface undergoes a deformation reminiscent of that of a

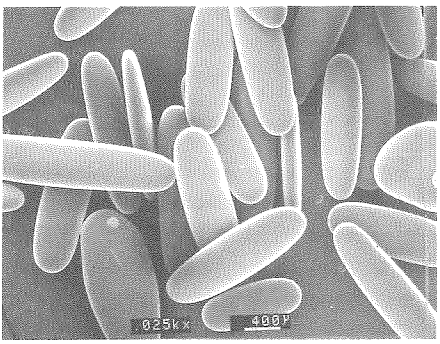
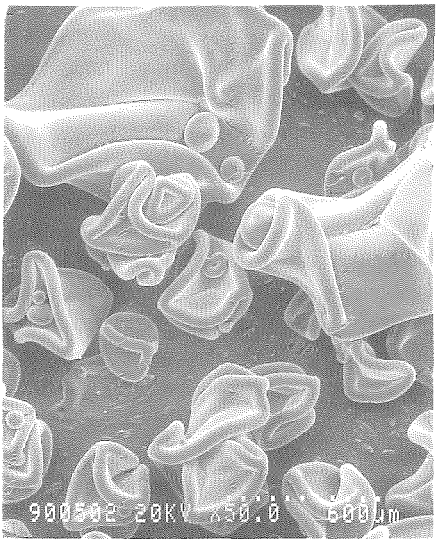
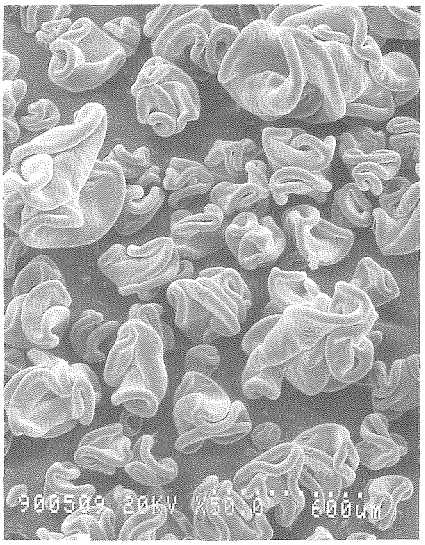


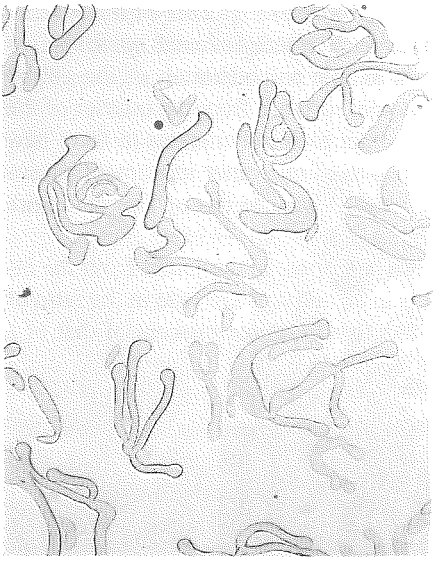
Figure 3.14. Elongated superabsorbent particles prepared by viscosifying the aqueous phase of a suspension polymerization. (Sample courtesy of Nippon Shokubai Co. Ltd.)



(a)



(c)



(b)



(d)

Figure 3.15. **(a–d)** Highly convoluted superabsorbent particles prepared by suspension polymerization: **(b)** and **(d)** are cross-sectional views of **(a)** and **(c)**, respectively.

ball being deflated. At low conversion, early in the polymerization, the particles are observed to be tetrahedral in shape with lobes of unreacted monomer forming the edges of the tetrahedra. This whole process continues to such an extreme that a second and even a third stage of bifurcation can occur in these lobes. The particles are fractal in nature in the sense that the surface area depends on the measurement scale, and there is self-similarity at each stage of bifurcation. After drying, the edges curl up to form the crinolated surfaces observed in Figure 3.15. The particles have such a high surface area that rate increases in fluid absorption of 30-fold over that of a sphere of equivalent cross section are achieved. The degree of convolution is controlled by the initial monomer droplet size, monomer concentration, crosslinker concentration, and hydroperoxide concentration.

3.3.5. Commercial Status of Suspension Technologies

There are three principal commercial superabsorbent processes that use suspension technology, and a description of the processing equipment and chemicals used is not available from public sources. Typically, the primary challenge in scaling-up a suspension process from the laboratory to a commercial scale is to manage agitation so that mass and energy transfer needs are met without adversely affecting the desired ability to control particle size. Due to the larger height of a full-scale reactor, more power input (higher continuous-phase fluid velocity) is required to prevent settling-out of the suspension. However, this additional power must not cause the particle size to decrease.

There are several inherent advantages of a suspension process over a bulk process. Most of these are a result of producing a product that needs no further size reduction. Temperature control during the polymerization reaction is easier as a result of the contact of the low viscosity (relative to the gelatinous polymer) continuous phase with the reactor walls. Surface crosslinking chemistry is easily carried out in the reactor either before or after drying. Drying is faster because the particle size, and therefore the diffusion path, is smaller relative to gel particles derived from the solution process. Azeotropic drying can be conveniently used. Particle size distribution is generally sharp and, in particular, fines production is much reduced compared with processes requiring sizing of dry product.

There are disadvantages to a suspension process as well. The continuous phase does not contribute to product performance and must be recycled for the process to be cost-effective. Even with recycling, the extra equipment required for recycling adds to the capital cost of a suspension process. Furthermore, the continuous phase is typically a volatile and flammable organic with the associated considerations for safety on a commercial scale. The reactor volume yield of product is limited by the operable phase ratio, which in turn is controlled by the stability of the system to suspension failure. Finally, as alluded to above, some diaper manufacturers have determined that the use of spherical particles is problematic in their processes due to the redistribution of the particles in the diaper.

To the best of our knowledge, in 1996 there were three commercial superabsorbent polymer manufacturers using a suspension process (Table 3.1). These were Kao Soap Co. and Sumitomo Seika in Japan and Elf Atochem S.A. in France.

Atochem sold about 11,800 tons into diapers and the medical market using a process licensed from Sumitomo Seika. Sumitomo sold about 10,000 ton into diapers, electrical cabling, and soil conditioning, and Kao produced 10,000 tons for captive use in the Japanese diaper market.

REFERENCES

1. F.L. Buchholz, N.A. Peppas, eds., *Superabsorbent Polymers: Science and Technology*, ACS Symp. Ser., No. 573, American Chemical Society, Washington D.C. (1994).
2. F.L. Buchholz, In *Absorbent Polymer Technology,* L. Brannon-Peppas, R.S. Harland, eds., Elsevier Science Publishers, Amsterdam (1990).
3. P.J. Flory, *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, N.Y. (1953).
4. J.E. Mark, B. Erman, *Rubberlike Elasticity, A Molecular Primer,* John Wiley and Sons, New York (1988).
5. B. Obenski, Superabsorbent Polymers—A Growing Commodity, *Nonwovens Industry,* **25,** 44–46 (1994).
6. *Chemical Marketing Reporter,* February 12,1996, Schnell Publishing Co., New York, pp. 10–11 (1996).
7. *Chemical Marketing Reporter,* March 11, 1991, Schnell Publishing Co., New York, p. 4 (1991).
8. *Chemical Week,* March 24, 1993, p. 49.
9. R. Po, *J.M.S. Rev. Macromol. Chem. Phys.*, **C34,** 607 (1994).
10. K. Nukushina, *Yuki Gosei Kagaku,* **38,** 546 (1980).
11. F. Masuda, *Kinoo Zairyo,* April, p. 36 (1982).
12. F. Masuda, K. Nishida, A. Nakamura, *U.S. Patent 4,076,663* (1978).
13. K.G. McCurdy, K.J. Laidler, *Can. J. Chem.*, **42,** 818 (1964).
14. T. Sutton et al., *U.S. Patent 5,064,582* (1991).
15. G.T. Woodrum, T.H. Majette, *Eur. Patent Appl. 463,388* (1992).
16. Y. Irie et al., *Eur. Patent Appl. 454,497* (1991).
17. A.T. Graham, H. Gartner, *U.S. Patent 5,342,899* (1994).
18. T. Tsubakimoto, T. Shimomura, *U.S. Patent 4,286,082* (1981).
19. Y.F. Irie et al., *Eur. Patent Appl. 574,260* (1993).
20. F.M. Wampler, *Plant/Operations Progress,* **7,** 183 (1988).
21. T. Sato, M. Baba, M. Okane, *U.S. Patent 4,317,926* (1982).
22. N. Kutepow, H. Doerful, *U.S. Patent 3,086,046* (1963).
23. T. Horlenko, A. Fisher, *U.S. Patent 3,868,410* (1975).
24. Anonymous, *RD 37,631 Res. Disclosures*, **376,** 538 (1995).
25. T. Shimomura et al., *Eur. Patent Appl. 372,706* (1990).
26. E.N. Zil'berman et al., Translation of *Zhur. Org. Khim.*, **19,** 33–37 (1983).
27. M. Chmelir, J. Pauen, *U.S. Patent 4,857,610* (1989).
28. J. Siddall, T. Johnson, *U.S. Patent 4,833,222* (1989).

used to determine particle size and particle size distribution in superabsorbent polymers.

The Rotap sieving, similar to the ASTM method used for polymer powders,[62] has been the technique of choice within the superabsorbent polymer industry. The process consists of placing a powder sample in a nest of sieves that are shaken horizontally while the column is being hit at the top with a hammer.[63] The idea is to reproduce the type of motion that has been successful when sieving shallow beds of powder by hand, combining a horizontal swirling action with a vertical jarring action. Care should be taken to eliminate blinding of the sieves.

The aerodynamic particle size analyzer,[64,65] based on the principle of particle lag in a flow field, has been used to quantify the relative concentration of particles of less than 10 μm. However, it has not been fully evaluated for general superabsorbent polymer particle sizing. The particles to be measured are first suspended in air using a disperser, and then the suspension is expanded through a nozzle into a partial vacuum. The air velocity remains constant in the measurement region and the particles accelerate at different rates according to their size. Two laser beams determine the particle velocity. As the particles pass through each laser beam, light is scattered and detected by two photomultipliers. The time between the measurements at the two photomultipliers is converted into particle size.

4.5.6. Bulk Density and Flowability

In commercial usage, polymer bulk density[66] and polymer flowability[67] affect equipment design in the polymer manufacturing plants and machine settings on diaper manufacturing lines. These characteristics are determined by timing the flow of a sample of superabsorbent granules through a funnel into a cylinder of known volume. The bulk density is the mass/volume ratio of polymer in the cylinder. The flowability is the time for the sample (typically 100 g) to flow through the funnel.

4.6. POLYMER ANALYSIS AND NETWORK STRUCTURE

4.6.1. Swelling Capacity: Theory and Practice

Certainly the first property, and arguably the most important, measured in a commercial superabsorbent used in the personal care market is the extent of swelling. This is true not only because swelling is related to the properties of the network, but also because the principal performance criterion for diapers is the amount of liquid contained per unit cost of diaper. For a complete discussion of these relationships, see Chapter 5. The following discussion is intended as a brief summary relating the methods of measurement to the equations describing swelling, modulus, and swelling rate and the assumptions that have entered into those equations.

Using the "phantom network approximation," and following the approach of Mark and Erman,[68] an expression (Eq. 5.10) for equilibrium swelling of polymers, q_m, is derived in Chapter 5 and is shown below as Eq. 4.2. Equilibrium swelling de-

pends on the polymer concentration v_{20} at the time of preparation (e.g., during crosslinking), the solvent (swelling liquid) interaction parameter, χ, the molar volume V_1 of the swelling liquid, the dry polymer density ρ_0, the backbone molecular weight M_n of the polymer, and the average molecular weight between junctions, M_c.

$$q_m^{5/3} = \frac{(1/2 - \chi)2M_c}{V_1 \rho_0 v_{20}^{2/3}(1 - 3M_c/M_n)} \tag{4.2}$$

q_m is defined as the swelling ratio from the reference state volume V_0, which is the volume at which the polymer was prepared, to the final volume, V_{eq}, so $q_m = V_{eq}/V_0$.

Restating Eq. 4.2 in terms of q_m yields Equation 4.3:

$$q_m = \left(\frac{2kM_c}{\rho_0 v_{20}^{2/3}(1 - 3M_c/M_n)} \right)^{3/5} \tag{4.3}$$

where

$$k = \frac{(1/2 - \chi)}{V_1}$$

The derivation of this equation assumes a "low concentration" of crosslinks and a "good" solvent, which means that chain deformation during swelling is small relative to the length of the extended chain. This derivation also does not specifically take into account the ionic character of the typical superabsorbent polymer backbone, but this effect can be accommodated by using an effective value of the interaction parameter χ.

To relate an experimentally determined swelling capacity to the derived theoretical capacity, the manner in which swelling measurements are made must be taken into account. First, the theoretically derived swelling equations assume a volumetric measurement of swelling in that the relevant quantities are volume fractions of polymer and solvent. However, swelling measurements are typically done gravimetrically. It is assumed implicitly that the density of the swollen gel is the sum of the densities of the components with the fraction of each component as a weighting factor. The experimental gravimetric swelling ratio, Q, is converted to a volumetric swelling ratio, q_m, using Eq. 4.4, assuming a polymer density, ρ_0, of 1.66 g/cm^3 and a density of swelling liquid of 1.00 g/cm^3.

$$q_m = \frac{\frac{1}{\rho_0}}{\frac{1}{\rho_0}} + Q = \frac{0.6024}{0.6024 + Q} \tag{4.4}$$

Second, the commonly measured swelling capacity of industry is taken from a minimum dried volume, V_{dry}, rather than from the volume of preparation, V_0. This is not a measurement of q_m, but rather of a different swelling, ratio q_{dry}, which is related to q_m through Eq. 4.5:

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$$q_{dry} = q_m \frac{V_0}{V_{dry}} \tag{4.5}$$

For measurements of swelling and modulus, this difference is not particularly significant. However, if the relationship between swelling and the volume of preparation is important, this difference becomes significant. Substituting into Eq. 4.2 for q_m, and treating $(1/2 - \chi)/V_1$ as a constant, gives Eq. 4.6:

$$(q_{dry})^{5/3}(V_{dry}/V_0)^{5/3} = \frac{2kM_c}{\rho_0 v_{20}^{2/3}(1 - 3M_c/M_n)} \tag{4.6}$$

In Eq. 4.6, the term v_{20} is the volume fraction of polymer at the time of crosslinking and is the volume of the polymer divided by the volume at the time of preparation, V_0. Rearranging Equation 4.6, collecting the terms in V_0, and solving for q_{dry} gives Eq. 4.7:

$$q_{dry} = \frac{(V_0)^{7/5}}{V_{dry}} \left(\frac{2kM_c}{\rho_0(1 - 3M_c/M_n)} \right)^{3/5} \tag{4.7}$$

Swelling from the dry state (neglecting any changes in the network structure caused by the processing steps) does not change the dependence of swelling on crosslink density and network characteristics. This also means that swelling from the dry state does not affect the correlation between measurements of modulus and swelling. However, the exponent on V_0 is 7/5 instead of 3/5. Also, q_{dry} is volume fraction based, as is q_m, and polymer and swelling liquid densities must still be taken into account for Eq. 4.7 to be used for gravimetric measurements.

4.6.1.1. Variables in the Swelling Analysis. A number of variables may affect the measured value of the swelling capacity. The discussion above described some of these explicitly. The swelling liquid has a strong impact on the equilibrium swelling. The size of the polymer particles before swelling affects the length of time required to reach equilibrium swelling, hence the absorption or swelling rate. Swelling liquid held between the particles by capillary forces must be accounted for, or excluded, when comparing the experimental results to theory. In relating swelling measurements to network characteristics, the theory assumes the volumetric measurement of an equilibrium swelling capacity. Either volumetric or gravimetric techniques may be used. However, in the latter case, it is implicitly assumed that the densities of the polymer and swelling liquid are additive in the swollen gel.

For the most direct comparison of experiment to theory, the volume of a polymer sample with regular geometry is measured in both the dry state and final swollen state. Yin[69] has adapted this technique to determine the swelling extent of rectangular slabs of polyacrylate superabsorbents. It has also been used to determine the swelling of poly(acrylamide) networks in acetone–water solvent systems.[70] Ricka and Tanaka,[71] using a microscopic technique, measured the swelling of cylinders polymerized in micropipets. We have also used the microscopic technique to mea-

sure the swelling of spheres produced in inverse emulsion polymerizations. These methods work well for swelling determinations over a range of swelling liquids and may be preferred for swelling of polyelectrolytes at low ionic strength.

Commercial superabsorbents, however, are sold as irregular granules. In addition, superabsorbents used in personal care products are used to absorb and retain body fluids of relatively high ionic strength (about 0.9 wt% NaCl), and the fluid is sensibly constant in composition. Thus, the issues surrounding swelling a polyelectrolyte gel in a low ionic strength swelling liquid are not of great concern, and differences in swelling that result from differences in the ionic strength of the liquid are very small (for instance, Donnan equilibrium and migration of counter ions from the gel to the outer solution, although important, are relatively constant factors in the personal care products). As a result, alternate swelling methods were developed that were suitable for the morphology of commercial superabsorbents.

4.6.1.1.1. Particle Size and Swelling Time. Swelling capacity methods described in the early patent literature did not specify a particle size distribution for the analysis. It seems likely that the interest of the inventors was the relative performance of polymers in the end-use, rather than in swelling as a method of characterizing the network structure. Later, the particle size used for analysis was limited to particle size distributions useful in diapers, covering the range of particle diameters from 100 to 850 μm.[72] More recent versions of industrial swelling methods have narrowed the particle diameter distribution specified for the analysis still further to 300–600 μm.[73,74]

Industrial swelling methods have not always considered swelling to equilibrium. In several cases swelling times of 10 min or less are described.[75–77] Gradually, as the industry has developed, the swelling times in the patent literature have lengthened to 30 min[73,74] or more.[78] Figure 4.20 shows the relationship between mean particle diameter, swelling time, and the approach of the measured swelling extent to an equilibrium value. As the particle size increases (smaller mesh number), the time required to reach equilibrium increases. Thus, for 40–45 mesh particles (385 μm average particle diameter), equilibrium swelling is achieved in about 20 min, while for 20–25 mesh particles (780 μm average particle diameter), only about 90% of equilibrium swelling is reached at 30 min. Depending on the size of the particles before swelling, the swelling time, and the amount of interparticle liquid, the swelling capacity result may be greater than or less than an equilibrium swelling value.

4.6.1.1.2. Interparticle Liquid. In early, industrially used analysis methods for determining the swelling extent of collections of small particles, the additional mass of interparticle, unabsorbed liquid was included in the swelling ratios. The developers had not attempted to meet the criteria of theory, just as theory had been neglected with respect to swelling time and particle size distribution. In one free swell capacity analysis,[79] the sample first was swollen in 0.9 wt% NaCl and then the gel particles were separated from the liquid by gravity filtration. Values from this analysis are typically larger than for methods where interparticle moisture is excluded. The particle size distribution of the sample and the modulus of the swollen

4.6.2. Kinetics of Swelling

Absorption rate or swelling rate involves diffusion of a liquid into the particle. As such, it is governed by Fick's law of diffusion (Eq. 4.10),[81] where C is concentration of the diffusing species and D is the diffusion coefficient of the diffusing species in the polymer. For a spherical particle, where D is a function of C, the diffusion equation reduces to

$$\frac{\partial}{\partial}\frac{C}{t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial}{\partial}\frac{C}{r}\right) \tag{4.10}$$

Thus, the swelling rate is a function of diffusion path length r, and the diffusion coefficient. Through the diffusion coefficient, the swelling rate is expected to depend on temperature (Chapter 5, section 5.2.4) and salt concentration (Chapter 5, section 5.2.5).

4.6.2.1. Swelling Kinetics Methods. Several methods have been used to obtain swelling kinetics for polymer networks. Simple gravimetry versus time is common.[82] Several optical methods have been described in which the dimensional change of the sample is measured by means of the attenuation of transmitted light,[83] microscopy,[84] or profile projection.[85] These latter two methods work well when a regular geometric shape is used as the sample. A viscometric technique has also been developed,[86] based on the dependence of suspension viscosity on the volume fraction of the suspended particles.

The swelling rate is often measured by determining the swelling extent as a function of time, for example, by means of the centrifuge capacity analysis (Fig. 4.20). (Gravimetric swelling ratios are measured because diffusion, the driving force for swelling, is a concentration-driven process, not merely a volume-driven process.) An absorption rate may also be obtained from data of swelling versus time using the Gravimetric Absorbency Testing apparatus or the apparatus described for the absorbency under load (AUL) measurement (Fig. 4.22). Data of absorbency versus time, at any load, may be fit to a simple exponential. The swelling may then be described as a simple process wherein the rate is first-order in the amount of capacity remaining unswollen:

$$\text{Rate of swelling} = \frac{dQ}{dt} = k(Q_{max} - Q[t]) \tag{4.11}$$

where Q_{max} and Q are the swelling capacities at equilibrium and at any time, t, under the conditions of the experiment. The first-order rate constant, k, depends on the diffusion coefficient and the particle radius. Equation 4.12 shows the inverse of the rate constant as a characteristic time, τ:

$$\tau = \frac{r^2}{\pi^2 D} \tag{4.12}$$

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swollen superabsorbent gel particles. It has been our experience that the relative shear modulus values obtained by this method give the correct relationship between swelling and modulus as predicted by Flory and Erman.[94]

A variety of oscillatory rheometers may be used. Instruments that have been reported in the superabsorbent patent literature include the Rheometrics Fluids Spectrometer,[73] Sangamo Visco Elastic Analyser, Bohlin Instruments Rheometer, and the Yamaden Co. Ltd. Creep Meter.[95] The rheometer comprises a circular lower plate on which the hydrogel is placed. An upper conical plate is positioned at the proper sample gap, at the point at which an untruncated cone would contact the lower plate. An oscillating torque, at a frequency of 100 Hz, is applied to the upper plate, and the resulting angular displacement of the cone is determined. The shear modulus of the hydrogel is calculated from the ratio of the applied stress to the appropriate strain. For a more complete discussion of the experimental and theoretical details of the measurement of modulus, the reader is referred to standard texts on the subject.[96]

The sample to be analyzed is screened to the desired particle size cut such that the particle size after swelling is smaller than the desired gap setting. The sample is swollen to its equilibrium swelling in the desired liquid. Synthetic urine or 0.9 wt% NaCl are typically used. Excess liquid is removed from the swollen hydrogel by blotting. If too little liquid is removed, the particles will move in the excess liquid, and the measured modulus will be too small as a result of interparticle slippage. If too much liquid is removed, the polymer will not be at its equilibrium swelling. This is a critical part of the method and may lead to discrepancies in measurements between analysts.

A useful modification to this procedure is to first measure the swelling capacity by a method that removes the interparticle water. Then, a quantity of polymer is swollen to 90%–95% of its measured equilibrium swelling capacity. No blotting is required. The measured modulus is corrected for the extent of swelling using Eq. 5.7 (see Chapter 5) to calculate the modulus at equilibrium swelling.

In either case, approximately 1.5 mL of the swollen hydrogel is placed on the bottom plate, and the upper conical plate is lowered to the desired gap. Excess hydrogel is carefully trimmed from around the edges of the plate and cone. Stress and strain measurements are taken. The temperature of the rheometer is typically held constant at about room temperature or 21.2°C. The strain amplitude is small, less than about 2.5%. Measurements can be taken at one strain or at a range of strains and extrapolated to the limit of zero strain.

4.6.4. Combining the Concepts: Swelling Under Load

4.6.4.1. Swelling Under an Applied Compressive Load. Superabsorbents in personal care articles must resist deformation and deswelling under an external load because this ability has been correlated to improved performance in pad analysis[91] and in diapers.[89,97,98] When a uniaxial compression is applied to the swelling polymer particle, it is forced to change shape. The magnitude of the deformation

depends on the modulus, which in turn depends on the initial crosslink density and extent of swelling. The change in shape will tend to close off channels in the gel mass that allow the convective flow of free liquids. Thus, the shutting off of liquid flow by compression of the gel mass depends on the elastic modulus and the porosity of the sample bed and on variables that affect them. Areal loading of the polymer in the test device and the particle size distribution in the sample are two of these variables. (This effect is discussed more fully in Chapter 5, section 5.3.5.5.) Therefore, for two reasons, more rigid particles of gel maintain their swelling capacity better under load than do the same size distribution of particles of a softer, smaller modulus, more deformable gel.

Water-absorbent crosslinked polymers have been analyzed for swelling capacity and wicking action (the movement of fluid through a bed of polymer particles) under an applied load since at least 1977.[99] The ability to control the liquid pressure head of the swelling liquid was primitive, and the areal loading was not clearly defined in this early method. (A 1-g sample is placed on a fritted-glass funnel of undefined dimensions.) However, the intent to swell polymer samples under loads ranging from 0.68 to 2.8 kPa (0.1–0.4 lb/in^2) is clearly stated. By 1985, measurements of swelling under load for fluff–polymer composites or polymer alone were reported.[100,101] The applied load in this analysis simulates the effect on the polymer of applied load during use. A 0.1-g sample of polymer is spread evenly over a circle of 4.88 cm diameter. This is a polymer loading of about 50 g/m^2 and is said to represent the loading of superabsorbent polymers in products of that time.

Turk and Werner[101] (as discussed by Painter[100]) state that "all superabsorbents absorb less fluid when the quantity of superabsorbent is increased on the same area." (Nagorski[91] shows this effect for two types of polymers.) Therefore, to predict performance of the superabsorbent in the diaper, the analysis should mimic the superabsorbent area density in the polymer–fluff composite product. Because an average of about 6 g of polymer was used in baby diapers with about 60 cm^2 of area, a polymer area density about twice that reported previously,[102] an analysis was developed that confined the polymer to the analysis cell and used a higher polymer loading.[98] The details of this procedure are discussed in section 4.6.5.2. This procedure and slight modifications of it have become an industry standard.

The earliest descriptions of methods of AUL indicate the use of the analysis for measuring absorption rate.[91,99,100] Considerations of polymer area density and particle size distribution affect the determination of swelling rate, just as they do the determination of equilibrium swelling under load. These variables affect the rate at which the bed porosity and permeability change, (see Chapter 5, sections 5.3.5.1 and 5.3.5.2). This prediction of the rate of swelling under pressure qualitatively, but not quantitatively, matches the absorption rate under pressure determined by these methods. The slowing of diffusion in gels of different shapes and, therefore, the decrease in the rate constant of swelling under a compressive load are discussed in Chapter 5, section 5.3.3, and in the following sections.

4.6.4.2. Measurement of Swelling Under a Compressive Load: Absorbency Under Load. Both the equilibrium swelling under a compressive load,

5

THE STRUCTURE AND PROPERTIES OF SUPERABSORBENT POLYACRYLATES

Fredric L. Buchholz

5.1. NETWORK STRUCTURE AND EQUILIBRIUM SWELLING PROPERTIES

5.1.1. Basic Network Theory

Polyacrylate superabsorbents are used principally to absorb liquids in personal care sanitary products. The polymer properties of principal commercial importance are the amount of liquid that can be absorbed, the amount of liquid retained in the gel under various compressions, and the rate at which the liquid is absorbed. The challenge for industrial chemists and engineers is to continually produce new materials with improved properties. To meet this challenge, it is necessary to have a thorough understanding of the polymer and its applications. Only through this understanding of the structure and property relationships is continuous progress assured. Unfortunately, the precise structure of these polyelectrolyte gels is unknown. They have been studied and modeled for over 50 years, and yet no mathematical description can model and predict all the intricacies of these materials. All is not hopeless, however, because much of the study has resulted in some very good partial descriptions of the structure and properties of these highly swellable, soft, and rubbery substances.

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Many models of swellable polymer networks have emerged, and a challenge is to choose model(s) of network structure and behavior that allow progress to be made in synthesizing materials that are more useful than preceding materials. Two types of models have emerged from the decades of study: the molecular models of rubber elasticity with ionic contributions added[1–4] and the scaling models of networks.[5–7] Many variants of these basic models have evolved as theory and experimental observations advance in lock-step. As chemists and engineers involved with the synthesis and manufacture of superabsorbent polymers, we find molecular models most useful in helping to solve product development problems because they most directly connect the synthetic conditions to the final properties. Nevertheless, the advances brought to the field by the scaling theories are very important, and they are used often to solve processing problems of a simplified nature. It is well beyond the scope of this book to develop new models of the structure and properties of polyelectrolyte gels, and the reader is directed to numerous other sources for the basic derivations of the models.[8] However we can show how the use of these models can help in the development of new and improved superabsorbent materials. Even though the models are not perfect, they are quite useful in showing how variations in the major structural features can affect the principal properties. The basic Flory–Rehner model, and its modern incarnation the Flory–Erman model, especially as modified to account for ionic effects, are frequently used to describe the behavior of superabsorbent polymers.

5.1.1.1. Network Free Energies. The basic model of ionic networks as described by Hooper et al.[4] incorporates the principles of the Donnan membrane equilibrium into the network theory of Flory and Erman[9] and relates the structure of nonionic networks to material quantities such as elastic modulus over a wide range of conditions. The Flory–Erman theory includes effects of polymer chain entanglements in the swelling and elasticity equation. The inclusion of the Donnan membrane equilibrium allows for a better understanding of the effects of the macro-ions of the polyacrylate network and how they interact with the ions of simple salts that are present in swelling liquids such as urine. Sophisticated modeling[10] is increasingly precise but more complex to use as well, and simplifications are frequently employed.

The principal structural factors contributing to the properties of superabsorbent polymers are the crosslink density and the charge density. Numerous structural features of the polymer system and the magnitude of their interaction, however, govern how the crosslink density and charge density affect the macroscopic properties. Key parameters that are involved in how the crosslink density and charge density interact to yield macroscopic properties are

1. The molecular weight of the polymer chain between crosslinks, M_c
2. The molecular weight of polymer chain if no crosslinks were present, M_n
3. The amount of uncrosslinked polymer present (the extractable fraction of polymer)
4. The extent of entangling of the chains

5. The volume of the polymer system during preparation
6. The spacing of the charges along the chains
7. The thermodynamic interaction of the solvent with the polymer chains
8. The number of polymer strands that meet at a crosslink point, f

The nonrandom aspects of structure related to the method of synthesis are also important.[11] For example, the reactivity ratios of the monomers affect both how and when the crosslinker is incorporated into the network during preparation and how much soluble and extractable polymer is present in the network.

Network behavior may be described by manipulating equations that describe the thermodynamic interaction of the free energies of the components of the network and how they change over time. The vast majority of models assume that the free energy of the network can be taken as a sum of free energies of (1) the mixing of solvent with the polymer segments, (2) the mixing and interaction of the ions of the network and the swelling liquid, and (3) the entropic changes of the connected network chains as their conformations change with swelling or deformation. Of course, an equilibrium state will be attained when the sum of the free energy changes is zero.

Because the polymer networks are used primarily to absorb liquids and salt solutions, the concentration of the polymer and other components in the gel is of primary interest. The free energies of the polymer network may be described in terms of the chemical potentials μ_i of the system, and the chemical potentials may be described in terms of osmotic pressures according to the following definitions:

$$dG_{T,P} \sum_i \left(\frac{\partial G}{\partial n_i} \right) = \sum_i \mu_i \, dn_i \tag{5.1}$$

where $dG_{T,P}$ is the change in Gibb's free energy at constant temperature and pressure, and μ_i is the chemical potential of component i in the system, which is composed of n_i moles of each component. The osmotic pressure π is given by

$$\pi = -(\mu_i - \mu_i^0)/V_i \tag{5.2}$$

where μ_i^0 is the chemical potential of component i in its reference state and V_i is the molar volume of component i. In terms of osmotic pressures, the additive contributions of the free energies can be written as

$$\pi = \pi_{mix} + \pi_{net} + \pi_{ion} \tag{5.3}$$

where the contributions of mixing, network conformation, and ions may be given additionally in terms of the structural features of the network, according to the particular theory.

The Flory–Erman description of how these factors affect the swelling and modu-

lus, with the ionic contribution added according to Hooper et al.,[4] is given in Eq. 5.4, which describes polymers swollen to their maximum with a solvent:

$$\pi = -\frac{RT}{V_1}[\ln(1-\upsilon_2)+\upsilon_2+\chi\upsilon_2^2]-RT\upsilon_2^{1/3}\left(\frac{\xi}{V_0}\right)[1+(\mu_e/\xi)K(\upsilon_2)]+RT\sum_j (c_j^{gel}-c_j^{ext}) \tag{5.4}$$

The three principal contributions are shown in the same order as in the general equation for the total osmotic pressure (Eq. 5.3). The first contribution, due to mixing of the polymer segments with solvent molecules, is taken as the Flory–Huggins description. The second contribution, due to the elastic response of the network, is taken as the Flory–Erman description. The third contribution is taken as the ideal Donnan description of ionic effects in polyelectrolyte systems. The mixing and ionic contributions tend to increase the solvent content, while the elastic contribution tends to decrease the solvent content. Once again, equilibrium is achieved when the sum of the contributions equals zero.

In Eq. 5.4, υ_2 is the volume fraction of polymer in the gel at equilibrium swelling and is commonly taken as the inverse of the equilibrium swelling capacity. The polymer–solvent interaction parameter is χ, the molar volume of solvent is V_1, the number (moles) of crosslinks is μ, the cycle rank of the network is ξ, and $K(\upsilon_2)$ is a complex function of the entanglements or constraints on junctions.[12] The measure of the magnitude of the constraints is given by an entanglement parameter, κ, which is used to calculate the value of the function $K(\upsilon_2)$. The ionic contribution contains two terms; c_j^{gel} is the concentration of all mobile ions in the gel phase, and c_j^{ext} is the concentration of all mobile ions in the external liquid phase, which is in equilibrium with the gel. The ions in the gel phase include the counterions of the polyelectrolyte and any ions that permeate into the gel from the external liquid. The number of ions that permeate into the gel is controlled by the polyelectrolyte concentration in the gel phase (the Donnan equilibrium). The partitioning of ions into the gel contributes to the swelling by increasing the value of c_j^{gel} in Eq. 5.4, but also is controlled by the crosslink density and the charge density (degree of neutralization) of the gel.

In the Flory–Erman treatment, polymer networks are characterized by their "cycle rank," ξ. The cycle rank incorporates the crosslink density and all other structural features of the crosslinked polymer (except for ionic effects). That is convenient mathematically, but would be synthetically more useful if broken out into conventional structural parameters such as M_c and M_n. For a random network such as is obtained approximately in co-polymerizations of vinyl and divinyl monomers, with crosslink functionality of four, the cycle rank density, ξ/V_0, is

$$\frac{\xi}{V_0}=\frac{\rho N_a}{2M_c}\left(1-\frac{3M_c}{M_n}\right) \tag{5.5}$$

where ρ is the density of the polymer as prepared, V_0 is the volume of the sample at preparation, and N_a is Avogadro's number.

5.1.1.2. Crosslink Density. The number density of effective crosslinks, μ_e/V_0, is

$$\frac{\mu_e}{V_0} = \frac{\rho N_a}{2M_c}\left(1 - \frac{M_c}{M_n}\right) \tag{5.6}$$

and the shear modulus of a swollen gel, G, is[13]

$$G = \xi RT\backslash N_a V_0 (\upsilon_2/\upsilon_{20})^{1/3} \tag{5.7}$$

where R is the gas constant, T is absolute temperature, υ_{20} is the volume fraction of polymer during network formation, and υ_2 is the volume fraction of polymer at which the measurement of shear modulus is made. Equations 5.4–5.7 provide the fundamental relationships between swelling capacity, modulus, and the crosslink density for polymer networks.

5.1.1.3. Modulus of Elasticity. When an elastic material is subjected to mechanical stress, it deforms or strains. In the most elementary form, the modulus of the material is the ratio of the applied stress to the resulting strain. The elastic modulus refers to the recoverable strain, or the strain that is recovered when the stress is removed. For crosslinked rubbery polymers such as swollen superabsorbent polymers, the magnitude of the elastic shear modulus depends on the molecular structure. Of course the structure is controlled by exactly how the material is made.

The molecular weight of polymer between crosslinks M_c in superabsorbent polymers made by a crosslinking co-polymerization depends on the ratio of the concentration of crosslinker to the concentration of monomer (acrylic acid). The value of M_c may be approximated by the molecular weight of the extractable polymer fraction, because most of the soluble polymer is made in the polymerization when the molecular weight of the forming chains drops below the molecular weight of chain between crosslinks, as estimated from the stoichiometric crosslink density. This occurs near the completion of the polymerization reaction when the monomer concentration is low, and, as a result, the kinetic chain length is also low. When combined with the molecular weight of the backbone polymer chain (if all the crosslinks are somehow cut), the mole fraction of "dangling chains" is accounted for in Eq. 5.5 by a factor of $2M_c/M_n$ inside the parentheses. The dependence of the modulus on crosslinker concentration is shown in Figure 5.1.

Expressing the shear modulus in terms of polymerization parameters, by inserting the expression for ξ/V_0 obtained from Eq. 5.5 into Eq. 5.7, yields

$$G = \frac{\rho_0 RT}{2M_c}\left(1 - \frac{3M_c}{M_n}\right)\upsilon_{20}^{2/3}\upsilon_2^{1/3} \tag{5.8}$$

The swollen modulus therefore depends on the molecular weight between crosslinks, M_c, the backbone molecular weight, M_n, the concentration during

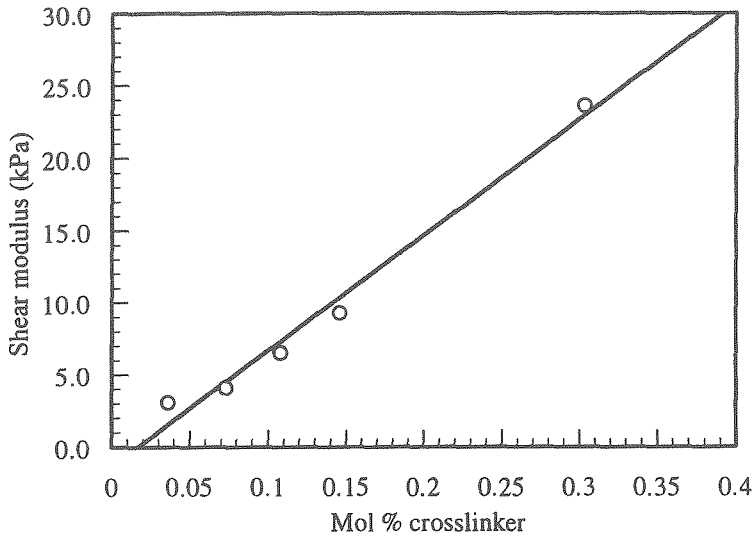


Figure 5.1. The shear modulus of sodium polyacrylate gels as a function of the stoichiometric ratio of crosslinker used in the polymerization, per mole of acrylic acid. The moduli have been normalized to the preparation volume according to Eq. 5.7.

crosslinking, v_{20}, and the extent of swelling during measurement as expressed through v_2. A slightly different form of this equation, and also of Eq. 5.10, is given in some of the original literature that describes the properties of rubber. These different forms result from the assumption that the networks are formed in the absence of any solvent, in which case $v_{20} = 1$, and V_0 contains no contribution from the volume of solvent.

The molecular weight between crosslinks and the molecular weight of the polymer backbone together define the amount of "dangling chains" in the network. The fraction of dangling chains, which are network chains having one end attached at a crosslink point and the other unattached to the network, is accounted for in Eq. 5.5 by a factor of $2M_c/M_n$ in the term $(1 - 3M_c/M_n)$. The number of elastic chains meeting at a crosslink that also is connected to a dangling chain is one fewer than if all the chains could support stress. This leads to a lower modulus and is accounted for by the extra factor of M_c/M_n in Eq. 5.5. Even though the dangling chains cannot support stress and therefore cannot contribute to the modulus, they do of course contribute to the swelling of the polymer by solvent (controlled by the thermodynamic solvation of the polymer units and the ions). Branching reactions during synthesis are an additional source of dangling chains that is not accounted for in Eq. 5.8. These reactions occur by radical chain-transfer to polymer coupled with chain termination to a radical not connected to the network.

The polymer concentration during crosslinking v_{20} defines the extent of entanglement of the network chains and therefore the number of configurations available to a chain in space. The extent of entanglement is determined by the distance be-

tween chains when the crosslinks are formed. The effect of entanglements on properties depends on the ratio of the distance between covalent crosslinks to the distance between entanglements. The concentration of monomer approximately fixes the concentration of chains at crosslinking, although strictly speaking the concentration of elastic chains continuously increases as a free-radical crosslinking co-polymerization proceeds. For example, suppose that a certain polymer at some concentration has an entanglement every 300 monomer units. The entanglements will have less effect on properties if the polymer is crosslinked every 250 monomer units than if the crosslinks are every 500 units.

The straightforward effects of concentration, as suggested by theory, are complicated in crosslinking co-polymerizations because many things change in concert with a change in monomer concentration. The solubility of crosslinkers may increase or decrease as the concentration of undissociated acrylic acid increases in the monomer solution, thereby changing the effective concentration of crosslinker. In addition, the molecular weight of the backbone polymer should increase, in general, as the monomer concentration that is loaded initially into the reactor increases, but decrease as the monomer is depleted during polymerization. Also, free-radical degradation of the polymer chains in the presence of sodium persulfate initiator occurs after the main polymerization is complete, when the polymer gel is still at elevated temperature. For chains attached to the network at only one place (dangling chains), only a single chain scission is required to cleave it from the network and form a soluble chain. As a result, the amount of extractable polymer increases as reaction time is extended. But for each extractable polymer chain formed, there must be many new dangling chains formed. Because only a small fraction of the network chains are initially dangling chains (most are elastic) and because the degradation process is random, the chains that will be most affected are those chains in largest number. The cleavage of chains during this side reaction affects the magnitude of the entanglement effect and hence the modulus. The general effects of concentration on the elastic shear modulus in the fully swollen state are shown in Table 5.1. In these polymers, the amount of crosslinker added to the polymerization, the amount of soluble polymer, and the equilibrium swelling capacity are all very similar, but the modulus increases as the acrylic acid concentration increases.

In deriving Eq. 5.5, the functionality of the crosslinks is taken to be four, as this

Table 5.1. The effect of monomer concentration on the modulus of swollen superabsorbent polymer.[a]

Monomer Concentration (wt%)	Swollen Modulus (kPa)
24	2.65
25	3.04
26	3.26
27	3.46

[a]The networks are all 65 mol% neutralized poly(acrylic acid), swollen in 0.9% NaCl solution to their maximum swelling extent.

is the crosslinker functionality for common divinyl crosslinking agents. Nevertheless, crosslinkers of higher functionality may be used, and this will also affect the modulus through the functionality f. Crosslinks of larger functionality will increase the modulus. The factor A used to account for the difference in modulus when different crosslinker functionalities are used is given in Eq. 5.9.

$$A = \left(1 - \frac{2}{f}\right) \tag{5.9}$$

N,N′-methylenebisacrylamide and ethyleneglycol diacrylate are both examples of crosslinkers that yield crosslinks of functionality four if both vinyl groups are reacted. 1,1,1-Trimethylolpropane triacrylate (TMPTA) and triallylamine have a theoretical functionality of six. However, if only two of the vinyl or allyl groups are actually used, perhaps due to steric problems in propagating a polymer chain through the crosslink as it forms,[14] the functionality of the crosslink would be four. We have determined by means of enhanced nuclear magnetic resonance spectroscopy (see Chapter 2, section 2.6.3) that residual vinyl groups are not found in superabsorbent polyacrylates made with acrylate ester crosslinkers. Inefficient crosslinking in these cases is most likely due to cyclo-polymerization of the crosslinker into the network structure and to clustering of crosslinks.[15] An example of the different efficiencies of crosslinker incorporation is shown in Figure 5.2. Over a range of crosslinker stoichiometries, the resulting equilibrium swelling capacities fall on separate curves.

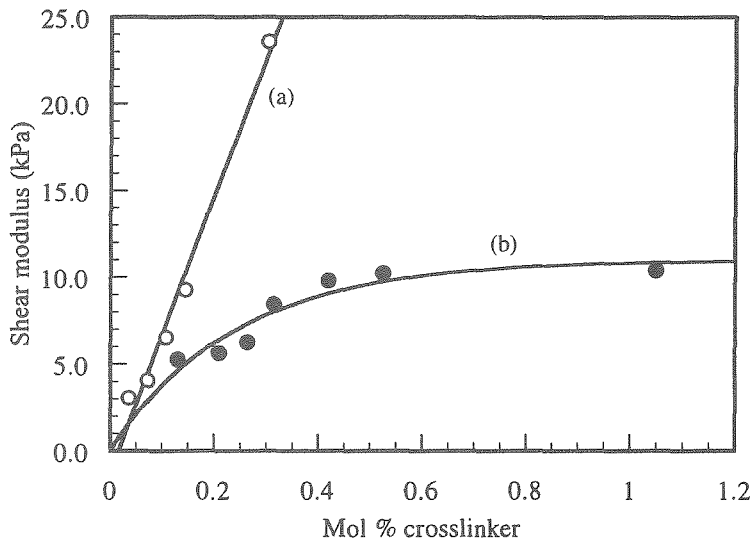


Figure 5.2. Shear modulus as a function of the amount of crosslinker used per mole of acrylic acid, for two structurally different crosslinkers, 1,3-butyleneglycol diacrylate **(a)** and triallylamine **(b)**.

This observation indicates a different efficiency of crosslinker incorporation into the final network polymer.

The extent of swelling of a crosslinked polymer affects the modulus. An increase in the swollen volume decreases the concentration of elastic chains and therefore decreases the modulus. In Eq. 5.8 the modulus of a swollen (non-ionic) polymer is proportional to the cube root of the ratio of the swelling change. The situation is more complex with polyelectrolyte networks. Over a wide range of charge density and ionic strength, the modulus decreases and then increases as swelling progresses. This is thought to be due to the very extended chain configurations that are possible at high charge density and low ionic strength, when the swelling extent is very large. However, for superabsorbent polymers used as liquid absorbents in personal care, the ionic strength of the absorbed fluid usually is sufficiently high that the chain configurations are not greatly extended.[16] The modulus behavior observed for a commercial polyacrylate absorbent polymer with increasing swelling is shown in Figure 5.3. The data were collected by the author by swelling a sample of polymer in a 0.9% NaCl solution to various amounts less than maximum swelling and measuring the modulus according to the methods described in Chapter 4. A fit of the data to a power law shows that the modulus (swollen) decreases as the 0.37 power of the change in swelling, very close to the theoretical value of 1/3 shown in Eq. 5.8. However, changing the concentration of salt in the swelling liquid does affect the magnitude of the modulus, as shown in Figure 5.4, even though an upturn is not observed over this range of swelling ratios. Ionic effects on the modulus of rubbers have been discussed numerous times.[17–20] These effects are not too important, how-

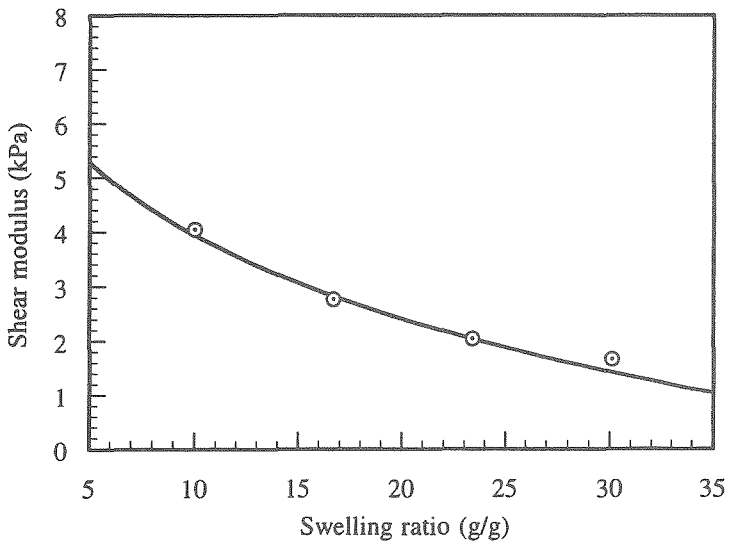


Figure 5.3. The shear modulus dependence on the swelling ratio of the sample. A single sample of superabsorbent polymer was swollen to less than equilibrium by limiting the fluid available. The modulus scales with the –0.37 power of the swelling ratio.

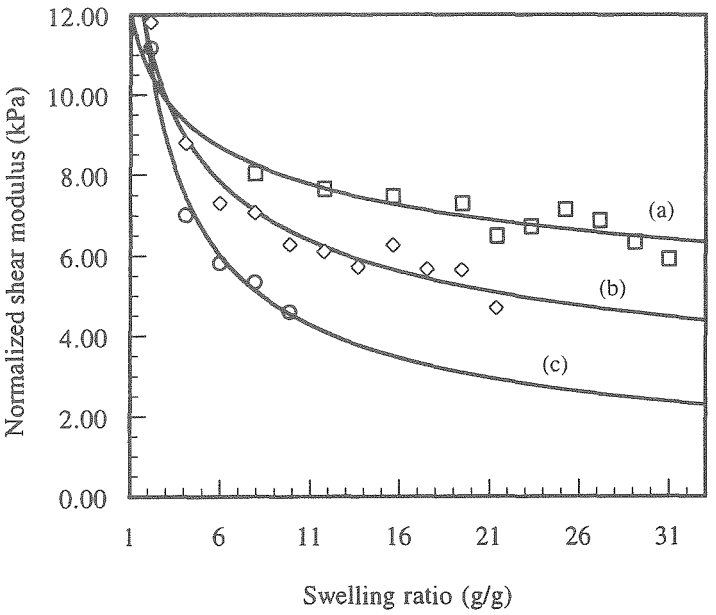


Figure 5.4. Shear modulus of partially neutralized poly(acrylic acid) gel, normalized to the volume of preparation, as a function of the swelling ratio in three different concentrations of sodium chloride, 0.0325% **(a)**, 0.125% **(b)**, and 0.9% **(c)**.

ever, for polyelectrolyte gels swollen in salt solutions of moderate electrolyte concentration (which is the case for superabsorbent polymer used in diapers).

Soluble polymer is that portion of the polymer chains that is unattached to the rest of the infinite network. The effect that this polymer has on modulus is difficult to treat and is usually neglected in the theories. These chains also do not contribute to the modulus but can be solvated and contribute to swelling. However, any soluble polymer may be extracted from the gel during the swelling process to some extent. The extent of extraction depends on the molecular weight of the soluble polymer chains, the extent of swelling of the gel network, the relative kinetics of the swelling and extraction processes, and whether the gel is bathed in excess liquid.

5.1.1.4. Swelling Capacity. From Eqs. 5.4–5.7, and assuming a randomly crosslinked, four-functional network (and neglecting the ionic effects), an equation for the swelling capacity in terms of the key polymerization parameters may be derived. The theory provides that networks prepared in the presence of diluent and then swollen greatly behave according to the so-called phantom network model. In this model the random, thermal fluctuations of the crosslinks are constrained only through the connectivity of the network and not by the presence of other chains in the same region of space. Therefore, the chains, when subjected to a stress, act only on the crosslink points to which they are directly connected. The chains do not af-

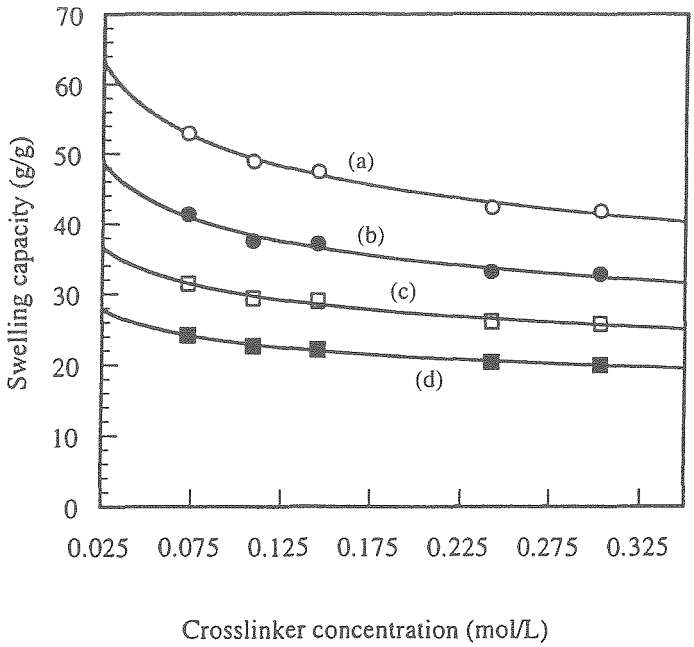


Figure 5.7. The dependence of the swelling capacity on the concentration of crosslinks during preparation of the gel and on the concentration of NaCl in the swelling liquid: **(a)** 0.225%, **(b)** 0.45%, **(c)** 0.90%, **(d)** 1.80%. The gels were polymerized at identical concentrations of monomer, using 1,3-butyleneglycol diacrylate as the crosslinker and with 65% of the carboxylic acid groups neutralized.

fiber fluff to retain water, the high retention ability of superabsorbent polymers is quite amazing. However, just as for fiber batts, liquid can be removed from a swollen superabsorbent gel by application of pressure, but the required pressures are much larger. This deswelling occurs because the application of pressure to the system causes an increase in its free energy and in the chemical potential of any species that can diffuse into or out of the system. The increase in chemical potential serves as a driving force to expel water from the gel into the surroundings when the gel is compressed.

The effect of adding pressure to the gel is similar to adding additional crosslinks to the gel. However, applying pressure to the gel does not change the network structure (the cycle rank) as does changing the crosslink density. The limitation of swelling under pressure and the related deswelling behavior are thus related to the osmotic pressure of the gel, which acts as a polymer solution confined inside a semipermeable membrane. In the following section, the effects of compression on the swelling of gels are described in more detail.

5.1.2.1. Osmotic Pressure of Networks. The osmotic pressure is defined by

$$\mu_1 - \mu_1^0 = RT \ln a_1 = -\pi \bar{v}_1 \tag{5.16}$$

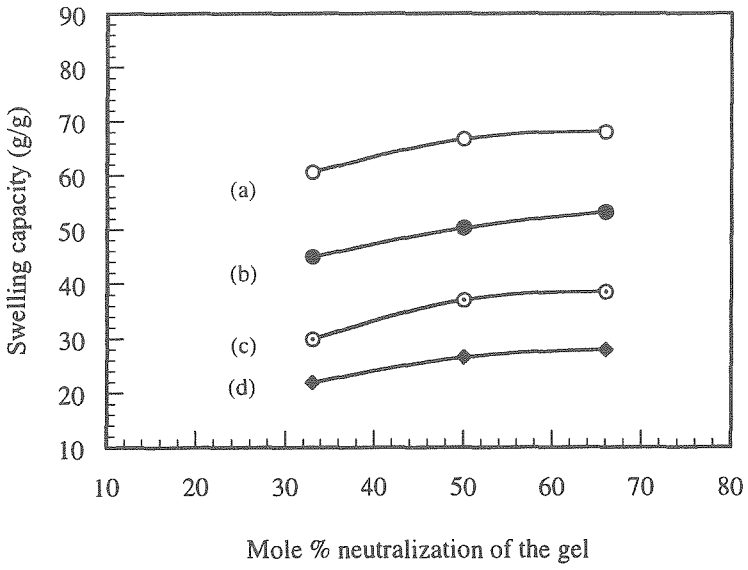


Figure 5.8. The dependence of swelling capacity on the extent of neutralization of the carboxylic acid groups and on the NaCl concentration (by weight) of the swelling liquid: **(a)** 0.225%, **(b)** 0.45%, **(c)** 0.9%, **(d)** 1.8%. The data are for one prepared gel that was neutralized to different extents after network formation.

where μ_1 and μ_1^0 are the chemical potentials of the solvent in the gel phase and in the pure solvent phase, respectively, R is the gas constant, T is the absolute temperature, a_1 is the activity of water in the gel phase, π is the osmotic pressure, and v_1 is the partial specific volume of the solvent. When the phases are not in equilibrium, the differences in the chemical potential of water in the two phases is a driving force for water to enter or leave the gel. The magnitude of this driving force is given by the activity of water in the gel phase and can be alternatively expressed as a pressure, the osmotic pressure π. When the phases are in equilibrium, there is no longer a difference in the chemical potential of water between the two phases and the osmotic pressure becomes zero. In gel swelling experiments, the osmotic pressure is often measured on a gel at constant volume in the presence of excess water. The measured pressure is frequently called the *swelling pressure*, which measures the force required to maintain the volume of the gel constant. The magnitude of this pressure varies with the concentration of polymer in the gel and varies from sample to sample depending on the structural characteristics of the gel and the nature of the swelling liquid.

5.1.2.2. Effect of Network Structure. The structural characteristics affecting the osmotic pressure of a gel are the same characteristics that affect the magnitude of the equilibrium swelling capacity and modulus of the gel. But in an application where limited swelling or deswelling is important, it is the sensitivity of the struc-

mixed together in the diaper, or even if they are mixed at all but reside instead in separate layers within the structure of the diaper. As absorbent products for personal care evolve to even thinner designs with less cellulose fluff, the fluff will play a decreasing role for the initial absorption. The behavior of the superabsorbent polymer when it is in the matrix of fluff and when it is under the influences of compressive stress in the device is of critical importance to the appropriate swelling kinetics. Additionally, when an application, such as adult incontinent devices, requires a fast rate of absorption, the fundamental aspects of the swelling process must be understood to endow the superabsorbent polymer with faster absorption rate. A number of methods that are useful for measuring the swelling kinetics are described in Chapter 4, section 4.6.2. In the next several sections the attributes of the polymer and swelling liquid that affect the kinetics of free swelling are discussed. Then the influence of the compressive stresses during use are included in order to gain a clearer understanding of how superabsorbent polymers behave.

5.2.1. Maximum Swelling and the Rate Constant of Swelling

The swelling process is a diffusive process, with water diffusing into the polymer as the polymer chains relax and diffuse outwardly into the liquid. The polymer chains must diffuse and move for the volume of the polymer to increase. Because of the diffusive mechanism, a principal factor in swelling kinetics is the size of the polymer particle, its morphology (e.g., monolithic, porous, smooth or rough surface) and its shape (e.g., spherical, irregular granular, flakes). In Table 5.4 is a comparison of the swelling kinetics of two different manufactured superabsorbents, as measured by a characteristic swelling time from the vortex time analysis (described in Chapter 4, section 4.6.2).

Sample A is principally a monolithic, granular product, and the swelling time changes smoothly as a function of the particle size. Sample B is an agglomerated sample and is quite different in its swelling rate character as shown by the nonregular dependence of swelling time on particle size.

Because the swelling rate is critical to the performance of the superabsorbent

Table 5.4. Dependence of the sorption time, t_v, as measured in the vortex time analysis, on particle radius, r, for two different samples

Mesh Size	r (cm)	Sample A (t_v, sec)[a]	Sample B (t_v, sec)[b]
20–25	0.0387	392.2	8.2
25–30	0.0325	280.7	316.7
30–35	0.0274	171.1	215.7
35–40	0.0230	130.2	5.5
40–50	0.0177	86.3	4.2
60–70	0.0115	46.6	38.3

[a]Sample A is from a homogeneously crosslinked, granular product.
[b]Sample B is from a granular, partially agglomerated, rapid swelling product.

from the synthetic conditions, and the physics of superabsorbent polymers, are described. In the following sections, many of the applications and emerging applications of superabsorbent polymers are described in more detail, with some attention paid to how the structure of the superabsorbent polymer affects its performance in the specific application.

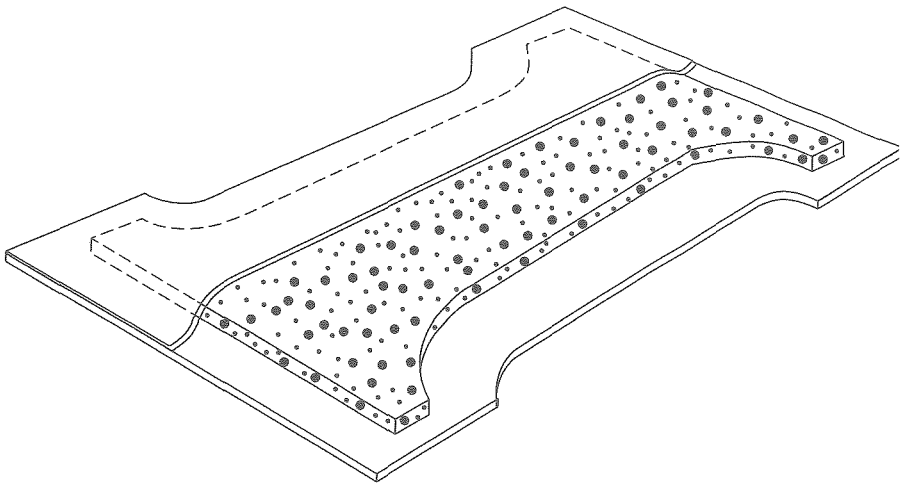
7.1. PERSONAL HYGIENE PRODUCTS

The largest use of superabsorbent polymers is in personal hygiene products. These consumer products include, in order of volume of superabsorbents used, disposable infant diapers, children's training pants, adult incontinence articles, and feminine sanitary napkins. Of these, infant diapers accounted for over 90% of the total superabsorbent polymer sold in 1995.[1] Because of this, the development of superabsorbent properties in general has been focused on optimizing absorbency of urine in a disposable diaper.

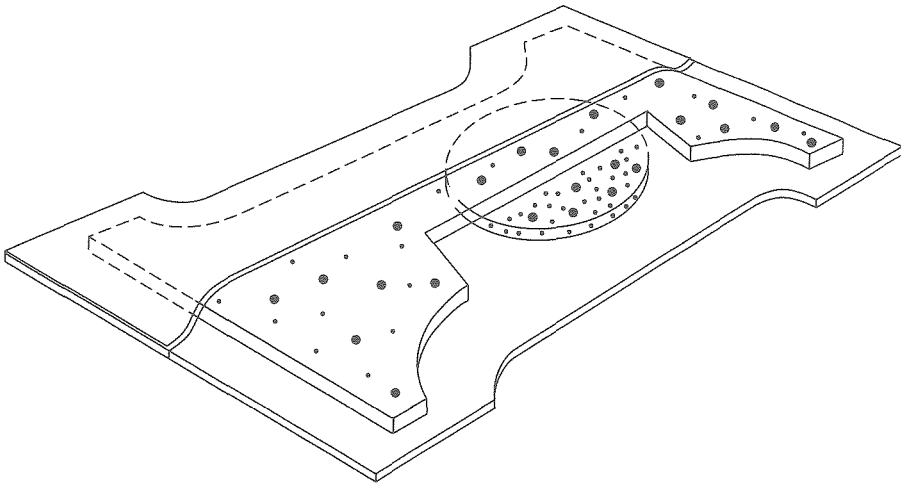
7.1.1. Disposable Infant Diapers

Disposable diapers have changed greatly during the past 30 years, but three basic design components are used in any diaper. A diaper consists of an absorbent core that is sandwiched between a porous top-sheet and an impermeable back-sheet, as in Figure 7.1a.[2] The top-sheet, which is next to the baby's skin, helps contain the absorbent core, especially when the core is wet and easily torn. The top-sheet must allow the urine to flow through it and not allow the liquid to remain near the baby's skin. Usually it is made of a porous, hydrophobic substance, for example, polyester or polypropylene nonwoven fabric. The back-sheet helps keep the baby's clothing dry and is a nonporous, hydrophobic substance, for example, polyethylene film. The absorbent core takes in the liquid, distributes it to distal regions of the core, and holds the liquid under pressure from the baby.

The absorbent cores of the earliest disposable diapers were made of multiple layers of creped tissue paper.[3] Liquid in the absorbent core was held only in the void space between the fibers of the paper. To hold a large volume of liquid, the core needed lots of void volume. To provide capillary pressure to wick and retain the liquid, the size of the voids or pores had to be small. The solution was to make a thick core, to have many small pores. Even then, the essential problems in creating an efficient diaper were known. The importance of total absorptive area, absorptive mass, density of the mass, and the location of this mass relative to the user's anatomy were recognized. The limitations of fit to the human body require that absorptive mass be less in the crotch area and more in the front and back. As a result, the distribution of liquid from the crotch to the rest of the diaper is essential. Reduced leakage from the diaper was recognized as a principal design criterion. Liquid distribution was enhanced by running the creping ridges along the length of the diaper, by folding the diaper in the lengthwise direction to yield simple channels for liquid flow, and by gradations in the density of the absorbent material along the length and



(a)



(b)

Figure 7.1. Schematic diagrams of diapers with **(a)** absorbent core of superabsorbent polymer and cellulose fluff sandwiched between the impermeable back sheet and the porous top sheet and **(b)** layered structure with higher density circular layer of superabsorbent polymer and fluff nearer the back sheet. (Adapted from *U.S. Patent 5,147,343* and *Br. Patent Appl. 2,215,609.*)

width of the diaper. The density gradations enhanced both the wicking of fluid (high density) and the liquid-holding, volumetric capacity (low density). This was accomplished by discrete layering of the fluff in regions having different densities or by graduating the density across the thickness of the pad. This trend toward layers is quite evident in modern diaper designs, which have numerous layers to accomplish the various tasks of liquid movement and storage. Layering has become more prevalent with the incorporation of superabsorbent polymer into absorbent cores.

The storage of liquid in a diaper was revolutionized by adding superabsorbent polymers to it.[4] Eventually this idea caught on with diaper manufacturers as a result of the superior liquid retention of superabsorbent polymer. Superabsorbent polymers absorb, and retain under a slight mechanical pressure (1–5 kPa in diapers), about 30 times their weight in urine. The swollen gel holds the liquid in a solid, rubbery state and prevents the liquid from leaking onto the baby's skin and clothing. In a diaper, the polymer is mixed with 1–10 times its mass of cellulose pulp fluff (processed wood fiber) to make up the absorbent core. In the first diapers containing superabsorbent polymer, the polymer amounted to about 12% of the mass of the absorbent core. More recently, diaper designs incorporate up to 60% of superabsorbent polymer[5] and more.[6,7] Cores containing superabsorbents can be made thinner because a smaller volume of dry superabsorbent polymer can absorb the same volume of aqueous liquid as a larger volume of fluff. The fraction of superabsorbent polymer in the absorbent core has increased as the properties of the polymer and the properties of the entire core become better understood.

The superabsorbent polymer must function in concert with the other components in the diaper to produce the desired performance. The absorbent core became a composite structure, with the fluff and superabsorbent polymer randomly mixed. Early in the development of superabsorbent-containing diapers (the early to mid-1980s), only the superior absorption and retention of water by superabsorbent polymers were recognized as important, and the absorption capacity for urine was maximized. This required superabsorbents having a low crosslink density. However, this also resulted in small gel modulus when swollen. As a result of their high deformability, early superabsorbents tended to "gel-block," or create swollen masses of gel that blocked the channels that allowed urine to penetrate into the diaper structure.[8] Because urine cannot flow as easily within a gel-blocked absorbent core, diapers containing superabsorbents with large capacity and small gel modulus are more likely to hold urine next to the wearer's skin and are more likely to leak. As the understanding of the new composite structures, containing both fluff and superabsorbent polymer increased, increased gel strength or modulus emerged as a means to prevent gel blocking. Increasing the crosslink density of the gel particles resulted in products with higher modulus and higher absorption under pressure, but lower free swelling capacity. Although the equilibrium swelling capacity was somewhat lower, the improved gel modulus led to an overall improvement in diaper performance.[9]

The swelling and deformation properties of the superabsorbent polymer caused the development of numerous designs either to work around the limiting properties of the composite or to work synergistically with improved superabsorbent polymer. The basic feature of low density of the core could be, at least partly, discarded be-

cause the absorbency function was largely taken on by the superabsorbent polymer instead of the void space between fibers. But the requirement of liquid flow and distribution remained as important as ever, and is complicated by the presence of superabsorbent polymer. Consider a dry, random mixture of superabsorbent polymer and cellulose fluff in a given ratio. As the superabsorbent polymer absorbs liquid, the volume and mass of each polymer particle increases, and the mass fraction of gel in the core increases. The change of the gel fraction with increasing swelling of the polymer in the core is shown for three initial ratios of polymer to fluff in Figure 7.2. The volume of the pores between the particles of superabsorbent polymer and the fibers of fluff is affected by the elastic properties of the core and the superabsorbent polymer, and different cores may be designed to optimize performance.

If the superabsorbent polymer is only slightly crosslinked, it is soft and deformable, and may expand into the pores between the fluff and polymer particle as it swells. In this case, flow is inhibited as the composite becomes less porous as swelling proceeds and the pore size decreases. Diaper absorbent cores may be designed and constructed with the limitations of the polymer in mind.[10] However, the large absorption capacity of the polymer still is desirable, and modified designs may be developed to alleviate the inhibition of flow during swelling. A general technique is to redistribute the superabsorbent polymer from a random distribution into layers (thickness or z-direction) or regions (x,y-directions, but mostly length) of the core. The superabsorbent polymer may be concentrated more toward the back-sheet, as in Figure 7.1b, or more toward the ends of the diaper (more distant from the crotch). These techniques concentrate the fluff near the point of initial wetting to

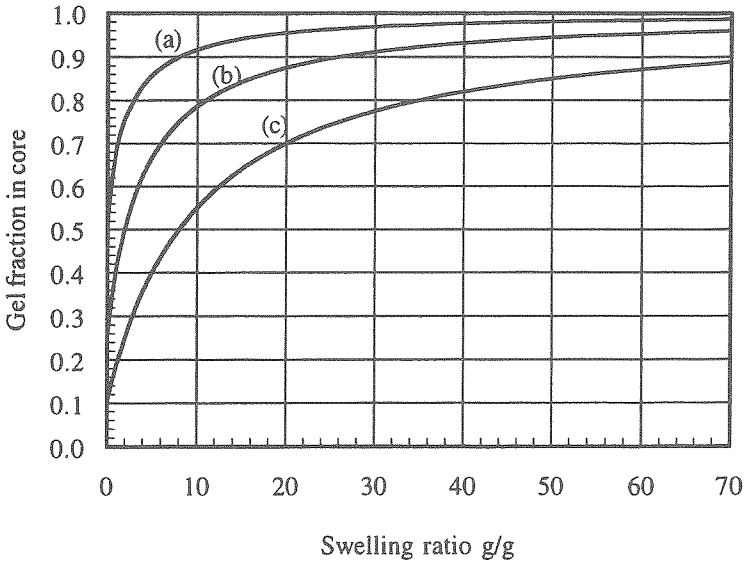


Figure 7.2. The fraction of gel in the absorbent core as a function of the swollen volume of the polymer for three different initial weight ratios of polymer to fluff: **(a)** $f_{SAP} = 0.5$, **(b)** $f_{SAP} = 0.25$, and **(c)** $f_{SAP} = 0.1$.

improve liquid flow before the superabsorbent polymer swells and during subsequent wettings of the same diaper. In practice, this is accomplished primarily by reducing the amount and density of the absorbent materials, particularly the superabsorbent polymer, at the urine insult point, as shown for example in Figure 7.1. This structure tends to draw urine away from the insult point as a result of higher density and hence higher capillary pressure of the distant regions and reduces the impact of gel blocking on initial containment of the liquid insult. In this way the design accommodates the superabsorbent polymer. Conversely, superabsorbent polymer design may be used to improve diaper performance.

If the superabsorbent polymer is more highly crosslinked, it is more rigid in the swollen state. Improving the rigidity of the particles enables the swelling particles actually to push aside the fiber component of the composite, thereby maintaining the porosity and permeability during subsequent contacts with liquid. Of course, if the swelling polymer opens the structure of the composite too much, the integrity of the composite may be destroyed, and leakage may increase. Therefore, the optimization of the polymer properties and location is required and is accomplished by a trial and error approach. A number of design challenges, and improvements, are evident from recent patent literature, which includes patents on sophisticated designs[11–17] and potential new attributes of the diaper, such as flushability.[18–20] In addition to the equilibrium properties of the superabsorbent polymer, the kinetic aspects of the swelling and absorption must be considered.

The absorption rate of the diaper must be optimized to the urination rate of the baby. If the absorbent core absorbs too slowly, the liquid will overflow the core and leak from the diaper. The absorption rate of the composite is influenced by, but not synonymous with, the absorption rate of the superabsorbent polymer. Fast swelling of the polymer may be desirable if it helps contain the liquid quickly. However, in some diaper designs, fast swelling may cause the diaper to leak if the porosity and permeability of the composite is reduced. As described in Chapter 5, the absorption rate of superabsorbent polymers is affected by the maximum absorption capacity of the polymer and its particle size and shape.[21] The placement of fast- or slow-absorbing polymers in the composite structure therefore has important implications for the effectiveness of the composite. Many different schemes for mixing fluff and superabsorbent polymer have been investigated in order to find optimum diaper performance. It should be expected that the particle size and shape of the superabsorbent polymer particles, and their change with swelling in relation to the size and shape of the fluff fibers, affect the porosity and permeability of the core. The relative amount of each component should also affect the optimum. Some effects of particle size and shape have been studied,[22,23] but much remains unknown. When the superabsorbent swelling is delayed in the wetting region of some diaper designs, there is more time to distribute urine through the diaper.[24,25] Improved distribution results in lower saturation of the core in the wetting region, so that subsequent insults may be more readily absorbed. The improved understanding of the impact of superabsorbent polymer on the absorbent core has resulted in some very thin diapers.

In the early 1990s, ultrathin diapers became possible. The amount of cellulose pulp fluff used in these diapers was reduced by half, yielding a thinner diaper with a

higher concentration of superabsorbent polymer in the absorbent core. A separate layer of nonwoven fibers was added to improve urine distribution in the diaper. This distribution layer was placed between the composite absorbent core (cellulose fiber and superabsorbent) and the porous cover sheet. The distribution layer has lower absorbency than either the standard cellulose fluff or superabsorbent polymer and a low density that allows fast liquid distribution within the diaper. It has been made from either chemically crosslinked cellulose fibers or a nonabsorbent nonwoven material, such as polypropylene fiber, and it is sufficiently porous to allow liquid to pass through freely.

To maintain the total absorbent capacity of the ultrathin diapers, the amount of superabsorbent polymer was about doubled over earlier versions, replacing bulky cellulose fluff. This increase in concentration of superabsorbent required the polymer to have still higher resistance to gel blocking because there were fewer fibers to help maintain open pores between swollen superabsorbent particles. The most common approach to improving resistance to gel blocking was to increase gel modulus by creating a structured superabsorbent particle, as detailed in Chapter 3, section 3.2.8.1. These products have a crosslink density gradient, increasing from the center of the particle to its exterior. The higher density crosslinks near the particle surface produce a rigid gel early in the swelling process, which reduces the tendency to gel-block and improves the absorbency under load of the superabsorbent. The low crosslink density in the particle interior maintains the free swell capacity compared to a homogeneously crosslinked particle, with the potential to improve the absorption efficiency of the diaper.

The structured particle has been a significant advance in superabsorbent polymer technology for diapers, and superabsorbent polymers are likely to change further as the composite absorbent core structure becomes understood even better. Other applications of superabsorbent polymer have different requirements, however, and these requirements are also in need of study and optimization.

7.1.2. Adult Incontinence Products

Adult incontinence products also employ superabsorbent polymer to absorb urine. The market for these products is growing as the members of the post-World War II baby boom age. Because the products are used to absorb urine, generally the technology learned and used for baby diapers is applied directly to adult incontinence products (certainly most of the criteria are similar). However, the application is unique in several ways and could likely benefit from some research focused on finding the optimum superabsorbent polymer properties. Adults are more concerned about discreetness when using the products and desire very thin, easily disposed-of products. The thinness of these products has improved dramatically with the use of superabsorbent polymer. Urination volume and rate are both larger for adults than infants, and the products must also absorb under the larger pressures exerted by adults. Fast-swelling superabsorbent polymer has long been desired for this application and has been incorporated into multilayered absorbent pads.[26] Approaches to fast-swelling superabsorbent polymer involve increasing the specific

area of the superabsorbent polymer, including using small particle sizes (higher surface area to volume ratio), using porous agglomerates of smaller particles,[27] and making highly wrinkled particles.[23] There is also more variability in the extent of incontinence in individuals, and, as a result, many different styles of products are available, including light- and heavy-duty personal pads, bed pads, and briefs.[28] Each of these is likely to need a slightly different superabsorbent polymer for optimum performance. Another application with many different product styles is feminine hygiene products.

7.1.3. Feminine Hygiene Products

Superabsorbent polymers are also used in some feminine hygiene products. In fact, the first commercial personal hygiene product with superabsorbent polymer was a feminine napkin in Japan. The reasons for using superabsorbent polymer in feminine care products are similar to those for diapers and incontinence products: leakage control and comfort. Good fitting, very thin, absorbent products are enabled by the properties of superabsorbent polymer. As in diapers, the superabsorbent must be able to absorb fluid under load, and therefore a high gel modulus product is useful. A challenge for the product developers, however, is the very significant difference between the fluids to be absorbed by feminine hygiene products and diapers. For diapers the fluid is a very low viscosity aqueous solution of (primarily) salt and urea. For feminine hygiene, the fluid is a complex, more viscous mixture of water, salts, and cells. The cells are far too large to diffuse into the network structure of the superabsorbent polymer, and may instead *adsorb* onto the surfaces of the superabsorbent polymer particles. The high osmotic pressure of partially swollen superabsorbent polymer can de-water the cells if they are in direct contact, and this can lead to a nearly impermeable surface layer of cells and protein and a severe reduction in the efficacy of the polymer. These factors suggest that the nature of the superabsorbent polymer for feminine hygiene should be different from the polymer used for urine absorption. In some respects the factors influencing the nature of the superabsorbent polymer for this application may be similar to those used to specify polymers for use in other blood applications. For example, polymers used in surgery and surgical appliances have been chemically modified to prevent undesired blood clotting.[29] Incorporating similar modifications into superabsorbent polymers may improve their performance in feminine hygiene products. Surface coating the superabsorbent polymer with surface-active agents improves blood dispersibility,[30] as does the addition of a variety of salts.[31] Potassium or lithium salt-neutralized superabsorbent polymers have also been disclosed for specific feminine hygiene needs.[32]

7.2. AGRICULTURAL AND HORTICULTURAL APPLICATIONS

Superabsorbents can also help conserve water in a variety of agricultural and horticultural applications. Mainly the polymers are used in the same way as mulch, to help the soil retain moisture. A comparison of the water-retention effectiveness of

the traditional moisture retention aid, peat, and of superabsorbent polymer shows excellent retention by both materials and an expected decrease in water holding ability of the superabsorbents as salinity of the water increases.[33] As soil additives, the polymers are mixed into soil at a concentration of about 0.1 wt%. Little benefit is achieved below this concentration, and the soil can become too spongy and soft if much more is used and it becomes fully saturated with water. Soils that receive little rainfall, or that are too porous to hold moisture in the root zone, can be improved by adding superabsorbent polymers. The resulting soil mixture retains moisture longer, and plants live longer after germination. In clay soils, superabsorbent polymer helps improve the air content of the soil as the polymer particles expand and contract during the cycle of moisture absorption and evaporation, at least when conditions are not too wet. Under wet and soggy soil conditions, which are often not conducive to plant growth due to low oxygen content in the soil, the use of absorbent polymers may actually prolong the unfavorable soil conditions. An excellent review of how the properties of the superabsorbents influence the behavior of soils is by Kazanskii and Dubrovskii.[34]

Superabsorbent polymers have found limited utility as soil additives because results from studies on the efficacy of superabsorbents in improving plant health or yield have been mixed. The conflicting results are a consequence of the varied soil conditions present in the experiments.[35,36] Most of the positive results occurred when small ratios of superabsorbent polymer to soil were used and the soil was normally drier than average. The superabsorbent polymer absorbs water more effectively and controls its release into the soil as conditions become drier. The polymers have shown positive results, for example, in cabbage seedling germination and survival[37] and under conditions of water economy in growing corn.[38] In one experiment, the yields of Chinese cabbage increased about 10% compared to the control plot without superabsorbent polymer, using the same amount of water.[39] Seed pellets have been disclosed that contain seed, a superabsorbent polymer, fertilizers, binders, and an inorganic filler such as vermiculite.[40] These pellets can be spread in remote areas and help the seed germinate and grow with no further attention.

The nursery/floriculture market consumes a large percentage of the superabsorbent volume used in the agricultural market. The primary function of the absorbent polymer in this case is to reduce the volume and frequency of watering for ornamentals such as flowering plants, trees, shrubs, and hanging baskets. In the professional landscaping business, superabsorbents also are used to reduce transplant failures resulting from improper watering. For the nursery market, light-weight, sterile, soil-less mixtures are often used to prevent soil-borne diseases from affecting the plants. These mixtures can benefit from the addition of relatively light-weight superabsorbent polymers as an efficient water-retention agent.[41]

Superabsorbent polymer may also be used as a soil additive for turf grasses on high value land such as golf courses, sod production, and athletic fields, where the health and vigor of the vegetation is vital, and maintenance is expensive. In addition to reducing maintenance costs, another advantage is improved durability for soccer, football, and other athletic fields. The superabsorbents are applied by broadcasting, by injecting the polymer under the turf after the turf has been sliced and lifted, or by

a liquid spray application wherein small, swollen, deformable gel particles can pass through the spray nozzles with relative ease.[42] The goal is to evenly distribute the polymer and any additives such as fertilizers or pesticides.

The type of superabsorbent used for these markets is typically based on polyacrylamide chemistry. Superabsorbents containing ionic functional groups, such as the polyacrylates used for infant diapers, show a reduction in swelling capacity when exposed to multivalent cations present in the soil or in the irrigation water. These cations form irreversible crosslinks between ionic functional groups, reducing the ability of the superabsorbent polymer to swell after numerous absorption cycles. Nonionic polyacrylamides maintain a larger percentage of the original absorbent capacity than polyacrylates when exposed to the polyvalent cations present in ground and irrigation waters.[39]

7.3. CONTROLLED RELEASE

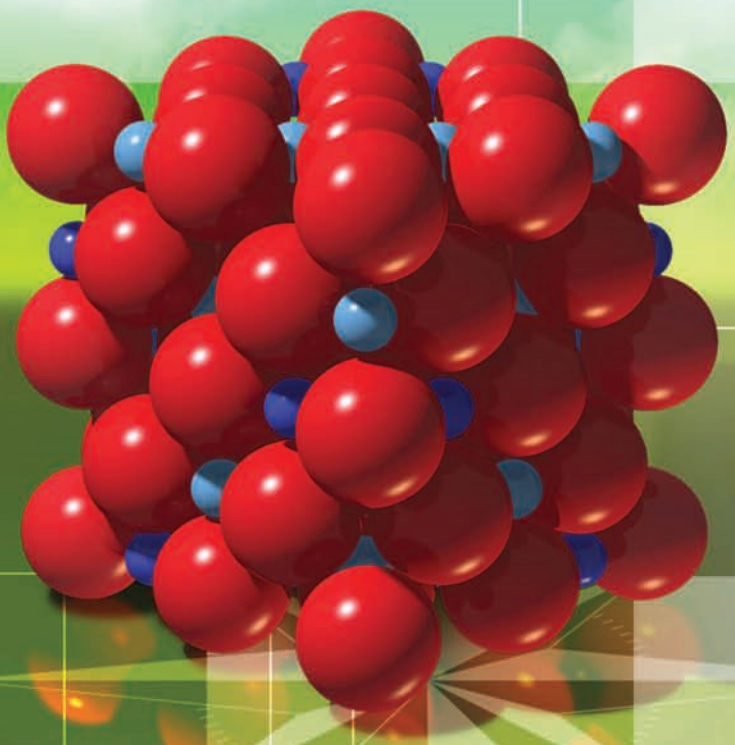
Superabsorbent polymer may also be used to control the release of substances that are initially dissolved or trapped within the polymer phase, such as pesticides, fertilizers, and pharmaceuticals. Just as the absorption of water by superabsorbent polymer is caused by unequal activities of water inside the gel and in the external liquid phase, substances that are initially at a higher activity in the polymer will diffuse out of the particle and into the surroundings. The initially dry polymer system is activated for release by swelling, and the control depends on the change in diffusibility of the releasable substance as the polymer phase changes its concentration. Numerous water-absorbent polymers share this essential feature for controlled release by swelling,[43] but superabsorbent polyelectrolytes possess additional useful features. The swelling of poly(acrylic acid) and other acidic or basic polymers depends on the pH and ionic strength of the swelling medium, and changes in pH or ionic strength may serve as switches for controlled release.[44] The crosslink density also affects the extent of swelling and is used to control the release characteristics of the polymers. To make the controlled-release particles, usually the polymer is prepared first and then the active substance is added to the polymer by swelling the polymer in a solution of the active substance, followed by drying of the impregnated gel. Adding the active substance to the polymerization may affect the course of the polymerization or alter the active substance, either of which is undesirable.

As an example, Levy et al.[45] describe using superabsorbent polymer as a reservoir for insecticide for the control of mosquitoes. Polyelectrolyte superabsorbent polymers were impregnated with insecticidal, film-forming compounds such as tridecyl alcohol or with insecticides such as malathion, or insect growth regulators. The formulations were stable when dry but swelled in water to release the active ingredients. The release was relatively slow, enabling the formulation to be active over long periods of time and in situations where the polymer cycled through periods of wetness and dryness. In a dry period, the water in the superabsorbent polymer gel evaporates. The remaining active ingredient is trapped and can be released again

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MATERIALS SCIENCE AND ENGINEERING
AN INTRODUCTION

EIGHTH EDITION



William D. Callister, Jr.
David G. Rethwisch

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Characteristics of Selected Elements

Element	*Symbol*	*Atomic Number*	*Atomic Weight (amu)*	*Density of Solid, 20°C (g/cm^3)*	*Crystal Structure, 20°C*	*Atomic Radius (nm)*	*Ionic Radius (nm)*	*Most Common Valence*	*Melting Point (°C)*
Aluminum	Al	13	26.98	2.71	FCC	0.143	0.053	3+	660.4
Argon	Ar	18	39.95	—	—	—	—	Inert	−189.2
Barium	Ba	56	137.33	3.5	BCC	0.217	0.136	2+	725
Beryllium	Be	4	9.012	1.85	HCP	0.114	0.035	2+	1278
Boron	B	5	10.81	2.34	Rhomb.	—	0.023	3+	2300
Bromine	Br	35	79.90	—	—	—	0.196	1−	−7.2
Cadmium	Cd	48	112.41	8.65	HCP	0.149	0.095	2+	321
Calcium	Ca	20	40.08	1.55	FCC	0.197	0.100	2+	839
Carbon	C	6	12.011	2.25	Hex.	0.071	~0.016	4+	(sublimes at 3367)
Cesium	Cs	55	132.91	1.87	BCC	0.265	0.170	1+	28.4
Chlorine	Cl	17	35.45	—	—	—	0.181	1−	−101
Chromium	Cr	24	52.00	7.19	BCC	0.125	0.063	3+	1875
Cobalt	Co	27	58.93	8.9	HCP	0.125	0.072	2+	1495
Copper	Cu	29	63.55	8.94	FCC	0.128	0.096	1+	1085
Fluorine	F	9	19.00	—	—	—	0.133	1−	−220
Gallium	Ga	31	69.72	5.90	Ortho.	0.122	0.062	3+	29.8
Germanium	Ge	32	72.64	5.32	Dia. cubic	0.122	0.053	4+	937
Gold	Au	79	196.97	19.32	FCC	0.144	0.137	1+	1064
Helium	He	2	4.003	—	—	—	—	Inert	−272 (at 26 atm)
Hydrogen	H	1	1.008	—	—	—	0.154	1+	−259
Iodine	I	53	126.91	4.93	Ortho.	0.136	0.220	1−	114
Iron	Fe	26	55.85	7.87	BCC	0.124	0.077	2+	1538
Lead	Pb	82	207.2	11.35	FCC	0.175	0.120	2+	327
Lithium	Li	3	6.94	0.534	BCC	0.152	0.068	1+	181
Magnesium	Mg	12	24.31	1.74	HCP	0.160	0.072	2+	649
Manganese	Mn	25	54.94	7.44	Cubic	0.112	0.067	2+	1244
Mercury	Hg	80	200.59	—	—	—	0.110	2+	−38.8
Molybdenum	Mo	42	95.94	10.22	BCC	0.136	0.070	4+	2617
Neon	Ne	10	20.18	—	—	—	—	Inert	−248.7
Nickel	Ni	28	58.69	8.90	FCC	0.125	0.069	2+	1455
Niobium	Nb	41	92.91	8.57	BCC	0.143	0.069	5+	2468
Nitrogen	N	7	14.007	—	—	—	0.01–0.02	5+	−209.9
Oxygen	O	8	16.00	—	—	—	0.140	2−	−218.4
Phosphorus	P	15	30.97	1.82	Ortho.	0.109	0.035	5+	44.1
Platinum	Pt	78	195.08	21.45	FCC	0.139	0.080	2+	1772
Potassium	K	19	39.10	0.862	BCC	0.231	0.138	1+	63
Silicon	Si	14	28.09	2.33	Dia. cubic	0.118	0.040	4+	1410
Silver	Ag	47	107.87	10.49	FCC	0.144	0.126	1+	962
Sodium	Na	11	22.99	0.971	BCC	0.186	0.102	1+	98
Sulfur	S	16	32.06	2.07	Ortho.	0.106	0.184	2−	113
Tin	Sn	50	118.71	7.27	Tetra.	0.151	0.071	4+	232
Titanium	Ti	22	47.87	4.51	HCP	0.145	0.068	4+	1668
Tungsten	W	74	183.84	19.3	BCC	0.137	0.070	4+	3410
Vanadium	V	23	50.94	6.1	BCC	0.132	0.059	5+	1890
Zinc	Zn	30	65.41	7.13	HCP	0.133	0.074	2+	420
Zirconium	Zr	40	91.22	6.51	HCP	0.159	0.079	4+	1852

Values of Selected Physical Constants

Quantity	*Symbol*	*SI Units*	*cgs Units*
Avogadro's number	N_A	6.022×10^{23} molecules/mol	6.022×10^{23} molecules/mol
Boltzmann's constant	k	1.38×10^{-23} J/atom · K	1.38×10^{-16} erg/atom · K 8.62×10^{-5} eV/atom · K
Bohr magneton	μ_B	9.27×10^{-24} A · m^2	9.27×10^{-21} erg/gauss[a]
Electron charge	e	1.602×10^{-19} C	4.8×10^{-10} statcoul[b]
Electron mass	—	9.11×10^{-31} kg	9.11×10^{-28} g
Gas constant	R	8.31 J/mol · K	1.987 cal/mol · K
Permeability of a vacuum	μ_0	1.257×10^{-6} henry/m	unity[a]
Permittivity of a vacuum	ϵ_0	8.85×10^{-12} farad/m	unity[b]
Planck's constant	h	6.63×10^{-34} J · s	6.63×10^{-27} erg · s 4.13×10^{-15} eV · s
Velocity of light in a vacuum	c	3×10^8 m/s	3×10^{10} cm/s

[a] In cgs-emu units.
[b] In cgs-esu units.

Unit Abbreviations

A = ampere	in. = inch	N = newton
Å = angstrom	J = joule	nm = nanometer
Btu = British thermal unit	K = degrees Kelvin	P = poise
C = Coulomb	kg = kilogram	Pa = Pascal
°C = degrees Celsius	lb_f = pound force	s = second
cal = calorie (gram)	lb_m = pound mass	T = temperature
cm = centimeter	m = meter	μm = micrometer (micron)
eV = electron volt	Mg = megagram	
°F = degrees Fahrenheit	mm = millimeter	W = watt
ft = foot	mol = mole	psi = pounds per square inch
g = gram	MPa = megapascal	

SI Multiple and Submultiple Prefixes

Factor by Which Multiplied	*Prefix*	*Symbol*
10^9	giga	G
10^6	mega	M
10^3	kilo	k
10^{-2}	centi[a]	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

[a] Avoided when possible.

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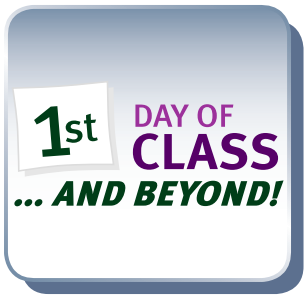


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MAKE IT YOURS!

EIGHTH EDITION

Materials Science and Engineering

An Introduction

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Front Cover: Depiction of a unit cell for the inverse spinel crystal structure. Red spheres represent O^{2-} oxygen ions; dark blue and light blue spheres denote Fe^{2+} and Fe^{3+} iron ions, respectively. (As discussed in Chapter 20, some of the magnetic ceramic materials have this inverse spinel crystal structure.)
Back Cover: The image on the right shows the ionic packing of a close-packed plane for the inverse spinel crystal structure. The relationship between this close-packed plane and the unit cell is represented by the image on the left; a section has been taken through the unit cell, which exposes this close-packed plane.

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Dedicated to

our wives, Nancy and Ellen, whose love, patience, and understanding have helped make this volume possible

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Mechanical Engineering Online Support Module



Biomaterials Online Support Module



Glossary G1

Answers to Selected Problems S0

Index I1

Many polymer properties are affected by the length of the polymer chains. For example, the melting or softening temperature increases with increasing molecular weight (for $\overline{M}$ up to about 100,000 g/mol). At room temperature, polymers with very short chains (having molecular weights on the order of 100 g/mol) will generally exist as liquids. Those with molecular weights of approximately 1000 g/mol are waxy solids (such as paraffin wax) and soft resins. Solid polymers (sometimes termed *high polymers*), which are of prime interest here, commonly have molecular weights ranging between 10,000 and several million g/mol. Thus, the same polymer material can have quite different properties if it is produced with a different molecular weight. Other properties that depend on molecular weight include elastic modulus and strength (see Chapter 15).

14.6 MOLECULAR SHAPE

Previously, polymer molecules have been shown as linear chains, neglecting the zigzag arrangement of the backbone atoms (Figure 14.1*b*). Single chain bonds are capable of rotating and bending in three dimensions. Consider the chain atoms in Figure 14.5*a*; a third carbon atom may lie at any point on the cone of revolution and still subtend about a 109° angle with the bond between the other two atoms. A straight chain segment results when successive chain atoms are positioned as in Figure 14.5*b*. On the other hand, chain bending and twisting are possible when there is a rotation of the chain atoms into other positions, as illustrated in Figure 14.5*c*.[5] Thus, a single chain molecule composed of many chain atoms might assume a shape similar to that represented schematically in Figure 14.6, having a multitude of bends, twists, and kinks.[6] Also indicated in this figure is the end-to-end distance of the polymer chain *r*; this distance is much smaller than the total chain length.

Polymers consist of large numbers of molecular chains, each of which may bend, coil, and kink in the manner of Figure 14.6. This leads to extensive intertwining and entanglement of neighboring chain molecules, a situation similar to a heavily tangled

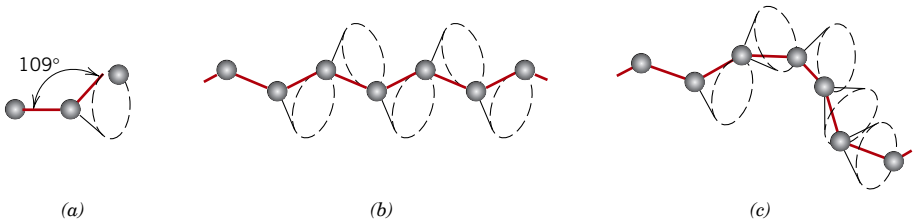


Figure 14.5 Schematic representations of how polymer chain shape is influenced by the positioning of backbone carbon atoms (gray circles). For (*a*), the rightmost atom may lie anywhere on the dashed circle and still subtend a 109° angle with the bond between the other two atoms. Straight and twisted chain segments are generated when the backbone atoms are situated as in (*b*) and (*c*), respectively. (From Askeland, *Science and Engineering of Materials,* 3E. © 1994 Cengage Learning, a part of Cengage Learning, Inc. Reproduced by permission. www.cengage.com/permissions)

[5] For some polymers, rotation of carbon backbone atoms within the cone may be hindered by bulky side group elements on neighboring chain atoms.

[6] The term *conformation* is often used in reference to the physical outline of a molecule, or molecular shape, that can be altered only by rotation of chain atoms about single bonds.

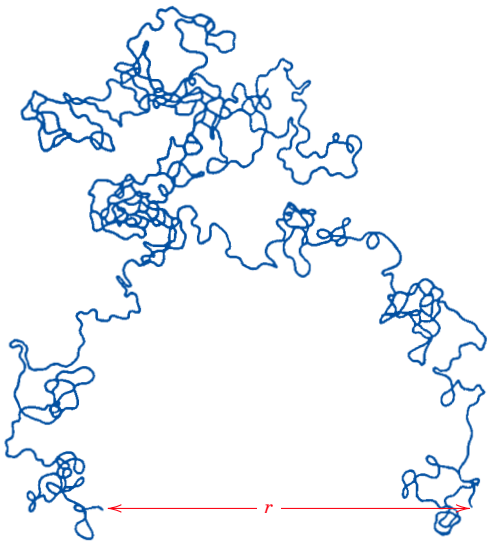


Figure 14.6 Schematic representation of a single polymer chain molecule that has numerous random kinks and coils produced by chain bond rotations. (From L. R. G. Treloar, *The Physics of Rubber Elasticity,* 2nd edition, Oxford University Press, Oxford, 1958, p. 47.)

fishing line. These random coils and molecular entanglements are responsible for a number of important characteristics of polymers, to include the large elastic extensions displayed by the rubber materials.

Some of the mechanical and thermal characteristics of polymers are a function of the ability of chain segments to experience rotation in response to applied stresses or thermal vibrations. Rotational flexibility is dependent on repeat unit structure and chemistry. For example, the region of a chain segment that has a double bond (C═C) is rotationally rigid. Also, introduction of a bulky or large side group of atoms restricts rotational movement. For example, polystyrene molecules, which have a phenyl side group (Table 14.3), are more resistant to rotational motion than are polyethylene chains.

14.7 MOLECULAR STRUCTURE

The physical characteristics of a polymer depend not only on its molecular weight and shape but also on differences in the structure of the molecular chains. Modern polymer synthesis techniques permit considerable control over various structural possibilities. This section discusses several molecular structures including linear, branched, crosslinked, and network, in addition to various isomeric configurations.

Linear Polymers

linear polymer

Linear polymers are those in which the repeat units are joined together end to end in single chains. These long chains are flexible and may be thought of as a mass of spaghetti, as represented schematically in Figure 14.7*a*, where each circle represents a repeat unit. For linear polymers, there may be extensive van der Waals and hydrogen bonding between the chains. Some of the common polymers that form with linear structures are polyethylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), nylon, and the fluorocarbons.

Mechanism of Elastic Deformation

As with other material types, elastic deformation of polymers occurs at relatively low stress levels on the stress–strain curve (Figure 15.1). The onset of elastic deformation for semicrystalline polymers results from chain molecules in amorphous regions elongating in the direction of the applied tensile stress. This process is represented schematically for two adjacent chain-folded lamellae and the interlamellar amorphous material as Stage 1 in Figure 15.12. Continued deformation in the second stage occurs by changes in both amorphous and lamellar crystalline regions. Amorphous chains continue to align and become elongated; in addition, there is bending and stretching of the strong chain covalent bonds within the lamellar crystallites. This leads to a slight, reversible increase in the lamellar crystallite thickness as indicated by Δt in Figure 15.12*c*.

Inasmuch as semicrystalline polymers are composed of both crystalline and amorphous regions, they may, in a sense, be considered composite materials. Therefore, the elastic modulus may be taken as some combination of the moduli of crystalline and amorphous phases.

Mechanism of Plastic Deformation

The transition from elastic to plastic deformation occurs in Stage 3 of Figure 15.13. (Note that Figure 15.12*c* is identical to Figure 15.13*a*.) During Stage 3, adjacent chains in the lamellae slide past one another (Figure 15.13*b*); this results in tilting of the lamellae so that the chain folds become more aligned with the tensile axis. Any chain displacement is resisted by relatively weak secondary or van der Waals bonds.

Crystalline block segments separate from the lamellae, in Stage 4 (Figure 15.13*c*), with the segments attached to one another by tie chains. In the final stage, Stage 5, the blocks and tie chains become oriented in the direction of the tensile axis (Figure 15.13*d*). Thus, appreciable tensile deformation of semicrystalline polymers produces a highly oriented structure. This process of orientation is referred to as **drawing,** and is commonly used to improve the mechanical properties of polymer fibers and films (this is discussed in more detail in Section 15.24).

drawing

During deformation the spherulites experience shape changes for moderate levels of elongation. However, for large deformations, the spherulitic structure is virtually destroyed. Also, to a degree, the processes represented in Figure 15.13 are reversible. That is, if deformation is terminated at some arbitrary stage, and the specimen is heated to an elevated temperature near its melting point (i.e., is annealed), the material will recrystallize to again form a spherulitic structure. Furthermore, the specimen will tend to shrink back, in part, to the dimensions it had prior to deformation. The extent of this shape and structural recovery will depend on the annealing temperature and also the degree of elongation.

15.8 FACTORS THAT INFLUENCE THE MECHANICAL PROPERTIES OF SEMICRYSTALLINE POLYMERS

A number of factors influence the mechanical characteristics of polymeric materials. For example, we have already discussed the effects of temperature and strain rate on stress–strain behavior (Section 15.2, Figure 15.3). Again, increasing the temperature or diminishing the strain rate leads to a decrease in the tensile modulus, a reduction in tensile strength, and an enhancement of ductility.

15.9 DEFORMATION OF ELASTOMERS

One of the fascinating properties of the elastomeric materials is their rubberlike elasticity. That is, they have the ability to be deformed to quite large deformations and then elastically spring back to their original form. This results from crosslinks in the polymer that provide a force to restore the chains to their undeformed conformations. Elastomeric behavior was probably first observed in natural rubber; however, the past few years have brought about the synthesis of a large number of elastomers with a wide variety of properties. Typical stress–strain characteristics of elastomeric materials are displayed in Figure 15.1, curve *C*. Their moduli of elasticity are quite small and, furthermore, vary with strain because the stress–strain curve is nonlinear.

In an unstressed state, an elastomer will be amorphous and composed of crosslinked molecular chains that are highly twisted, kinked, and coiled. Elastic deformation, upon application of a tensile load, is simply the partial uncoiling, untwisting, and straightening, and the resultant elongation of the chains in the stress direction, a phenomenon represented in Figure 15.15. Upon release of the stress, the chains spring back to their prestressed conformations, and the macroscopic piece returns to its original shape.

Part of the driving force for elastic deformation is a thermodynamic parameter called *entropy,* which is a measure of the degree of disorder within a system; entropy increases with increasing disorder. As an elastomer is stretched and the chains straighten and become more aligned, the system becomes more ordered. From this state, the entropy increases if the chains return to their original kinked and coiled contours. Two intriguing phenomena result from this entropic effect. First, when stretched, an elastomer experiences a rise in temperature; second, the modulus of elasticity increases with increasing temperature, which is opposite to the behavior found in other materials (see Figure 6.8).

Several criteria must be met for a polymer to be elastomeric: (1) It must not easily crystallize; elastomeric materials are amorphous, having molecular chains that are naturally coiled and kinked in the unstressed state. (2) Chain bond rotations must be relatively free for the coiled chains to readily respond to an applied force. (3) For elastomers to experience relatively large elastic deformations, the onset of plastic deformation must be delayed. Restricting the motions of chains past one another by crosslinking accomplishes this objective. The crosslinks act as anchor points between the chains and prevent chain slippage from occurring; the role of crosslinks in the deformation process is illustrated in Figure 15.15. Crosslinking in many elastomers is carried out in a process called vulcanization, to be discussed shortly. (4) Finally, the elastomer must be above its glass transition temperature (Section 15.13). The lowest

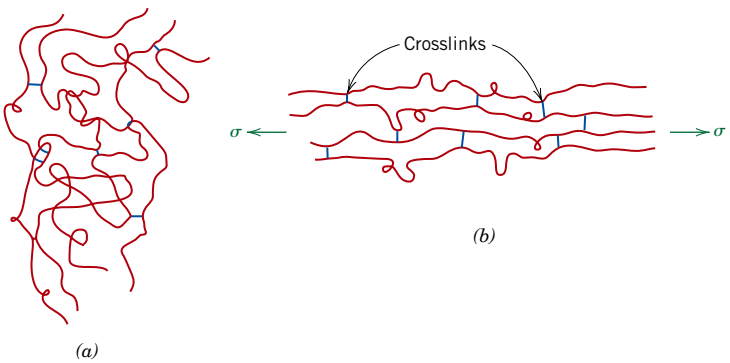


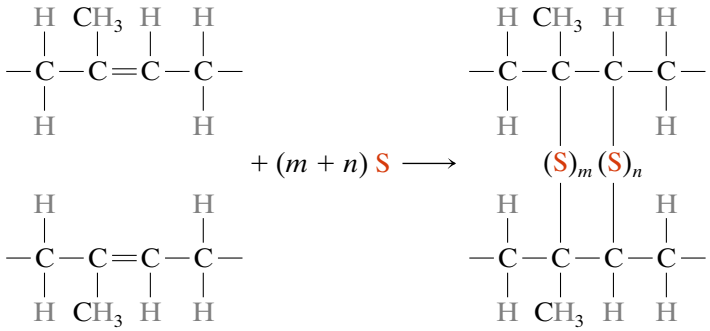
Figure 15.15 Schematic representation of crosslinked polymer chain molecules (*a*) in an unstressed state and (*b*) during elastic deformation in response to an applied tensile stress. (Adapted from Z. D. Jastrzebski, *The Nature and Properties of Engineering Materials,* 3rd edition. Copyright © 1987 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

temperature at which rubberlike behavior persists for many of the common elastomers is between −50 and −90°C (−60 and −130°F). Below its glass transition temperature, an elastomer becomes brittle such that its stress–strain behavior resembles curve *A* in Figure 15.1.

Vulcanization

vulcanization

The crosslinking process in elastomers is called **vulcanization,** which is achieved by a nonreversible chemical reaction, ordinarily carried out at an elevated temperature. In most vulcanizing reactions, sulfur compounds are added to the heated elastomer; chains of sulfur atoms bond with adjacent polymer backbone chains and crosslink them, which is accomplished according to the following reaction:



(15.4)

in which the two crosslinks shown consist of *m* and *n* sulfur atoms. Crosslink main chain sites are carbon atoms that were doubly bonded before vulcanization but, after vulcanization, have become singly bonded.

VMSE



Polymers: Rubber

Unvulcanized rubber, which contains very few crosslinks, is soft and tacky and has poor resistance to abrasion. Modulus of elasticity, tensile strength, and resistance to degradation by oxidation are all enhanced by vulcanization. The magnitude of the modulus of elasticity is directly proportional to the density of the crosslinks. Stress–strain curves for vulcanized and unvulcanized natural rubber are presented in Figure 15.16. To produce a rubber that is capable of large extensions without rupture of the primary chain bonds, there must be relatively few crosslinks, and these

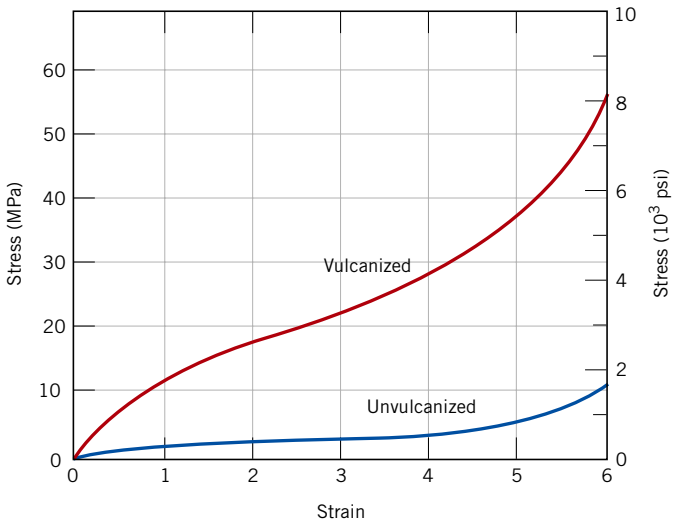


Figure 15.16 Stress–strain curves to 600% elongation for unvulcanized and vulcanized natural rubber.

Ceramic materials are frequently used because of their resistance to corrosion. Glass is often used to contain liquids for this reason. Refractory ceramics must not only withstand high temperatures and provide thermal insulation but, in many instances, must also resist high-temperature attack by molten metals, salts, slags, and glasses. Some of the new technology schemes for converting energy from one form to another that is more useful require relatively high temperatures, corrosive atmospheres, and pressures above the ambient. Ceramic materials are much better suited to withstand most of these environments for reasonable time periods than are metals.

Degradation of Polymers

Polymeric materials also experience deterioration by means of environmental interactions. However, an undesirable interaction is specified as degradation rather than corrosion because the processes are basically dissimilar. Whereas most metallic corrosion reactions are electrochemical, by contrast, polymeric degradation is physiochemical; that is, it involves physical as well as chemical phenomena. Furthermore, a wide variety of reactions and adverse consequences are possible for polymer degradation. Polymers may deteriorate by swelling and dissolution. Covalent bond rupture as a result of heat energy, chemical reactions, and radiation is also possible, ordinarily with an attendant reduction in mechanical integrity. Because of the chemical complexity of polymers, their degradation mechanisms are not well understood.

To briefly cite a couple of examples of polymer degradation, polyethylene, if exposed to high temperatures in an oxygen atmosphere, suffers an impairment of its mechanical properties by becoming brittle. Also, the utility of poly(vinyl chloride) may be limited because this material may become discolored when exposed to high temperatures, although such environments may not affect its mechanical characteristics.

17.11 SWELLING AND DISSOLUTION

When polymers are exposed to liquids, the main forms of degradation are swelling and dissolution. With swelling, the liquid or solute diffuses into and is absorbed within the polymer; the small solute molecules fit into and occupy positions among the polymer molecules. Thus the macromolecules are forced apart such that the specimen expands or swells. Furthermore, this increase in chain separation results in a reduction of the secondary intermolecular bonding forces; as a consequence, the material becomes softer and more ductile. The liquid solute also lowers the glass transition temperature and, if depressed below the ambient temperature, will cause a once-strong material to become rubbery and weak.

Swelling may be considered a partial dissolution process in which there is only limited solubility of the polymer in the solvent. Dissolution, which occurs when the polymer is completely soluble, may be thought of as just a continuation of swelling. As a rule of thumb, the greater the similarity of chemical structure between the solvent and polymer, the greater the likelihood of swelling and/or dissolution. For example, many hydrocarbon rubbers readily absorb hydrocarbon liquids such as gasoline. The responses of selected polymeric materials to organic solvents are contained in Tables 17.4 and 17.5.

Swelling and dissolution traits also are affected by temperature as well as characteristics of the molecular structure. In general, increasing molecular weight, increasing degree of crosslinking and crystallinity, and decreasing temperature result in a reduction of these deteriorative processes.

In general, polymers are much more resistant to attack by acidic and alkaline solutions than are metals. For example, hydrofluoric acid (HF) will corrode many

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Superabsorbent Polymers and Superabsorbent Polymer Composites

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ABSTRACT: This article briefly describes the general aspects and cross-linking polymerization of superabsorbent polymers (SAPs) and superabsorbent polymer composites (SAPCs). Research and development of SAPs has become very active after the Northern Region Laboratory of the United States Department of Agriculture invented the first SAP, used as a soil conditioner. Based on the advancements in organic/inorganic syntheses, SAPs are produced and used in a wide range of applications for fluid absorption. The rapid growing nanotechnology has led to more explorations of SAPs and SAPCs for applications in biomedical, biotechnology and advanced technologies. Examples of research work of SAPs and SAPCs published in refereed, reviewed articles are introduced.

KEYWORDS: Superabsorbent polymers; Superabsorbent polymer composites; Water absorption capacity; Cross-linking reaction; Ionic functional groups.

INTRODUCTION

Superabsorbent polymers (SAPs) or hydrogels are loosely cross-linked, three-dimensional networks of flexible polymer chains that carry dissociated, ionic functional groups. They are basically the materials that can absorb fluids of greater than 15 times their own dried weight, either under load or without load, such as water, electrolyte solution, synthetic urine, brines, biological fluids such as urine sweat, and blood. They are polymers which are characterized by hydrophilicity containing carboxylic acid, carboxamide, hydroxyl, amine, imide groups and so on, insoluble in water, and are cross-linked polyelectrolytes. Because of their ionic nature and interconnected structure, they absorb large quantities of water and other aqueous solutions without dissolving by solvation of water molecules via hydrogen bonds, increasing the entropy of the network to make the SAPs swell tremendously. The factors that supply absorbing power to polymers are osmotic pressure, based on movable counter-ions, and affinity between the polymer electrolyte and water. The factor that suppresses absorbing power, in contrast, is found in the elasticity of the gel resulting from its network structure. Not only are they of high fluid absorbing capacity, but the absorbed fluid is hard to release, as they merely immobilize the fluid by entrapment rather than by holding it in the structure

SAPs possess a number of attributes that make them attractive in many different applications. SAPs have supplanted much of the traditional absorbents in infant diapers and have made significant improvements in the performance of feminine hygiene products and adult incontinence products as a result of superior water-absorbing properties. Because of their excellent characteristics, SAPs are widely used in many fields, such as agriculture, horticulture, sanitary goods, and medicine. The basic property of water absorption has suggested the use of SAPs in many other applications, including paper towels, surgical sponges, meat trays, disposable mats for outside doorways and in bathrooms, household pet litter, bandages and wound dressings. The ability of the swollen gels to release the water to the surroundings as vapor has also been used in various ways, for example, as humidity-controlling products or as soil conditioners. SAPs may also be used to release water-soluble substances from within the network structure into the surroundings as a solution. For example, pharmaceuticals and fertilizers may be incorporated into SAPs to yield controlled release products. Another characteristic of the swollen polymer is its rubbery nature, which has been used to control the consistency of products as diverse cosmetics or concrete or to contribute a soft, yet dry, feel to a product like hot or cold packs for sore muscles. The soft, rubbery nature may also be employed to impact sealing properties to products that are in contact with water or aqueous solutions, for example, underground wires and cables. Since they are widely applied not only in the fields of personal care products, bio-sorbent, bio-material, pharmaceutical, drug delivery systems, but also in agriculture, forestation, industrial, construction, communication industries, and environmental applications, SAPs provide ways for water management for both wanted or unwanted water depending on its particular purpose. Therefore, water absorption

capacity (WAC) is the most important characteristics of SAPs and SAPCs. This can be measured by volumetric, gravimetric, spectroscopic and microwave methods.

Synthesis Techniques

From a material resource point of view, SAPs can also be divided into natural macromolecules, semi-synthetic polymers, and synthetic polymers. From a preparation point of view, they can be synthesized by graft polymerization, cross-linking polymerization, networks formation of water-soluble polymer and radiation cross-linking, etc. There are many types of SAPs presently in the market. Mostly, they are lightly cross-linked copolymers of acrylate and acrylic acid, and grafted starch-acrylic acid polymers prepared by inverse suspension, emulsion polymerization, and solution polymerization. The polymerization techniques have been described[1].

Bulk polymerization

Bulk polymerization is the simplest technique which involves only monomer and monomer-soluble initiators. High rate of polymerization and degree of polymerization occur because of the high concentration of monomer. However, the viscosity of reaction increases markedly with the conversion which generates the heat during polymerization. These problems can be avoided by controlling the reaction at low conversions. The advantage of bulk polymerization is that it produces high molecular weight polymer with high purity. Polyacrylate SAPs are prepared by this technique.

Solution polymerization/cross-linking

In solution co-polymerization/cross-linking reactions, the ionic or neutral monomers are mixed with the multifunctional cross-linking agent. The polymerization is initiated thermally, by UV-irradiation, or by a redox initiator system. The presence of solvent serving as a heat sink is the major advantage of the solution polymerization over the bulk polymerization. The prepared SAPs need to be washed with distilled water to remove the unreacted monomers, oligomers, cross-linking agent, the initiator, the soluble and extractable polymer, and other impurities. Phase separation occurs and the heterogeneous SAP is formed when the amount of water during polymerization is more than the water content corresponding to the equilibrium swelling. The best example is preparation of poly(2-hydroxy ethyl methacrylate) SAPs from hydroxyl ethyl methacrylate, using ethylene glycol dimethacrylate as a cross-linking agent. Using this method, a great variety of hydrogels has been synthesized. The SAPs can be made pH-sensitive or temperature-sensitive by incorporating methacrylic acid or *N*-isopropyl acrylamide as monomers.

Suspension polymerization or inverse suspension polymerization

Suspension polymerization is a method to prepare spherical SAP microparticles with size range of 1 μm to 1 mm. In suspension polymerization, the monomer solution is dispersed in the non-solvent forming fine monomer droplets, which are stabilized by the addition of stabilizer. The polymerization is initiated by radicals from thermal decomposition of an initiator. The newly formed microparticles are then washed to remove unreacted monomers, cross-linking agent, and initiator. Some SAPs microparticles of poly(hydroxy ethyl methacrylate) have been prepared by this method. Recently, the inverse suspension technique has been widely used for polyacrylamide-based SAPs because of its easy removal and management of the hazardous, residual acrylamide monomer in the polymer.

Polymerization by irradiation

Ionizing high energy radiation, like gamma rays[2] and electron beams[3], has been used as an initiator to prepare the SAPs of unsaturated compounds. The irradiation of aqueous polymer solution results in the formation of radicals on the polymer chains. Also, radiolysis of water molecules results in the formation of hydroxyl radicals, which also attack the polymer chains, resulting in the formation of macroradicals. Recombination of the macroradicals on different chains results in the formation of covalent bonds, so finally a cross-linked structure is formed. Examples of polymers cross-linked by the radiation method are poly(vinyl alcohol), poly(ethylene glycol) and poly(acrylic acid). The major advantage of the radiation initiation over the chemical initiation is the production of relatively pure and initiator-free SAPs.

Cross-linking in Superabsorbent Polymers

There are two main types of cross-linking, bulk and surface cross-linking in most advanced SAPs, especially those used in diapers and napkins. The difference between the surface cross-linking and bulk cross-linking is shown below. Network formation is caused by post-polymerization cross-linking or curing in the case of using a UV source[1]. A bi-functional or multi-functional monomer is first mixed with the pre-formed polymer chains and a coupling reaction between the cross-linker and the functional groups on the pre-formed polymer is triggered by low temperature mixing, followed by heating. Ionic cross-linking and covalent cross-linking are the two different types of post-polymerization cross-linking[4].

a) Bulk or core/bulk cross-linking: Such a cross-

linking of the polymer normally takes place during the polymerization stage of the monomer to form a network in which a cross-linking agent is actually a co-monomer with a higher functionality than the main monomer. The reactivity ratio of the cross-linker and the monomer is very important. If the reactivity ratio of the cross-linker is higher than that of the monomer, it will react at low monomer conversion. On the other hand, if the reactivity ratio of the cross-linker is lower than that of the monomer, it will react at a high monomer conversion. Extractable product contains low molecular weight polymer chains that are not incorporated in the polymer network and can be readily extracted in excess liquid. The degree of soluble polymer is important in determining the optimum cross-linking level, since too low a cross-linking level gives high WAC with low strength and high extractable product, while too high a cross-linking level induces low extractable product with non-tacky gel and having low WAC. To obtain an acceptable level for most SAP users, a balance is required with a small amount of extractable, high gel strength and high WAC.

b) Surface cross-linking: This type of surface cross-linking is a new process that improves the absorption against a pressure profile of the polymer gel, such as for feminine napkins. For the surface cross-linking reaction, surface treatment is necessary. Because high swelling capacity is obtained, but poor absorption against pressure occurs due to low elastic gel strength, caused by the low core cross-linking level. Swollen particles are easily deformed and clump together under load. The liquid supplying voids are closed. When the swelling under load is increased, the capacity under load is decreased. Therefore, gel blocking happens, so post-treatment is necessary to solve this problem This takes place during the final stages of SAP manufacture, and can be used to tune the desired properties of the SAP. Surface treatment is also a necessary step to provide better SAP products. A compound having at least two functional groups, capable of reacting with the carboxylate groups on the polymer backbone, such as polyhydric alcohol (monopropylene glycol), diglycidyl ethers (ethylene glycol diglycidyl ether), or quaternary amines, is usually used as a cross-linking agent. The cross-linking agent can be incorporated to the SAP by dissolving it into a solution containing water and a swelling suppressant solvent. Generally, the cross-linking reaction of the coated SAP particles can be performed by heating the polymer for a predetermined time. The amount of the cross-linking agent and heating time can be varied to give SAPs products with different swelling properties, such as absorption against pressure and saline flow conductivity. By the surface treatment, a highly cross-linked shell results with increased rigidity and a lower level of cross-linking core. The shell is of finite thickness, which can be fully controlled by adjusting the coating solvents and particle size of SAPs. The harder surface prevents gel blocking or fish eyes and allows liquid to flow freely to the SAP particles for fluid absorption.

Particle size and particle size distribution (PSD) are one of the important parameters for performance quality of the final products. Generally particle size and PSD have a direct effect on a free swell rate of the SAPs, where the small particle size can absorb faster than the larger particle size. The PSD controls the extent of fluid absorption; inter-particle voids resulting from a broad PSD hold unabsorbed water, which may cause problems with the products. Therefore, controls in polymerization technique, optimization of grinding machine and particle size classification are the keys to success in industrial production of diapers or napkins.

Many kinds of SAPs have been commercialized since the hydrolyzed starch-polyacrylonitrile graft copolymer; the super slurper was first developed by the Northern Regional Laboratory of the United States Department of Agriculture in 1961[4]. Since then tremendous amounts of research and development have been made in an attempt to modify SAPs structure and morphology to enhance WAC, gel strength and absorption rate. New types of SAPs and superabsorbent polymer composites (SAPCs) are emerging for more advanced applications, especially in the nanotechnology field. A well-known example of SAP is an acrylate family which is widely used in many industrial applications especially in personal care products.

Polyacrylate superabsorbent polymers are one of the largest families of the polymer. They are prepared by free-radical initiated polymerization of acrylic acid and its salts with a cross-linker in aqueous solution or as suspension drops of aqueous solution in a hydrocarbon solvent. Furthermore, copolymerization of acrylic acid with other hydrophilic vinyl monomers such as acrylamide has expanded widely the applications of SAPs. The types of co-monomer and cross-linker monomer play an important role in designing SAPs properties and applications. Bulk, solution, and suspension polymerizations are the major production processes for polyacrylate SAPs. In addition, polymerization by radiation has also gained much attention for future clean technology production. The monomer and cross-linker concentrations, the initiator type and concentrations, pre-neutralization or post-neutralization of the carboxylic acid groups, the relative reactivities of the monomer pairs and cross-linker polymerization additives, the medium pH, the reaction temperature, in conjunction with the types of initiator, are all significant factors in both polymerization processes. Several initiating sources for a particular monomers and special additives include thermal

initiator, redox initiator, and photochemical initiator, such as non-ionizing radiation or ionizing radiation. The types of cross-linking agent modify the final properties of SAPs. Without a cross-linking agent incorporated in the SAPs, soluble polymers are always obtained. Cross-linking polymerization plays a significant role in the properties of superabsorbent polymers. Three principal bonding types, namely, covalent, ionic and physical cross-links are used to bind the polymer chains together. The copolymerizing cross-linkers used in SAPs range from di-functional compounds such as *N, N'*-methylenebisacrylamide or diacrylate esters to tri-functional compounds like 1,1,1-trimethyolpropanetricarylate to tetra-functional compounds such as tetraallyloxyethane. In addition, covalently cross-linked SAPs can also be produced. The preformed polymers with the above-mentioned functional monomers react with the carboxylic acid groups by means of a condensation polymerization. Ionic cross-links are formed in which a polyvalent ion of opposite charge reacts with the charged polymer chains. The cross-linking points are thus formed as a result of charge association of the unlike charges. Physical cross-links are formed by means of hydrogen bonding of segments of one polymer chain with the segments of another polymer chain. This type of cross-link is not quite stable, because it is easily destroyed under heat or pressure.

Although there are a few researchers in the area of SAPs in Thailand, SAPs research work carried out here falls into the categories of redox initiation, radiation initiation and polymerization, either by copolymerization or graft copolymerization as follows. Polysaccharide can be a very good substrate for preparing biodegradable SAPs. Starch and chitosan are the most suitable substrates for graft co-polymerization[5-10] to produce SAPs. Syntheses of SAPs by hydrophilic vinyl monomers by inverse suspension polymerization have been widely carried out[11-12] and by solution polymerization[13-15], via radiation initiation and polymerization[16-22].

Superabsorbent polymer composites (SAPCs)

Theoretically, there is a wide range of inorganic materials with expandable layers available for utilization for the preparation of SAPCS. In recent years, the study of organic-inorganic nanocomposites has become a very important field. Currently, reinforcing polymers with small amounts of smectite clays has attracted increasing interest, because the derived hetero-structural materials exhibit impressive mechanical, thermal, optical, and other properties that increase their technological values. The organic/inorganic phases are quite different in nature and incompatible, leading to phase separation. Interfacial bonding and adhesion is introduced to avoid phase separation by covalent bonding. Phyllosilicate is an appropriate material to prepare SAPCs. Clays have sandwich types of structure with an octahedral Al sheet and two tetrahedral Si sheets. There are many types of phyllosilicate: kaolinite, montmorillonite, hectrite, saponite and, synthetic mica, etc. The commonly used layered silicate for the preparation of polymer/layered silicate nanocomposites belongs to the same general family of 2:1 layered phyllosilicate. Their crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of aluminium or magnesium hydroxide. The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. Isomorphic substitution within the layers (for example, Al^{3+} is replaced by Mg^{2+} or Fe^{2+}, or Mg^{2+} is replaced by Li^{+}) generates negative charges that are counterbalanced by alkali and alkali earth cations situated inside the galleries. In the case of tetrahedrally substituted layered silicates, the negative charge is located on the surface of silicate layers, and hence, the polymer matrices can react interact more readily with these than with octahedrally-substituted material. Therefore, intercalation structures can be produced in SAPCs. The SAPCs find many new applications beyond those of SAPS, such as nanocomposite materials, for example, fabrication of silver or zinc nanoparticles in SAP or SAPC networks. The proven applications are for catalysis, optics, electronics, bio-medicals and quantum-sized domain applications. Some potential application of SAPCs in water treatments have been described[23-26].

Future prospects

SAPs and SAPCs are very dynamic research areas in polymer sciences due to the advances in polymer syntheses resulting in better WAC, higher gel strength and faster absorption rate, as well as other materials properties for comfort and safety. Nanotechnology will likely play a major role in the production of the higher performance SAPs and SAPCs.

References

1. Staples TL, Henton DE, and Buchholz FL (1998) Chemistry of Superabsorbent Polyacrylates. In *Modern Superabsorbent Polymer Technology* (Eds: Buchholz, FL and Graham, AT), Wiley-VCH, New York, Chapter 2.
2. Karadað E., Saraydin D., Gûven O. (2001) Radiation Induced Superabsorbent Hydrogels. Acrylamide/Itaconic Acid

Copolymers, *Macromol. Mater. Eng* **286**: 34-42.
3. Garnett JL., Ng L-T., Virngkhou V. (1999) Grafting of Methyl Methacrylate to Cellulose and Polypropylene with UV and Ionising Radiation in the Presence of Additives Including CT Complexes, *Radiation Phys Chem* **56**: 387-403.
4. United States Department of Agriculture (1961) U.S. Patent 3,981,100.
5. Faullimmel JG, Kiatkamjornwong S, and Rungsriwong N (1988) Graft Copolymerization of Acrylonitrile onto Cassava Starch. I. Synthesis of saponified starch-*g*-polyacrylonitrile by manganic pyrophosphate initiation. *J. Sci Res Chulalongkorn Univ* **13**: 42 – 9.
6. Faullimmel JG, Kiatkamjornwong S and Rungsriwong N (1988) Graft Copolymerization of Acrylonitrile onto Cassava Starch. II. Water absorption properties of saponified cassava starch-*g*-polyacrylonitrile. *J. Sci Res Chulalongkorn Univ* **13**: 103 –10.
7. Faullimmel, JG, Kiatkamjornwong S and Rungsriwong N (1989). Graft Copolymerization of Acrylonitrile onto Cassava Starch. III. Effect of gelatinization temperature on water absorption. *J Sci Res Chulalongkorn Univ* **14**: 12 –7.
8. Kiatkamjornwong S, and Faullimmel, JG (1991) Synthesis of Cassava Starch-Based Water-Absorbing Polymer for Agriculture Application, *J. Nat Res Council Thailand* **23**: 15-35.
9. Sangsirimongkolying R, Damronglerd S and Kiatkamjornwong S (1999) Pilot-Scale Production of Highly Water Absorbing Polymer from Native Cassava Starch by Hydrogen Peroxide-Ascorbic Acid Initiation. *J. Sci Res Chulalongkorn Univ* **24**: 1 –12.
10. Damronglerd S, Kiatkamjornwong S and Sangsirimongkolying, R (1999) Expanded-Scale Production of Highly Water Absorbing Polymer from Cassava Starch. *J Royal Inst Thailand, Acad Sci* **24**: 90 – 103.
11. Kiatkamjornwong S, Siwarungson N and Nganbunsri A (1999) *In Situ* Immobilization of Alkaline Protease during Inverse Suspension Polymerization of Polyacrylamide and Poly(Acrylamide-*co*-Methacrylic Acid) Hydrogel Beads. *J. Appl Polymer Sci* **73**: 2273 – 91.
12. Kiatkamjornwong S and Phunchareon P (1999) Influences of Reaction Parameters on Water Absorption of Neutralized Poly(Acrylic Acid-*co*-Acrylamide) Synthesized by Inverse Suspension Polymerization. *J. Appl Polym. Sci* **72**: 1349-66.
13. Kiatkamjornwong S and Wongwatthanasatien R (2004) Superabsorbent Polymer of Poly[acrylamide-*co*-(acrylic acid)] by Foamed Polymerization. I. Synthesis and Water Swelling Properties. *Macromol Symp* **207**: 229-40.
14. Lanthong P, Nuisin R and Kiatkamjornwong S (2006) Graft Copolymerization, Characterization and Degradation of Cassava Starch-*g*-Acrylamide/Itaconic Acid Superabsorbents, *Carbohydr Polym* **66**: 229 – 45.
15. Yeamsawas D, Kangwasupamonkon W, Chailapakul O and Kiatkamjornwong, S (2007) Synthesis and Swelling Properties of Poly[Acrylamide-*co*-(Crotonic Acid)] Superabsorbents, *React Funct. Polym*. **67**: 865-82.
16. Kiatkamjornwong S, Chvajarernpun J and Nakason C (1993) Modification on Liquid Retention Property of Cassava Starch by Radiation Grafting with Acrylonitrile. I. Effect of γ-Irradiation on Grafting Parameters. *Radiation Phys Chem* **42**: 47–52.
17. Kiatkamjornwong S and Meechai N (1997) Enhancement of the Grafting Performance and of the Water Absorbing of Cassava Starch Graft Copolymer by Gamma Radiation. *Radiation Phys Chem* **49**: 689 – 96.
18. Kiatkamjornwong S and Suwanmala P (1997) Effect of Total Dose on Water Absorption of Partially Hydrolyzed Polyacrylamide-*co*-Poly(Vinyl Pyrrolidone) Superabsorbent by Gamma Irradiation. *Radiation Phys Chem* **50**: 617 – 24.
19. Kiatkamjornwong S and Suwanmala P (1998) Partially Hydrolyzed Poly[acrylamide-*co*-Poly(1-Vinyl-2-Pyrrolidone)] Synthesized by Gamma Irradiation. *J Appl Polymer Sci* **68**: 191 – 203.
20. Kiatkamjornwong S and Suwanmala P (1998) Effect of Dose Rate on Water Absorption of Partially Hydrolyzed Poly[acrylamide-*co*-Poly(Vinyl Pyrrolidone)] Superabsorbent by Gamma Irradiation. *Radiation Phys Chem* **52**: 217 – 21.
21. Kiatkamjornwong S, Chomsaksakul W and Sonsuk M (2000) Radiation Modification of Water Absorption of Cassava Starch by Acrylic Acid/Acrylamide. *Radiation Phys Chem* **59**: 413-27.
22. Kiatkamjornwong S, Mongkolsawat K and Sonsuk, M (2002) Synthesis and Property Characterization of Cassava Starch-*g*-Poly[acrylamide-*co*-(maleic acid)] via gamma-irradiation. *Polymer* **43**: 3915-24.
23. Jiraprasertkul W, Nuisin R, Jinsart W and Kiatkamjornwong S (2006) Synthesis and Characterization of Cassava Starch Graft Poly(acrylic acid) and Poly[(Acrylic Acid)-*co*-Acrylamide] and Polymer Flocculants for Wastewater Treatment. *J Appl Polymer Sci* **102**: 2915 –28.
24. Nanakorn P, Noppakundilograt S, Seetapan N and Kiatkamjornwong S (2007) Synthesis and Characterization of Acrylamide-Based Aluminium Flocculant for Turbidity Reduction in Wastewater. *Europ Polymer J,* submitted.
25. Noppakundilograt S, Nanakorn P and Kiatkamjornwong S (2007) Removal of Congo Red and Direct Blue 71 by Acrylamide/Acrylic Acid-Based Aluminium Flocculants. *J Hazard Mat*, submitted.
26. Phattanarudee S, Foungfung D and Kiatkamjornwong S (2007) Effect of Mica on Water Absorption of Acrylamide–Itaconic Acid Superabsorbent Nanocomposites. *Europ Polymer J*, submitted.

PRINCIPLES OF POLYMERIZATION

Fourth Edition

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here. All monomers can be polymerized by any of the various processes. However, it is usually found that the commercial polymerization of any one monomer is best carried out by one or two of the processes. The laboratory techniques for carrying out polymerizations have been discussed [Sandler and Karo, 1992, 1993, 1998; Sorenson et al., 2001]. Up-to-date technological details of commercial polymerizations are difficult to ascertain, although general descriptions are available [Arpe, 2002; Brydson, 1999; Grulke, 1989; Matsumoto et al., 1977; Menikheim, 1988; Munzer and Trommsdorff, 1977; Salamone, 1996; Saunders, 1988; Schildknecht, 1977].

3-13a Bulk (Mass) Polymerization

Bulk or *mass polymerization* of a pure monomer offers the simplest process with a minimum of contamination of the product. However, bulk polymerization is difficult to control because of the characteristics of radical chain polymerization. Their highly exothermic nature, the high activation energies involved, and the tendency toward the gel effect combine to make heat dissipation difficult. Bulk polymerization requires careful temperature control. Further, there is also the need for strong and elaborate stirring equipment since the viscosity of the reaction system increases rapidly at relatively low conversion. The viscosity and exotherm effects make temperature control difficult. Local hot spots may occur, resulting in degradation and discoloration of the polymer product and a broadened molecular weight distribution due to chain transfer to polymer. In the extreme case, uncontrolled acceleration of the polymerization rate can lead to disastrous ''runaway'' reactions [Sebastian and Biesenberger, 1979]. Bulk polymerization is not used commercially for chain polymerizations nearly as much as for step polymerizations because of the difficulties indicated. It is, however, used in the polymerizations of ethylene, styrene, and methyl methacrylate. The heat dissipation and viscosity problems are circumvented by carrying out the polymerizations to low conversions with separation and recycling of unreacted monomer. An alternative is to carry out polymerization in stages—to low conversion in a large reactor and to final conversion in thin layers (either on supports or free-falling streams).

3-13b Solution Polymerization

Polymerization of a monomer in a solvent overcomes many of the disadvantages of the bulk process. The solvent acts as diluent and aids in the transfer of the heat of polymerization. The solvent also allows easier stirring, since the viscosity of the reaction mixture is decreased. Thermal control is much easier in *solution polymerization* compared to bulk polymerization. On the other hand, the presence of solvent may present new difficulties. Unless the solvent is chosen with appropriate consideration, chain transfer to solvent can become a problem. Further, the purity of the polymer may be affected if there are difficulties in removal of the solvent. Vinyl acetate, acrylonitrile, and esters of acrylic acid are polymerized in solution.

3-13c Heterogeneous Polymerization

Heterogeneous polymerization is used extensively to control the thermal and viscosity problems. There are three types of heterogeneous polymerization: *precipitation, suspension*, and *emulsion*. Emulsion polymerization is discussed in Chap. 4. Precipitation polymerizations begin

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Water-Absorbent Polymers: A Patent Survey

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N,N'-methylenebisacrylamide. After reaction completion, a second portion (5–25% by weight) of acrylic comonomer [methyl methacrylate, (meth)-acrylic acid, 2-hydroxyethyl methacrylate] is added, and polymerization restarts.

Water absorbent poly(acrylate)s themselves serve as seeds for polymerization of sodium acrylate in organic solvents [193]. The aqueous monomer solution is absorbed by the poly(acrylate) particles dispersed in hydrocarbon and polymerized.

Polymerization of acrylic acid can be accomplished directly in a fibrous matrix [162, 163]. A solution containing monomer, sodium hydroxide, initiator, and *N,N'*-methylenebisacrylamide [163] is sprayed over cotton and polymerized. The product is mixed with unreacted cotton and used for diapers, napkins, surgical pads, etc. manufacture. Similar methods have been experimented with polyester fibers, fabrics [225, 239, 270], or webs [188]. Addition of poly(ethylene glycol) dilaurate (or other surfactants having HLB values greater than 7) in order to facilitate fiber impregnation is claimed [239]. One patent [225] claims neutralization of acrylic acid with ammonia, alkali metal hydroxides, or vinylpyridine. Monomer polymerization can be initiated by ascorbic acid solution sprayed on fiber preimpregnated with monomers and peroxide solution [225, 239]. A water-absorbent fabric, manufactured by impregnating a synthetic fiber fabric with an alkali metal acrylate, crosslinking agent, initiator, and a water-soluble polymer solution [poly(*N*-vinylpyrrolidone) or poly(ethylene oxide)] [310], is used as a water cutoff layer in optical fiber cables and shows good flexibility.

2.1.2. Monomers

As already pointed out, (meth)acrylic acid and amides are the typical monofunctional comonomers used for absorbent polyacrylate manufacture. Although a great variety of other unsaturated comonomers were claimed in patents, specific examples concern only a limited number of chemical compounds. Nonetheless, some particular monomers are explicitly disclosed in patent documents.

Unsaturated sulfonic acid salts are used in the synthesis of homopolymers [187] and copolymers [124, 53, 45, 67, 70, 116, 278, 135, 305].

Acrylamidoalkyl sulfonic salts **(II)** like

$$CH_2=CH-(C=O)-NH-R-SO_3M \qquad \textbf{(II)}$$

are described [187] (in the examples, R = isobutylene; M = Na, ammonium). The synthesis was performed in water in the presence of a peroxide initiator and crosslinking agents (polyallyl compounds or *N,N'*-methylene-

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bisacrylamide). Use of **(II)** comonomers is also reported in other patents [124, 135, 305]. Acrylamide/sodium 2-acrylamido-2-methylpropansulfonate copolymers are useful for removing acidic water from fuels, battery casings, etc., maintaining their absorbent properties at low pH values [135].

In other patents [53, 67, 70], copolymers are described of acrylic acid (<50% by weight), *N*-substituted (meth)acrylamides **(III)** (<5% by weight), and an olefinically unsaturated sulfonic salt; for instance, a vinylsulfonate, a styrenesulfonate, or a vinylbenzylsulfonate (>25% by weight).

$$CH_2{=}CR^1{-}(C{=}O){-}NH{-}CH_2OR \qquad \textbf{(III)}$$

where R = alkyl; R^1 = H, methyl. The *N*-substituted (meth)acrylamides used, also cited in another patent [71], allow a peculiar kind of crosslinking that will be discussed in the following section.

Ampholitic ion pair monomers **(IV)** are copolymerized with (meth)acrylic acids, esters, salts, amides, or nitriles in the presence of *N,N'*-methylenebisacrylamide [278].

$$CH_2{=}C(CH_3){-}(C{=}O){-}OCH_2CH_2{-}N(CH_3)_3^{+}{}^{-}SO_3{-}R{-}CH{=}CH_2 \qquad \textbf{(IV)}$$

where R = alkylene, arylene.

Dialkylaminoalkyl (meth)acrylates or (meth)acrylamides **(V)** are emulsion polymerized in the presence of *N,N'*-methylenebisacrylamide [294].

$$CH_2{=}CR^1{-}(C{=}O){-}A{-}CH_2NR^2R^3 \qquad \textbf{(V)}$$

where R^1 = H, methyl; R^2, R^3 = alkyl; A = OCH_2, NCH_2CH_2. Postreacting the emulsion with an acid, a salt (aluminum sulfate, ferric chloride, etc.), or a quaternarizing agent (alkyl halide or sulfate) gives rise to a polymer with water-swelling properties. The emulsion shows better solubility than a powder product and has excellent stability, so the posttreatment can be carried out any time before use.

Hydrogels with bacteriostatic properties are prepared by polymerizing acrylamide and/or acrylic acid with *N,N'*-methylenebisacrylamide and 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride [76, 96]. The resulting polymer is suitable for applications requiring contact of the material with the human body, e.g., wound dressing or coating for medical devices.

Copolymers of heterocyclic *N*-vinyl monomer containing a carbonyl function (*N*-vinyl-2-pyrrolidone, *N*-vinyl-2-caprolactam, *N*-vinyl-2-morpholinone, etc.) and alkyl acrylates are prepared in organic solvents (alco-

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hols or hydrocarbons) using diacrylates as crosslinking agents. They are used in surgical tools manufacturing [27].

Vinylpyridine (ortho or para) is added in small amounts (< 1%) to solutions containing acrylic acid, potassium acrylate, and *N,N'*-methylenebisacrylamide [225]. A polyester nonwoven fabric is impregnated with the aqueous mixture before initiating polymerization. Vinylpyridine in greater amounts (up to 20%) is claimed in other patents [247, 254].

Oxygen permeability of polymers, a desired characteristic for contact lens materials, increases with their water content. Thus, some water-absorbent polymers are very suitable for the manufacture of contact lenses. Examples are reported by Nakashima et al. [206]. Their patent discloses radical polymerization of vinyl acetate in the presence of crosslinked methyl methacrylate/hydroxyalkyl methacrylate copolymers (0–9% mol of hydroxyalkyl methacrylate in the copolymer; 70–98% by weight of vinyl acetate in the polymerization mixture). The resulting copolymers are saponified to give transparent, permeable gels.

Polymer absorbent emulsions prepared by the polymerization of dimethylaminoethyl methacrylate in the presence of *N,N'*-methylenebisacrylamide are described [260].

Copolymers of methacrylic acid, 3-*O*-methacryloyl-D-glucose, and *N,N'*-methylenebisacrylamide are prepared and neutralized with NaOH [223].

Crosslinked copolymers of acrylic acid and long chain acrylic esters (C_{10-30}) are prepared in hydrocarbon solvent; stearyl methacrylate is used in the examples [31]. The presence of crosslinking agent is optional; the insolubility in water is caused by hydrophobic alkyl chains. The polymers described in this patent have an improved rheological behavior because they do not drop sharply in viscosity compared with other water-absorbent polymers when a salt is present in the fluid. Thus, they are potentially useful for thickening ion-containing water or solutions.

A substantial improvement of absorption rate and capacity with respect to these polymers is claimed in a group of four patents of the same company [60, 61, 89, 90]. Copolymers of partially neutralized unsaturated carboxylic acids (30–90% by weight), C_{10-30} alkyl (meth)acrylates (2–30%), C_{1-8} alkyl (meth)acrylates, or (meth)acrylamides (5–40%) are claimed. The radical polymerization is accomplished in chlorofluorocarbons, and the crosslinking agent, when present, enhances absorbent properties. Further addition of C_{3-8} diols or poly(etherdiol)s [61] makes the polymer more easily extrudable due to a plasticizing effect.

Acrylic acid neutralized to at least 70% and a comonomer selected from styrene or its derivatives or C_{6-18} α-olefins (7–93% by weight of monomer mixture) are dispersed in water and polymerized by photochemical initia-

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tion [110]. Styrene is also claimed to be a comonomer in other patents [235, 177, 253].

Long-chain alkyl acrylates as plasticizing monomers are cited in several patents [32, 49, 55, 139, 218].

Soft water absorbent polymers useful for fibers and coated articles production are synthesized without using external plasticizers [32, 49, 55]; in this way there is no possibility of releasing low molecular weight compounds by the polymer. C_{4-10} alkyl methacrylate or C_{1-10} alkyl acrylate (50–92% by weight), unsaturated carboxylic acids (8–50%), and C_{1-4} ω-hydroxyalkyl acrylates (0–15%) are used; partial saponification is made with an alkali metal hydroxide solution, and a crosslinking agent (diglycidyl derivatives, haloepoxides, dihalo alcohols) is added. Saponification is made in such a way that 30–70% of the acrylic ester units are left intact.

Water swellable polymers with a relatively high hydrophobic character may be used as viscosifiers for hydrocarbons instead of traditional hydrocarburic polymers [211]. They are obtained by copolymerizing about 1% of a hydrophilic monomer (acrylic acid) and a hydrophobic polar monomer (C_{6-10} alkyl acrylates; a preferred monomer is ethylhexyl acrylate). A nonpolar hydrophobic comonomer can be added to the formulation; a crosslinking agent is usually not necessary. The emulsion is directly added as obtained to the hydrocarbon in an amount of about 0.5–5% by weight after polymerization.

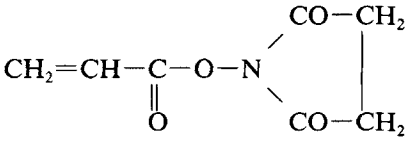
C_{1-4} alkyl acrylates and hydroxyalkyl (meth)acrylates (molar ratio 12–5:1) are copolymerized in aqueous medium, partially saponified with strong alkali alcoholic solutions, and neutralized with HCl [136]. No crosslinking agent is used because the hydroxyalkyl acrylate, according to the author, acts as a crosslinking site.

Glycidyl methacrylate and diethyleneglycol dimethacrylate are polymerized by suspension polymerization to give crosslinked poly(glycidyl methacrylate) [298]. The polymer is swollen with dioxane or tetrahydrofuran, so the glycidyl groups may be hydrolyzed with acid-water solutions to obtain poly(glycerol methacrylate). Treatment of poly(glycerol methacrylate) with 2-chloroethyldiethylamine hydrochloride solutions leads to anionic resin-bearing ammonium groups, while treatment of swollen poly(glycidyl methacrylate) with sulfite or hydrogenosulfite solutions leads to a cationic sulfonated resin. These resins, which have a controlled pore size, can be employed as gel filtration chromatography media to separate and recover ionizable macromolecular substances (especially proteins) from aqueous solutions.

Copolymer beads able to bond biological substrates bearing amino or hydroxyl groups (enzymes, antigens, peptides, hormones, etc.) are prepared by radical polymerization in heptane/tetrachloroethylene/formamide solu-

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tions. The copolymer is a crosslinked copoly(acrylic acid) or copoly(acrylamide) modified with about 15–50% of a comonomer having epoxidic, anhydridic, or succinimidic groups [66]. Examples of such comonomers are (meth)acrylic anhydride, glycidyl acrylate or other epoxyalkyl (meth)acrylates, and acryloyl *N*-oxysuccinimide (**VI**).



(**VI**)

Other comonomers may be used (allyl methacrylate, sulfoethyl methacrylate, *N*-vinylpyrrolidone, 2-hydroxyethyl methacrylate).

Copoly(acrylate)s are prepared by (co)polymerizing acrylonitrile and/or methacrylonitrile with crosslinking divinyl monomers and partially saponifying the resulting product [144, 198]. The final polymer bears carboxylate and amide groups. By incorporating a reducing agent (sodium hydrosulfite or thiosulfate) before the saponification stage and an oxidizing agent (benzoyl or hydrogen peroxide, sodium perborate) after the saponification stage, a white product is obtained, otherwise the product is dark [208].

A poly(styrene–acrylic acid–sodium acrylate) block copolymer is prepared by reacting a methacryloyl-terminated poly(styrene) (molecular weight about 7000) with acrylic acid in a cyclohexane/toluene/methylethylketone solution [244]. Seventy-five percent of the carboxylic groups are neutralized with NaOH.

2.1.3. Crosslinking

Crosslinking of polymer chains is basically carried out in two ways. The first involves free-radical copolymerization with small amounts of polyvinylic comonomers. The second way consists of a nucleophilic or condensation reaction between the carboxylate or carboxylic pendant group of the *linear* polymer, respectively, with suitable polyfunctional compounds; poly(epoxides), haloepoxides, and polyols are the most common of them.

As previously pointed out, spontaneous thermal crosslinking takes place in some other cases [74, 107, 179] or involves intermolecular reactions between chemical functions already present in the polymer chains as pendant groups [83, 136, 217, 218, 241, 264], such as carboxyls and hydroxyls. Alkoxymethylamido groups of *N*-alkoxymethyl (meth)acrylamides (**III**) copolymers may undergo nucleophilic attack of carboxylate groups present on the chain, on heating, and by splitting out alcohol molecules and giving rise to crosslinked structures [53, 67, 70, 71]. Uncrosslinked polymeric film

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where X = Cl, Br, or I.

2.3. Maleic Anhydride Copolymers

Copolymers of maleic anhydride (MA) and hydrophobic comonomers represent a third class of superabsorbent polymers. The hydrophobic comonomer could be either an olefin or a vinyl ether. Free-radical polymerization is accomplished in organic solvents (ketones, benzene, chlorohydrocarbons). The anhydridic ring is transformed to the salified or hemisalified form to impart hydrophilicity to the polymer, and it can serve as a reaction site for crosslinking agents. Absorbent properties of maleic anhydride absorbent copolymers are reported in Table 5.

One patent claims crosslinked MA/indene water swellable copolymers [73].

Styrene/MA/*N*-vinylpyrrolidone, styrene/MA/isobutyl acrylate, and styrene/MA copolymers are synthesized in ketonic solvents, mixed with glycols (0.5–2.5% by weight) as crosslinking agents and extruded through a spinnerette in a water bath [44]. Fibers are stretched and heated at 50°C to complete the crosslinking reaction, then are treated with gaseous ammonia or alkali metal hydroxide solutions to transform anhydridic rings to their salt form and render the material hydrophilic. Polyethoxylated and polypropoxylated glycerine (molecular weight 500–6000) are used as alternative crosslinking agents (10% based on the weight of polymer) in analogous processes [38].

Styrene/MA and isobutylene/MA copolymers are partially hydrolyzed with alkaline solutions (about 30–70% of total carboxylic groups) and crosslinked with alkylene carbonates, gylcols, poly(etherdiol)s, or oligosac-

TABLE 5

Absorption Properties of Absorbent Olefin/Maleic Anhydride Copolymers (the best values among those of patent examples are reported.)

References	Water absorption capacity (g/g polymer)	Saline or physiological solution absorption capacity (g/g polymer)
38	119	22
197	69.5	
157, 181	160	24
186, 205		44.7
46		34

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charides (especially sucrose) [197, 232, 229, 214, 219] at high temperatures. Epoxy resins, styrene oxide, propylene oxide, glycidyl methacrylate, epichlorohydrin, and glycidol are also used for copolymers of MA with methyl vinyl ether, ethylene, isobutylene, or styrene [8].

Williams et al. describe the polymerization in benzene of MA, alkyl vinyl ethers (alkyl = methyl in the examples) and divinyl ether as a crosslinking agent [109, 117]. The polymer is then reacted with ammonia or alkylamines; copolymerized anhydridic rings are opened and amide and ammonium carboxylate groups are formed. The choice of the length of amine alkyl chain depends on the desired balance in the final polymer between hydrophilic and hydrophobic properties (namely, the degree of swelling).

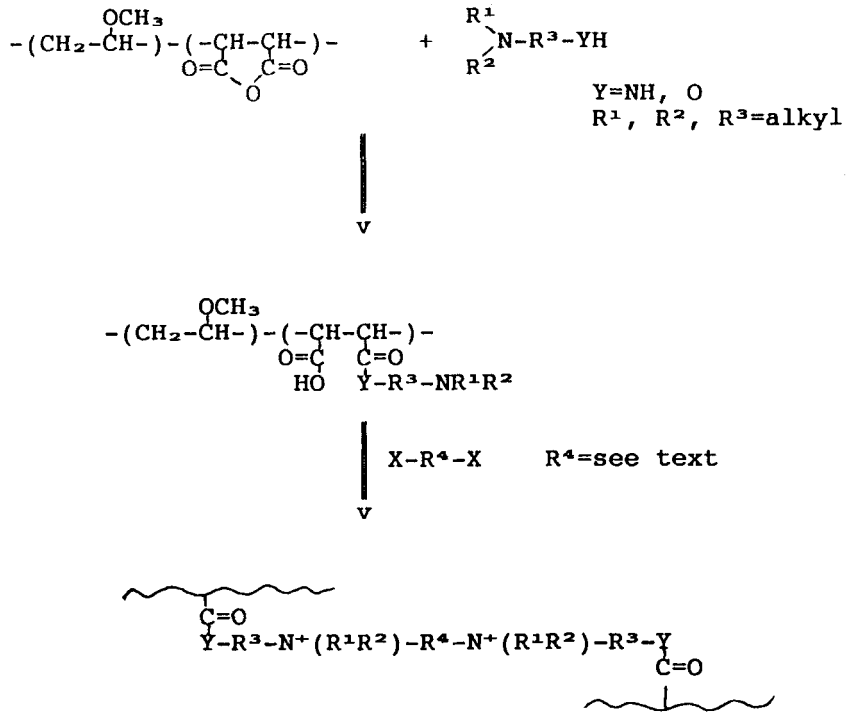
Copolymers of MA and C_{2-4} olefins are synthesized in dichloroethylene or benzene solution with peroxide initiator [4]. Crosslinking agents are allyl esters of olefinically unsaturated acids [maleic, itaconic, crotonic, (meth)acrylic, etc.]. The author has found that other polyunsaturated compounds, such as divinylbenzene, alkyl vinyl ethers, triallyl isocyanurate, ethyleneglycol methacrylate, *N,N'*-methylenebisacrylamide, and others, are ineffective in crosslinking this class of copolymers. Treatment with a base provides the final hydrophilic product.

All the crosslinking agents described by Gross for acrylic polymers and summarized in Section 2.1.3 are also useful for MA copolymers [47, 50, 54].

Polyethyleneimine as a crosslinking agent is described by Murakami et al. [118]. Coating kaolin with the said copolymer gives rise to a water-retaining agent for horticulture.

The preparation of water absorbent semi-interpenetrating polymer networks (SIPN) is described by Stofko et al. [301, 302]. A methyl vinyl ether/MA copolymer (matrix polymer) is functionalized with dialkylaminoalkylamine or dialkylaminoalcohols [301] according to Scheme 2. A polymer solution is then mixed with a water-soluble polymer [poly(*N*-vinylpyrrolidone) or poly(ethyloxazoline)] or with a water-swellable poly(acrylate) (acrylic acid/methyl methacrylate/hydroxyethyl methacrylate copolymers), and crosslinked through reaction between pendant amino groups with difunctional alkylating compounds [α,α'-dibromo-*m*-xylene, dibromoneopentyl glycol, or 3,3,-bis(iodomethyl)oxetane]. Functionalization of the matrix polymer can also be performed with aminoalkyltrialkoxysilanes and (poly)alkoxyalkylamine mixtures [302] according to Scheme 3. The functionalized matrix polymer is then mixed with poly(*N*-vinylpyrrolidone) or poly(vinyl alcohol). Addition of water causes hydrolysis of trialkoxysilyl groups and crosslinking. The SIPN obtained are useful in manufacturing contact lenses and ink-receptive layers for transparent imageable materials. Typical inks for plotter pens contain solvents with low volatility in order

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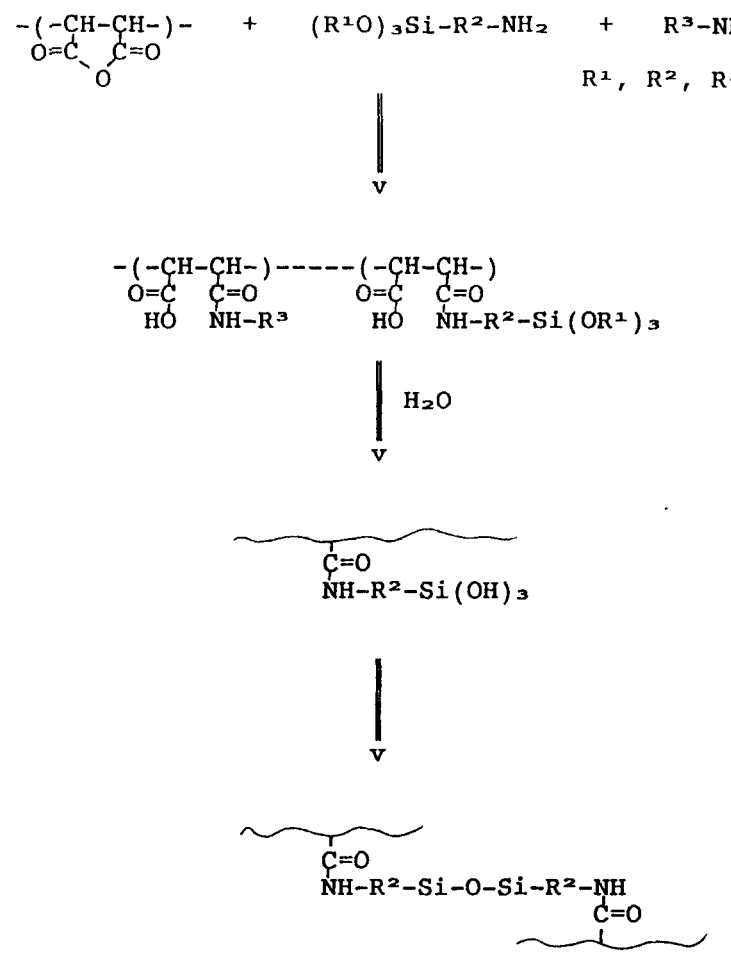
SCHEME 2.

to avoid desiccation due to prolonged exposure of pens to air. Water or water-miscible solvents are commonly used. They give good results on paper supports because paper absorbs such solvents very efficiently. However, because of low volatility, image drying on polymeric transparent films would be very slow. Thus, to avoid this problem, water absorbent materials should be blended to a polymeric matrix support, but blending is often unsatisfactory since demixing, lack of transparency, haze, and brittleness occur due to phase separation. The use of the SIPN described is a way to solve all these problems.

Blends of crosslinked MA copolymers are described in several patents. Multi-arm block styrene/ethylene oxide copolymers are mixed with styrene/MA copolymers [157, 181]. Cast films are immersed in KOH solutions to enhance absorptivity. Fibrous materials based on blends with block poly(ethylene oxide-*co*-propylene oxide) are also described [186, 205].

Chloroprene rubbers, neoprene rubbers, styrene–butadiene rubbers, and

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SCHEME 3.

styrene–isoprene rubbers are mixed with crosslinked isobutylene/MA copolymers [111, 115] to give water-absorbent rubber compositions, useful as water leak stoppers.

Styrene/MA or isobutylene/MA copolymers crosslinked with *N,N'*-methylenebisacrylamide are synthesized, and water dispersions of them are added to cellulose slurry employed for the preparation of paper handsheets [46]. After treatment with ammonia or NaOH, the paper shows high water absorptivity.

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Finally, blends of styrene/MA copolymer and poly(vinyl acetate) are reported by Heslinga et al. [105, 106]. Cellulose acetate, cellulose acetobutyrate, poly(methyl methacrylate), and poly(ethyl acrylate) are also used instead of poly(vinyl acetate). Blends are employed for fibers or foams manufacture.

Water-absorbent laminates useful as a cover for greenhouses are manufactured by superimposing a polyester nonwoven fabric and a film of isobutylene/maleic anhydride/sodium maleate copolymer, and heat-treating [147].

2.4. Miscellaneous

In this section polymers not belonging to previous classes are described. Their absorbent properties are reported in Table 6.

2.4.1. Synthesis

Diallyl dialkyl quaternary ammonium salts **(IX)** polymerize in water/heptane mixture and in the presence of polyfunctional divinyl compounds to give water-absorbent materials [133]. The use of a crosslinking agent is

TABLE 6

Absorption Properties of Miscellaneous Absorbent Polymers [the best values among those of the patent examples are reported. The values corresponding to the comparative example in the patent are reported in parentheses. "Absorption rate ratio" is the amount of fluid absorbed in a fixed time (or reverse time of absorption of a fixed amount of fluid) ratio between the polymer and a reference polymer.]

References	Water absorption capacity (g/g polymer)		Saline or physiological solution absorption capacity (g/g polymer)	Absorption rate ratio
148	158		31	
149	44		31	
29, 40	592			
152	95	(13.8)		
281	45			
289	99[a]			
176, 204				1.29
72			87	
295			50	
267				40

[a]pH 8.5 solution.

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posed of polyols, diisocyanates, a suitable catalyst, and water as a foaming agent [287]; the addition of organic carbonates is said to lower the viscosity of the mixture.

Absorbent fibrous materials are prepared by dispersing cellulosic fibers and particles of an absorbent polymer in an excess of water [80]. The slurry is added to a water-miscible solvent which is unable to swell the fiber or the polymer (for example, acetone). Fibers are recovered by filtration and dried.

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REFERENCES

1. J. B. Ingraham, D. L. Gibson, and C. H. Kucera, US 3,336,979 (1967), Dow Chemical Co.
2. M. F. Katzer, US 3,354,084 (1967), Dow Chemical Co.; *Chem. Abstr.*, *68*, 13798 (1968).
3. J. W. Adams and H. W. Hoftiezer, US 3,366,582 (1968), American Can Co.
4. J. H. Johnson, US 3,393,168 (1968), Monsanto Co.; *Chem. Abstr.*, *69*, 44372 (1968).
5. W. M. Welsh and B. L. Atkins, US 3,428,470 (1969), Dow Chemical Co.
6. R. E. Anderson and G. D. Giffin, US 3,438,893 (1969), Dow Chemical Co.
7. I. Sobolev, US 3,457,198 (1969), ITT Rayonier Inc.
8. B. B. Darlow and A. R. M. Gibb, US 3,514,419 (1970), ICI.
9. M. F. Katzer, US 3,520,140 (1970), Dow Chemical Co.
10. T. H. Sheperd and F. E. Gould, US 3,520,949 (1970), National Patent Development Co.
11. L. H. Eilers and C. F. Parks, US 3,554,287 (1971), Dow Chemical Co.
12. T. H. Sheperd and F. E. Gould, US 3,575,123 (1971), National Patent Development Co.
13. W. T. Grubb and C. E. Cliche, US 3,629,008 (1971), General Electric Co.
14. W. I. Lang and J. I. Krajewski, US 3,640,826 (1972), International Minerals and Chemical Co.
15. E. W. Merril and P. S. L. Wong, US 3,658,745 (1972), MIT.
16. T. Smith, US 3,661,815 (1972), Grain Processing Co.
17. J. W. Adams and A. H. Tilloson, US 3,682,856 (1972), American Can Co.
18. W. L. Livingston, US 3,684,707 (1972).
19. R. A. Nelson, US 3,686,024 (1972), Dow Chemical Co.

20. N. S. Chu, US 3,734,876 (1973), Union Carbide Co.
21. G. W. Neal and L. D. Booth, US 3,746,666 (1973), Dow Chemical Co.
22. C. W. Neefe, US 3,803,093 (1974).
23. B. G. Harper, R. N. Bashaw, and B. L. Atkins, US 3,810,468 (1974), Dow Chemical Co.
24. W. T. Grubb and C. E. Cliche, US 3,819,416 (1974), General Electric Co.
25. H. W. Hoftiezer and A. H. Tilloson, US 3,838,077 (1974), American Can Co.
26. O. K. Kim, US 3,872,063 (1975), American Cyanamid Co.
27. R. Steckler, US 3,878,175 (1975), Plastik Devices Inc.
28. P. K. Chatterjee and R. F. Schwenker Jr., US 3,889,678 (1975), Personal Products Co.
29. P. G. Assarsson and P. A. King, US 3,898,143 (1975).
30. S. N. Yen and F. D. Osterholtz, US 3,900,378 (1975) Union Carbide Co.
31. R. K. Schlatzer Jr., US 3,915,921 (1975), B.F. Goodrich Co.
32. J. R. Gross and R. T. McFadden, US 3,926,891 (1975), Dow Chemical Co.
33. D. D. Duchane, US 3,932,322 (1976), Kimberly-Clark Co.
34. M. O. Weaver, E. B. Bagley, G. F. Fanta, and W. M. Doane, US 3,935,099 (1976), USA Secretary of Agriculture.
35. N. D. Burkholder, R. L. Winser, and D. A. Taber, US 3,935,363 (1976), Dow Chemical Co.
36. A. Holst, M. Kostrzewa, and H. Lask, US 3,936,441 (1976), Hoechst AG.
37. M. F. Fein, N. D. Field, and E. P. Williams, US 3,954,682 (1976), GAF Co.
38. J. R. Gross, US 3,954,721 (1976), Dow Chemical Co.
39. N. S. Chu, US 3,956,224 (1976), Union Carbide Co.
40. P. G. Assarsson and P. A. King, US 3,957,605 (1976), Union Carbide Co.
41. N. D. Burkholder, US 3,959,569 (1976), Dow Chemical Co.
42. J. R. Gross, US 3,966,679 (1976), Dow Chemical Co.
43. J. R. Gross, US 3,980,663 (1976), Dow Chemical Co.
44. R. N. Bashaw and B. L. Atkins, US 3,983,095 (1976), Dow Chemical Co.
45. M. O. Weaver, E. B. Bagley, G. F. Fanta, and W. M. Doane, US 3,985,616 (1976), USA Secretary of Agriculture.
46. R. N. Bashaw, B. L. Atkins, and J. R. Gross, US 3,989,586 (1976), Dow Chemical Co.
47. J. R. Gross, US 3,993,616 (1976), Dow Chemical Co.
48. M. O. Weaver, E. B. Bagley, G. F. Fanta, and W. M. Doane, US 3,997,484 (1976), USA Secretary of Agriculture.
49. J. R. Gross and R. T. McFadden, US 4,008,353 (1977), Dow Chemical Co.
50. J. R. Gross, US 4,017,653 (1977), Dow Chemical Co.
51. J. R. Gross, US 4,018,951 (1977), Dow Chemical Co.
52. A. R. Reid, US 4,028,290 (1977), Hercules Inc.
53. J. R. Gross, US 4,041,020 (1977), Dow Chemical Co.
54. J. R. Gross, US 4,041,228 (1977), Dow Chemical Co.
55. J. R. Gross and R. T. McFadden, US 4,041,231 (1977), Dow Chemical Co.
56. S. H. Ganslaw and H. G. Katz, US 4,043,952 (1977), National Starch and Chemical Co.

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57. G. F. Fanta and W. M. Doane, US 4,045,387 (1977), USA Secretary of Agriculture.
58. A. R. Reid, US 4,051,086 (1977), Hercules Inc.
59. M. L. Zweigle and J. C. Lamphere, US 4,059,552 (1977), Dow Chemical Co.
60. I. J. Westerman, US 4,062,817 (1977), B.F. Goodrich Co.
61. D. C. Spaulding, US 4,066,583 (1978), B.F. Goodrich Co.
62. T. C. Allen and D. B. Denning, US 4,066,584 (1978), Akzona Inc.
63. A. Holst, H. Lask, and M. Kostrzewa, US 4,066,828 (1978), Hoechst AG.
64. A. Holst, H. Lask, and M. Kostrzewa, US 4,068,068 (1978), Hoechst AG.
65. T. Smith, US 4,069,177 (1978).
66. D. Kraemer, K. Lehmann, H. Pennewiss, H. Plainer, and R. Schweder, US 4,070,348 (1978), Rohm GmbH.
67. J. R. Gross, US 4,071,650 (1978), Dow Chemical Co.
68. F. Masuda, K. Nishida, and A. Nakamura, US 4,076,663 (1978), Sanyo Chemical Ind.
69. N. D. Burkholder, US 4,076,673 (1978), Dow Chemical Co.
70. J. R. Gross, US 4,076,928 (1978), Dow Chemical Co.
71. J. R. Gross, US 4,079,029 (1978), Dow Chemical Co.
72. S. H. Ganslaw and H. G. Katz, US 4,090,013 (1978), National Starch and Chemical Co.
73. G. W. Dirks, G. S. Li, and J. F. Jones, US 4,090,998 (1978), Standard Oil Co.
74. S. Aoki and H. Yamasaki, US 4,093,776 (1978), Kao Soap Co.
75. P. Chatterjee and G. Morbey, US 4,105,033 (1978), Personal Products Co.
76. C. H. Beede, H. L. Waldman, and T. Bluming, US 4,111,922 (1978), Johnson & Johnson.
77. A. H. Young and F. Verbanac, US 4,115,332 (1978), A. E. Staley Manufacturing Co.
78. G. F. Fanta and W. M. Doane, US 4,116,899 (1978), USA Secretary of Agriculture.
79. R. E. Erickson and R. M. Krajewski, US 4,117,184 (1978), Dow Chemical Co.
80. A. R. Reid, US 4,128,692 (1978), Hercules Inc.
81. N. D. Burkholder, US 4,132,695 (1979), Dow Chemical Co.
82. G. F. Fanta, E. I. Stout, and W. M. Doane, US 4,134,863 (1979), USA Secretary of Agriculture.
83. K. E. Polmanteer, US 4,138,382 (1979), Dow Corning Co.
84. J. W. Adams, US 4,151,130 (1979), American Can Co.
85. N. D. Burkholder, US 4,154,898 (1979), Dow Chemical Co.
86. R. A. Mooth, US 4,155,888 (1979), A. E. Staley Manufacturing Co.
87. P. J. George, US 4,167,464 (1979), B.F. Goodrich Co.
88. M. L. Zweigle and J. C. Lamphere, US 4,172,066 (1979), Dow Chemical Co.
89. I. J. Westerman and D. J. Janda, EP 5363 (1979), B.F. Goodrich Co.
90. I. J. Westerman, US 4,190,562 (1980), B.F. Goodrich Co.
91. J. A. Ward, US 4,192,727 (1980), Union Carbide Co.

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92. A. Holst, M. Kostrzewa, and H. Lask, US 4,200,558 (1980), Hoechst AG.
93. R. L. Durham and J. H. McKenzie, US 4,238,374 (1980), Agritec Inc.
94. H. Markham, C. R. Mason, and D. Bedford, WO 80/2031 (1980), British Steel Co.
95. T. Tsubakimoto, T. Shimomura, Y. Irie, and Y. Masuda, US 4,286,082 (1981), Nippon Shokubai Kagaku Kogyo Co.
96. C. H. Beede, H. L. Waldman, and T. Bluming, US 4,248,685 (1981), Johnson & Johnson.
97. R. E. Erickson, US 4,293,609 (1981), Dow Chemical Co.
98. L. R. Parks, US 4,295,987 (1981), Proctor & Gamble Co.
99. R. B. Dehnel, EP 33,235 (1981), Unilever.
100. L. F. Elmquist, EP 39,542 (1981), Henkel Co.
101. T. P. N. Laszlo, EP 41,934 (1981), Aktiebolag Ferrosan.
102. P. J. George, WO 81/1850 (1981), B.F. Goodrich Co.
103. J. R. Gross, US 4,310,593 (1982), Dow Chemical Co.
104. D. A. Jones and L. F. Elmquist, US 4,323,487 (1982), Henkel Co.
105. A. Heslinga and P. J. Greidanus, US 4,332,917 (1982), Nederlandse Cent. Org. voor Toegepast-Natuurwetenschappelijk Onderzoek.
106. A. Heslinga and P. J. Greidanus, US 4,338,417 (1982), Nederlandse Cent. Org. voor Toegepast-Natuurwetenschappelijk Onderzoek.
107. S. Obayashi, M. Nakamura, K. Fujiki, and T. Yamamoto, US 4,340,706 (1982), Seitetsu Kagaku Co.
108. S. L. Kopolow, US 4,354,901 (1982), Personal Products Co.
109. E. P. Williams and D. H. Lorenz, US 4,366,294 (1982), GAF Co.
110. P. J. George, EP 47,009 (1982), B.F. Goodrich Co.
111. Y. Yoshioka and H. Harima, EP 55,848 (1982), Kuraray Co.
112. H. Harima, Y. Yoshioka, T. Kimura, and K. Takasaki, EP 59,062 (1982), Kuraray Isoprene Chemical Co., C. I. Kasei Co.
113. K. R. Shah, US 4,369,229 (1983), Kendall Co.
114. R. Korpman, US 4,415,388 (1983), Johnson & Johnson.
115. Y. Yoshioka and H. Harima, US 4,420,588 (1983), Kuraray Co.
116. F. Engelhardt, H. Schmitz, H. J. Kleiner, H. Lask, and A. Holst, EP 68,159 (1983), Cassella AG.
117. E. P. Williams and D. H. Lorenz, EP 68,847 (1983), GAF Co.
118. T. Murakami, H. Miyazaki, and H. Harima, EP 72,569 (1983), Kuraray Co.
119. M. Samejima, G. Hirata, Y. Koida, Y. Kobayashi, and A. Kida, EP 76,428 (1983), Tanabe Seiyaku Co.
120. S. Obayashi, M. Nakamura, T. Yamamoto, and M. Fujikaka, EP 83,022 (1983), Seitetsu Kagaku Co.
121. R. E. Erickson, US 4,424,247 (1984), Dow Chemical Co.
122. R. E. Erickson, US 4,444,830 (1984), Dow Chemical Co.
123. E. Richman and M. A. Thorn, US 4,454,055 (1984), National Starch and Chemical Co.
124. H. Yamasaki, Y. Sumida, and S. Harada, US 4,459,396 (1984), Kao Soap Co.

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125. G. F. Fanta, W. M. Doane, and E. I. Stout, US 4,483,950 (1984), USA Secretary of Agriculture.
126. P. H. Stelzer, US 4,486,374 (1984), Dow Chemical Co.
127. P. J. George, US 4,486,489 (1984), B.F. Goodrich Co.
128. J. B. Clarke, EP 101,253 (1984), Allied Colloids Ltd.
129. N. Honda, H. Wakumoto, T. Nakano, H. Ueki, and J. Hiratsuka, EP 122,797 (1984), Mitsui Petrochemical Ind.
130. H. Yamasaki, T. Kobayashi, and Y. Sumida, US 4,497,930 (1985), Kao Co.
131. R. E. Erickson, US 4,500,585 (1985), Dow Chemical Co.
132. M. J. McKinley and D. P. Sheridan, US 4,500,670 (1985), Dow Chemical Co.
133. S. Obayashi, M. Nakamura, T. Yamamoto, and M. Fujikake, US 4,507,438 (1985), Seitetsu Kagaku Co.
134. D. Chaudhuri and M. R. Stebles, US 4,508,705 (1985), Lever Brother Co.
135. M. J. McKinley and J. W. Sanner, US 4,511,477 (1985), Dow Chemical Co.
136. H. Nagase, US 4,524,186 (1985), Fujikura Kasei Co.
137. H. Takeda and Y. Taniguchi, US 4,525,527 (1985), American Colloid Co.
138. L. J. Scott, R. E. Erickson, and T. C. Wallace, US 4,529,739 (1985), Dow Chemical Co.
139. S. Evani, J. H. Oswald, T. L. Staples, and B. T. Polak, US 4,535,098 (1985), Dow Chemical Co.
140. D. Lim, C. L. Kulkarni, and D. A. Repella, US 4,536,554 (1985), Barnes-Hind Inc.
141. S. Obayashi, M. Nakamura, T. Yamamoto, and M. Fujikake, US 4,541,871 (1985), Seitetsu Kagaku Co.
142. S. L. Kopolow, US 4,552,618 (1985), Personal Products Co.
143. M. Makita, S. Tanioku, and T. Touda, US 4,552,938 (1985), American Colloid Co.
144. A. P. Kightlinger and D. Hubbard, US 4,558,100 (1985), Grain Processing Co.
145. M. Hawe, D. Marshall, and J. R. Walker, EP 133,803 (1985), Allied Colloids Co.
146. R. Ofstead, EP 137,686 (1985), Minnesota Mining & Manufacturing Co.
147. Y. Fujimoto and H. Miyazaki, EP 159,165 (1985), Mitsui Petrochemical Ind. Ltd., Tokyo Serofan Co.
148. K. W. Dixon, EP 161,762 (1985), Atlantic Richfield Co.
149. K. W. Dixon, EP 161,763 (1985), Atlantic Richfield Co.
150. P. Fydelor, R. A. Miller, B. J. Ringrose, and J. W. A. Ramsay, WO 85/5364 (1985), Defence Secretary of Great Britain.
151. J. S. Kim, US 4,581,413 (1986), B.F. Goodrich Co.
152. H. Lüissi and P. Geistlich, US 4,587,284 (1986), Ed. Geistlich Sohne.
153. M. Makita and S. Tanioku, US 4,587,308 (1986), Arakawa Kagaku Kogyo Kabushiki Kaisha.
154. D. H. Walley and J. C. Fitch, US 4,588,505 (1986), Frontier Technology.
155. R. E. Hefner Jr. and D. I. Haynes, US 4,611,015 (1986), Dow Chemical Co.

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156. H. Takeda and Y. Taniguchi, US 4,612,250 (1986), American Colloid Co.
157. B. Le-Khac, US 4,616,063 (1986), Atlantic Richfield Co.
158. H. Takeda and Y. Taniguchi, US 4,618,631 (1986), American Colloid Co.
159. T. Tsubakimoto, T. Shimomura, and Y. Irie, US 4,625,001 (1986), Nippon Shokubai Kagaku Kogyo.
160. M. Nakamura, S. Obayashi, T. Yamamoto, T. Nakanishi, H. Tanaka, and Y. Sakamoto, EP 176,664 (1986), Seitetsu Kagaku Co.
161. M. Nakamura, S. Obayashi, S. Takemori, H. Tanaka, and M. Hirakawa, EP 179,937 (1986), Seitetsu Kagaku Co.
162. K. Saotome, EP 189,163 (1986), Hayashikane Shipbuilding & Engineering Co.
163. K. Saotome, EP 192,216 (1986), Hayashikane Shipbuilding & Engineering Co.
164. K. Itoh and T. Shibano, EP 195,406 (1986), Mitsubishi Petrochemical Co.
165. P. Flesher, J. Clarke, and D. Marshall, EP 195,550 (1986), Allied Colloids Co.
166. W. Alexander, M. Anderson, and M. Teppo, EP 206,808 (1986), American Colloid Co.
167. A. Bucceri, WO 86/2936 (1986); *Chem. Abstr.*, *105*, 135046 (1986).
168. M. J. McKinley and D. P. Sheridan, WO 86/4910 (1986), Dow Chemical Co.
169. A. Bucceri, WO 86/7373 (1986), Permasnow Ltd.
170. W. K. Larson and S. T. Hedrick, US 4,638,017 (1987), Minnesota Mining and Manufacturing Co.
171. R. L. Durham, US 4,645,605 (1987), Agritec Inc.
172. M. Matsubara, US 4,645,698 (1987), Showa Denko Kabushiki Kaisha.
173. R. Gelman, US 4,650,716 (1987), Hercules Inc.
174. M. Makita, S. Tanioku, and T. Touda, US 4,654,393 (1987), American Colloid Co.
175. C. O. Walker, US 4,664,816 (1987), Texaco Inc.
176. T. Tsubakimoto, T. Shimomura, and Y. Irie, US 4,666,983 (1987), Nippon Shokubai Kagaku Kogyo Co.
177. W. Alexander, B. R. Regan, and M. Anderson, US 4,677,174 (1987), American Colloid Co.
178. M. Nakamura, S. Obayashi, T. Yamamoto, T. Nakanishi, H. Tanaka, and Y. Sakamoto, US 4,683,274 (1987), Seitetsu Kagaku Co.
179. J. R. Cramm and K. M. Bailey, US 4,698,404 (1987), Nalco Chemical Co.
180. M. Makita, S. Tanioku, and T. Touda, US 4,703,067 (1987), American Colloid Co.
181. B. Le-Khac, US 4,705,773 (1987), ARCO Chemical Co.
182. F. W. Stanley Jr., J. C. Lamphere, and Y. Chonde, US 4,708,997 (1987), Dow Chemical Co.
183. W. Alexander, M. Teppo, and M. Anderson, EP 207,714 (1987), American Colloid Co.
184. K. Saotome, EP 208,945 (1987), Hayashikane Shipbuilding & Engineering Co.

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185. T. Sugimoro, H. Habara, K. Inukai, and A. Furuno, EP 209,864 (1987), Mitsubishi Rayon Co., Nitto Chemical Ind. Co., Diafloc Co.
186. B. Le-Khac, EP 210,754 (1987), ARCO Chemical Co.
187. W. Howland, EP 216,147 (1987), Henkel Co.
188. T. Nakazawa, EP 223,908 (1987).
189. S. Obayashi, M. Nakamura, T. Yamamoto, H. Tanaka, Y. Sakamoto, and Y. Shimada, EP 224,923 (1987), Seitetsu Kagaku Co.
190. W. K. Larson and S. T. Hedrick, EP 225,800 (1987), Minnesota Mining & Manufacturing Co.
191. M. Chmelir and J. Pauen, EP 228,638 (1987), Stockhausen GmbH.
192. T. R. Burrow and P. R. Laity, EP 232,121 (1987), Courtalds PLC.
193. P. Flesher and D. Farrar, EP 233,014 (1987), Allied Colloids Ltd.
194. H. Shirai, F. Yamai, S. Inada, H. Ike, and Y. Nakahara, EP 233,067 (1987), Sekisui Plastics Co.
195. S. Obayashi, M. Nakamura, T. Yamamoto, H. Tanaka, and Y. Sakamoto, EP 234,202 (1987), Seitetsu Kagaku Co.
196. B. H. Nowakowsky, J. Beck, H. Hartmann, and C. Vamvakaris, EP 238,050 (1987), BASF.
197. B. Le-Khac, EP 239,223 (1987), ARCO Chemical Co.
198. M. Diamantoglou, C. Josefiak, and H. Maegerlein, EP 241,885 (1987), AKZO.
199. K. Saotome, EP 248,437 (1987), Hayashikane Shipbuiding & Engineering Co.
200. R. E. Hafner Jr. and D. L. Haynes, EP 248,934 (1987), Dow Chemical Co.
201. W. Alexander, M. Anderson, and B. R. Regan, EP 248,963 (1987), American Colloid Co.; *Chem. Abstr.*, *108*, 205671 (1988).
202. S. Obayashi, M. Nakamura, T. Yamamoto, H. Tanaka, and Y. Sakamoto, EP 249,391 (1987), Seitetsu Kagaku Co.
203. T. Kobayashi, H. Yamasaki, and Y. Sumida, US 4,727,097 (1988), Kao Co.
204. T. Tsubakimoto, T. Shimomura, Y. Irie, Y. Masuda, K. Kimura, and T. Hatsuda, US 4,734,478 (1988), Nippon Shokubai Kagaku Kogyo Co.
205. B. Le-Khac, US 4,743,244 (1988), ARCO Chemical Co.
206. T. Nakashima, N. Toyoshima, and Y. Sasai, US 4,745,158 (1988), Toyo Contact Lenses Co.
207. W. Alexander, M. Anderson, and B. R. Regan, US 4,755,562 (1988), American Colloid Co.
208. A. P. Kightlinger and R. B. Hudson, US 4,769,414 (1988), Grain Processing Co.
209. R. F. Ofstead, US 4,771,089 (1988), Minnesota Mining & Manufacturing Co.
210. H. Shirai, F. Yamai, S. Inada, H. Ike, and Y. Nakahara, US 4,771,105 (1988), Sekisui Kaseihin Kogyo Kabushiki Kaisha.
211. B. Dymond, J. Langley, and M. Hawe, US 4,777,200 (1988), Allied Colloids Ltd.
212. K. M. Bailey and J. R. Cramm, US 4,777,231 (1988), Nalco Chemical Co.
213. K. Heidel, US 4,777,232 (1988), Starchem GmbH.

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214. B. Le-Khac, US 4,788,237 (1988), ARCO Chemical Co.
215. Y. Hosokawa and T. Kobayashi, EP 257,951 (1988), Kao Co.
216. Y. Hosokawa and T. Kobayashi, EP 259,037 (1988), Kao Co.
217. A. Allen, D. Farrar, and P. Flesher, EP 268,498 (1988), Allied Colloids Ltd.
218. A. Allen, D. Farrar, and P. Flesher, EP 269,393 (1988), Allied Colloids Ltd.
219. B. Le-Khac, EP 272,074 (1988), ARCO Chemical Co.
220. K. Itoh, T. Shibano, and K. Yoshinaga, EP 280,541 (1988), Mitsubishi Petrochemical Co.
221. J. M. Kendall, D. H. Maes, and R. Figueroa Jr., EP 281,395 (1988), Richardson-Vicks Inc.
222. J. Cornell, EP 282,316 (1988), Medi-Tech Int. Co.
223. T. Graafland, EP 283,090 (1988), Shell Int. Res. Maatschappij.
224. C. Jacquement, J. Rousset, P. Martineu, and C. Saunier, EP 291,422 (1988), Conservatome, Societe COATEX.
225. K. Itoh and T. Shibano, EP 293,762 (1988), Mitsubishi Petrochemical Co., Uni-Charm Co.
226. C. S. Freeman, WO 88/8440 (1988).
227. R. E. Erickson, WO 88/9801 (1988), Dow Chemical Co.
228. F. E. Gould, E. K. Morgan, and S. D. Reduker, US 4,798,876 (1989), Tyndale Plains-Hunter Ltd.
229. B. Le-Khac, US 4,813,945 (1989), ARCO Chemical Co.
230. W. Alexander, M. Anderson, and B. R. Regan, US 4,820,773 (1989), American Colloid Co.
231. D. Farrar, P. Flesher, M. Skinner, J. Clarke, D. Marshall, and M. Hawe, US 4,880,858 (1989), Allied Colloids Ltd.
232. B. Le-Khac, US 4,880,868 (1989), ARCO Chemical Co.
233. S. Doi and S. Ohnishi, EP 301,542 (1989), Mitsubishi Petrochemical Co.
234. K. Kimura, T. Hatsuda, Y. Irie, and T. Shimomura, EP 303,440 (1989), Nippon Shokubai Kagaku Kogyo Co.
235. W. Alexander, M. Anderson, and B. R. Regan, EP 303,518 (1989), American Colloid Co.
236. R. Fukushima and K. Aoyama, EP 304,143 (1989), Kyoritsu Yuki Co.
237. J. M. Lesniak, F. Boardman, W. G. Koci, and J. E. McCann, EP 309,187 (1989), Johnson and Johnson.
238. J. Siddall and T. C. Johnson, EP 312,952 (1989), Dow Chemical Co.
239. K. Itoh and T. Shibano, EP 315,185 (1989), Mitsubishi Petrochemical Co.
240. K. Nagasuma, K. Kadonaga, K. Kimura, and T. Shimomura, EP 317,106 (1989), Nippon Shokubai Kagaku Kogyo Co.
241. Y. Irie, S. Morihiro, T. Fujiwara, M. Sasabe, and K. Iwasaki, EP 323,243 (1989), Nippon Shokubai Kagaku Kogyo Co.
242. F. L. Buchholz, EP 324,385 (1989), Dow Chemical Co.
243. D. Farrar, J. R. Field, and P. Flesher, EP 326,382 (1989), Allied Colloids Ltd.
244. M. Takizawa, M. Nakamura, H. Takeuchi, S. Sakamoto, and S. Horiguchi, EP 335,410 (1989), Dainichiseika Color and Chemical Manufacturing Co.

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245. D. Farrar, A. Allen, and P. Flesher, EP 342,919 (1989), Allied Colloids Ltd.
246. Y. Hosoya, N. Watanabe, I. Takagi, and A. Miyoshi, EP 342,996 (1989), Mitsui Cyanamid Ltd.
247. K. Itoh, T. Shibano, S. Yada, and S. Tsunoi, EP 347,241 (1989), Mitsubishi Petrochemical Co.
248. S. Yada, T. Shibano, K. Itoh, and K. Yoshinaga, EP 348,180 (1989), Mitsubishi Petrochemical Co.
249. R. W. Harding, WO 89/3865 (1989), Permasnow Ltd.
250. C. S. Freeman, WO 89/9371 (1989).
251. W. H. Lewis and K. M. Bailey, US 4,950,692 (1990), Nalco Chemical Co.
252. W. Kobayashi, S. Otaka, and M. Nagai, US 4,952,243 (1990), Ube Ind. Ltd.
253. M. Anderson, US 4,954,562 (1990), American Colloid Co.
254. K. Itoh, T. Shibano, S. Yada, and S. Tsunoi, US 4,957,984 (1990), Mitsubishi Petrochemical Co.
255. K. Kimura, K. Nagasuna, T. Namba, K. Kadonaga, K. Miyake, and T. Shimomura, EP 349,240 (1990), Nippon Shokubai Kagaku Kogyo Co.
256. K. Nagasuna, T. Namba, K. Miyake, K. Kimura, and T. Shimomura, EP 349,241 (1990), Nippon Shokubai Kagaku Kogyo Co.
257. S. Tsuji, H. Musika, M. Itoh, J. Hayakawa, and E. Miyashita, EP 356,161 (1990), Mitsui Toatsu Chem. Ltd.
258. J. H. Manning, D. H. Hollenberg, and K. B. Makoui, EP 357,474 (1990), James River Co.
259. H. Takahashi, K. Kajikawa, J. Saga, T. Fujiwara, and T. Hatsuda, EP 372,706 (1990), Nippon Shokubai Kagaku Kogyo Co.
260. N. Watanabe, T. Arai, H. Fujiyoshi, and M. Shirota, EP 385,627 (1990), Mitsui Cyanamid Ltd.
261. Y. Takahashi, T. Shimomura, and N. Shirane, EP 386,723 (1990), Ahsu Kurin K.K., Nisshin Seifun K.K., Nippon Shokubai Kagaku Kogyo Co.
262. N. Harada, T. Okuno, and T. Shimomura, EP 386,897 (1990), Nippon Shokubai Kagaku Kogyo Co.
263. K. Yoshinaga, H. Hosaka, and T. Nakamura, EP 388,120 (1990), Mitsubishi Petrochemical Co.
264. A. S. Allen, EP 397,410 (1990), Allied Colloid Co.
265. K. Yoshinaga, T. Nakamura, and K. Itoh, EP 398,653 (1990), Mitsubishi Petrochemical Co.
266. P. Vondracek, P. Lopour, and J. Sulc, EP 399,518 (1990), Ceskoslovenksa Akademie Ved.
267. E. F. Tai, WO 90/8789 (1990), Dow Chemical Co.
268. J. W. Shell, WO 90/11,757 (1990), Depomed Systems Inc.
269. D. Farrar, WO 90/14,387 (1990), Allied Colloids Ltd.
270. S. Tseng and E. Reilly, WO 90/15,825 (1990), Weyerhaeuser Co.
271. S. B. Choi, H. M. Lee, M. J. Kim, and T. H. Chang, WO 90/15,829 (1990), Lucky Ltd.
272. R. Kilian, J. Poccia, and E. P. Reilly, WO 90/15,830 (1990), Weyerhaeuser Co.

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273. S. F. Nielsen and D. W. Kim, US 4,990,541 (1991), Hoechst Celanese Co.
274. D. Farrar, A. Allen, and P. Flesher, US 4,997,714 (1991), Allied Colloids Co.
275. S. F. Nielsen and D. W. Kim, US 5,011,864 (1991), Hoechst Celanese Co.
276. S. B. Choi and H. M. Lee, US 5,032,628 (1991), Lucky Ltd.
277. T. Miyajima, US 5,070,133 (1991), Kyoritsu Yuki Co.
278. I. Ahmed and H. L. Hsieh, US 5,075,399 (1991), Phillips Petroleum Co.
279. F. L. Buchholz, A. T. Graham, and T. C. Johnson, EP 409,136 (1991), Dow Chemical Co.
280. E. Otsuka, EP 410,669 (1991), C. I. Kasei Co.
281. T. G. Grasel and J. L. Guthrie, EP 420,515 (1991), W. R. Grace & Co.
282. C. M. Herron and D. J. Cooper, EP 427,316 (1991), Procter & Gamble Cellulose Co.
283. C. M. Herron and D. J. Cooper, EP 429,112 (1991), Procter & Gamble Cellulose Co.
284. Y. Miura, K. Hirano, T. Nate, T. Kambayashi, M. Ohtsuka, and T. Nagai, EP 440256 (1991), Tonen Co., Osaka Organic Chemical Ind., Sanyo Electric Co.
285. M. Nakamura, T. Yamamoto, H. Tanaka, H. Ozawa, and Y. Shimada, EP 441,507 (1991), Sumitomo Seika Chemical Co.
286. K. Kimura, T. Hatsuda, and K. Nagasuna, EP 450,924 (1991), Nippon Shokubai Kagaku Kogyo Co.
287. B. Le-Khac and U. E. Younes, EP 453,286 (1991), ARCO Chemical Technology Inc.
288. K. Nagasuna, K. Kajikawa, T. Hatsuda, Y. Irie, and T. Fujiwara, WO 91/3497 (1991), Nippon Shokubai Kagaku Kogyo Co.
289. C. R. L. Barcus and D. W. Bjorkquist, WO 91/9916 (1991), Procter & Gamble Co.
290. S. Tanioku, N. Oshima, K. Takeuchi, Y. Maeda, and A. Kitagawa, WO 91/16,380 (1991), Arakawa Chemical Ind.
291. J. M. Ball, WO 91/18,042 (1991), Dow Chemical Co.
292. Y. Haruna, A. Yano, Y. Irie, and T. Fujihara, US 5,124,416 (1992), Nippon Shokubai Kagaku Kogyo Co.
293. N. D. Sachinvala, US 5,126,438 (1992), Hawaiian Sugar Planters Association.
294. N. Watanabe, T. Arai, H. Fujiyoshi, and M. Shirota, US 5,132,358 (1992), Mitsui-Cyanamid Ltd.
295. G. T. Woodrum and T. H. Majette, EP 463,388 (1992), Hoechst Celanese Co.
296. K. Ukita, S. Hirota, and M. Inoue, EP 464,788 (1992), Nippon Zeon Co.
297. T. Sumiya, M. Date, and T. Kenji, EP 467,073 (1992), Sanyo Chemical Ind. Ltd.
298. T. Ito and H. Takayanagi, EP 467,339 (1992), Mitsubishi Kasei Co.
299. U. Conte, A. LaManna, and P. Giunchedi, EP 468,392 (1992), Farma Resa Srl.
300. K. Itoh, S. Yada, and K. Yoshinaga, EP 472,362 (1992), Mitsubishi Petrochemical Co.

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301. J. J. Stofko Jr. and M. Iqbal, EP 482,836 (1992), Minnesota Mining & Manufacturing Co.
302. J. J. Stofko Jr. and M. Iqbal, EP 482,837 (1992), Minnesota Mining & Manufacturing Co.
303. N. Harada, K. Wada, H. Obara, Y. Sano, and T. Shimomura, EP 493,011 (1992), Nippon Shokubai Co.
304. Y. Fujiura, K. Mita, and K. Shinoda, EP 494,599 (1992), Sanyo Chemical Ind. Ltd.
305. T. Sumiya, M. Date, and T. Kenji, EP 496067 (1992), Sanyo Chemical Ind. Ltd.
306. H. Tanaka, T. Kambayashi, Y. Sugiyama, T. Nagai, K. Nagata, K. Kubota, and K. Hirano, EP 501,482 (1992), Miura Dolphins Co., Tonen Co., Osaka Organic Chemical Ind., Sanyo Electric Co.
307. H. Gartner and J. Burgert, EP 509,708 (1992), Dow Chemical Co.
308. A. T. Graham and H. Gartner, EP 513,780 (1992), Dow Chemical Co.
309. P. E. Buckle, R. J. Davies, and D. V. Pollard-Knight, WO 92/21,976 (1992), Fisons PLC.
310. M. Umeda, Y. Sakuraba, and H. Baba, US 5,204,175 (1993), Tokai Rubber Ind. Ltd., Sumitomo Electric Ind. Ltd.
311. K. Itoh, S. Tsunoi, and T. Yamamoto, EP 521,355 (1993), Mitsubishi Petrochemical Co. Ltd.
312. K. Itoh, S. Yada, M. Omori, and T. Nakamura, EP 522,570 (1993), Mitsubishi Petrochemical Co. Ltd.
313. K. Hirakawa, K. Tanaka, M. Kawamoto, and T. Tsuda, EP 530,591 (1993), Kuraray Co., Unitika Ltd.
314. T. H. Chang, S. B. Choi, H. M. Lee, and M. J. Kim, EP 533,192 (1993), Lucky Ltd.
315. P. Trijasson, T. Pith, and M. Lambla, *Makromol. Chem., Macromol. Symp., 35/36*, 141 (1990).

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Superabsorbent Polymer Materials: A Review

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ABSTRACT

Superabsorbent polymer (SAP) materials are hydrophilic networks that can absorb and retain huge amounts of water or aqueous solutions. They can uptake water as high as 100,000%. Common SAPs are generally white sugar-like hygroscopic materials, which are mainly used in disposable diapers and other applications including agricultural use. This article reviews the SAP literature, background, types and chemical structures, physical and chemical properties, testing methods, uses, and applied research works. Due to variability of the possible monomers and macromolecular structure, many SAP types can be made. SAPs are originally divided into two main classes; i.e., synthetic (petrochemical-based) and natural (e.g., polysaccharide- and polypeptide-based). Most of the current superabsorbents, however, are frequently produced from acrylic acid (AA), its salts, and acrylamide (AM) via solution or inverse-suspension polymerization techniques. The main synthetic (internal) and environmental (external) factors affecting the acrylic anionic SAP characteristics are described briefly. The methods for quantifying the SAP practical features, i.e., absorption capacity (both load-free and under load), swelling rate, swollen gel strength, wicking capacity, sol fraction, residual monomer, and ionic sensitivity were discussed. The SAP applications and the related research works, particularly the hygienic and agricultural areas are reviewed. Meanwhile, the research findings on the effects of SAP in soil and agricultural achievements in Iran, as an arid country are treated as well. Finally, the safety and environmental issues concerning SAP practical applications are discussed as well.

Key Words:

hydrogel;
superabsorbent;
swelling;
water;
polymerization.

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INTRODUCTION

Hydrophilic gels that are usually referred to as hydrogels are networks of polymer chains that are sometimes found as colloidal gels in which water is the dispersion medium [1]. In another word, they are water absorbing natural or synthetic polymers (they may contain over 99% water). Hydrogels have been defined as polymeric materials which exhibit the ability of swelling in water and retaining a significant fraction (>20%) of water within their structure, without dissolving in water [2-4]. They possess also a degree of flexibility very similar to natural tissue due to their large water content.

The applications of hydrogels are grown extensively [3-6]. They are currently used as scaffolds in tissue engineering where they may contain human cells in order to repair tissue. Environmental sensitive hydrogels have the ability to sense environmental stimuli, such as changes of pH, temperature, or the concentration of metabolite and then release their load as a result of such a change. Hydrogels that are responsive to specific molecules, such as glucose or antigens can be used as biosensors as well as in drug delivery systems (DDS). These kinds of hydrogels are also used as controlled-release delivery devices for bio-active agents and agrochemicals. Contact lenses are also based on hydrogels.

Special hydrogels as superabsorbent materials are widely employed in hygienic uses particularly disposable diapers and female napkins where they can capture secreted fluids, e.g., urine, blood, etc. Agricultural grade of such hydrogels are used as granules for holding soil moisture in arid areas.

Absorbing versus Superabsorbing Materials

The hygroscopic materials are usually categorized into two main classes based on the major mechanism of water absorption, i.e., chemical and physical absorptions. Chemical absorbers (e.g., metal hydrides) catch water via chemical reaction converting their entire nature. Physical absorbers imbibe water via four main mechanisms [8]; (i) reversible changes of their crystal structure (e.g., silica gel and anhydrous inorganic salts); (ii) physical entrapment of water via capillary forces in their macro-porous structure (e.g., soft polyurethane sponge); (iii) a combination of the mechanism (ii) and hydration of functional groups (e.g., tissue paper); (iv) the mechanism which may be anticipated by combination of mechanisms of (ii) and (iii) and essentially dissolution and thermodynamically favoured expansion of the macromolecular chains limited by cross-linkages. Superabsorbent polymer (SAP) materials fit in the latter category, yet, they are organic materials with enormous capability of water absorption.

SAPs as hydrogels, relative to their own mass can absorb and retain extraordinary large amounts of water or aqueous solution [2,3]. These ultrahigh absorbing materials can imbibe deionized water as high as 1,000-100,000% (10-1000 g/g) whereas the absorption capacity of common hydrogels is not more than 100% (1 g/g). Visual and schematic illustrations of an acrylic-based anionic superabsorbent hydrogel in the dry and water-swollen states [7] are given in Figure 1.

Commercial SAP hydrogels are generally sugar-

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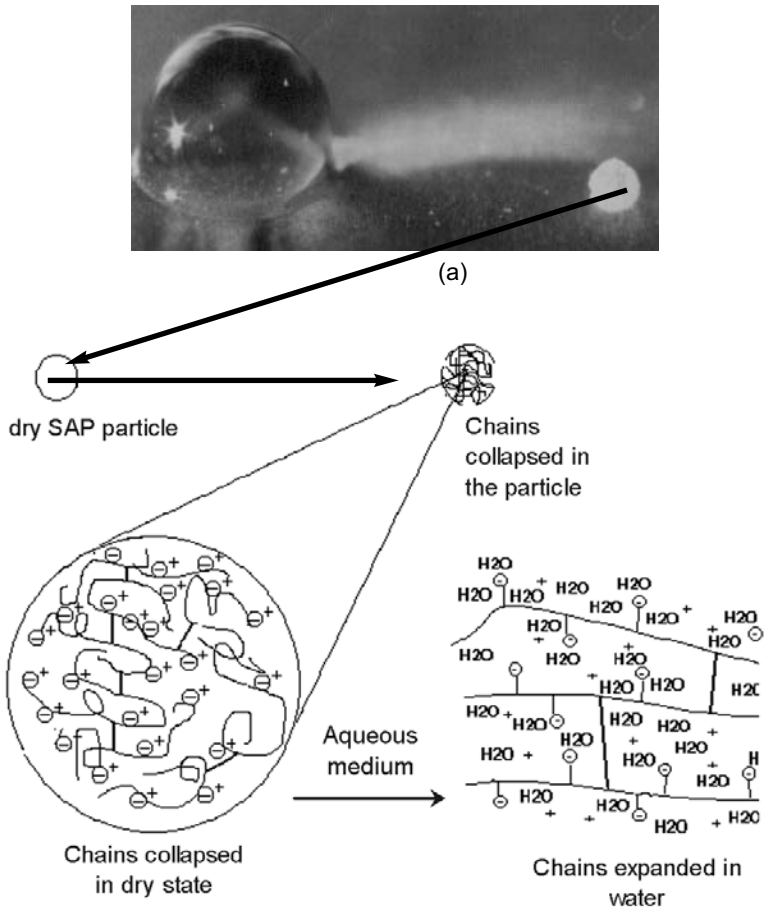


Figure 1. Illustration of a typical acrylic-based anionic SAP material: (a) A visual comparison of the SAP single particle in dry (right) and swollen state (left). The sample is a bead prepared from the inverse-suspension polymerization technique. (b) A schematic presentation of the SAP swelling.

like hygroscopic materials with white-light yellow colour. The SAP particle shape (granule, fibre, film, etc.) has to be basically preserved after water absorption and swelling, i.e., the swollen gel strength should be high enough to prevent a loosening, mushy, or slimy state. This is a major practical feature that discriminates SAPs from other hydrogels.

Table 1. Water absorbency of some common absorbent materials [2] in comparison with a typical commercial SAP sample.

Absorbent Material	Water Absorbency (wt%)
Whatman No. 3 filter paper	180
Facial tissue paper	400
Soft polyurethane sponge	1050
Wood pulp fluff	1200
Cotton ball	1890
Superab A-200[a]	20200

[(a)] Agricultural SAP produced by Rahab Resin Co., Ltd., Iran [9].

Traditional absorbent materials (such as tissue papers and polyurethane foams) unlike SAPs, will lost most of their absorbed water when they are squeezed. Table 1 compares water absorptiveness of some common absorbent materials [2] with a typical sample of a commercially available SAP [9].

History and Market

The synthesis of the first water-absorbent polymer goes back to 1938 when acrylic acid (AA) and divinylbenzene were thermally polymerized in an aqueous medium [2]. In the late 1950s, the first generation of hydrogels was appeared. These hydrogels

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been published about acrylic SAPs by the Stanford Research Institute, SRI [20].

Two valuable books on the synthetic SAP materials were published in 1990-1998 [2,3] and the fundamental phenomena dealing with the synthetic hydrogels were reflected very clearly [3]. In 2002, another valuable book was published, focused mainly on the fibres and textiles with high water absorbency characteristics [21].

In spite of the foresaid reviewing sources, to the best of our knowledge, there is no other published review with a comprehensive perspective on SAP hydrogels. The present article represents a different outlook; it gives an account of all types of SAP materials with a practical viewpoint from structure to usage, based on either the current literature or our long experience on these materials. The main target is appraisal the SAPs to be useful for either academies or industries. Meanwhile, a very beneficial section related to the practical methods of the SAP testing and evaluation has also been included in the analytical evaluation section.

SAPs TYPES AND PREPARATION

Classification

Resembling the hydrogel family, the SAPs can also be classified based upon different aspects. SAPs may be categorized to four groups on the basis of presence or absence of electrical charge located in the cross-linked chains [8]:

1- non-ionic

2- ionic (including anionic and cationic)

3- amphoteric electrolyte (ampholytic) containing both acidic and basic groups

4- zwitterionic (polybetaines) containing both anionic and cationic groups in each structural repeating unit

For example, the majority of commercial SAP hydrogels are anionic. SAPs are also classified based on the type of monomeric unit used in their chemical structure, thus the most conventional SAPs are held in one of the following categories [5, 8]:

(a) cross-linked polyacrylates and polyacrylamides

(b) hydrolyzed cellulose-polyacrylonitrile (PAN) or starch-PAN graft copolymers

(c) cross-linked copolymers of maleic anhydride

However, according to original sources, SAPs are often divided into two main classes; i.e., synthetic (petrochemical-based) and natural. The latter can be divided into two main groups, i.e., the hydrogels based on polysaccharides and others based on polypeptides (proteins). The natural-based SAPs are usually prepared through addition of some synthetic parts onto the natural substrates, e.g., graft copolymerization of vinyl monomers on polysaccharides.

It should be pointed out when the term "superabsorbent" is used without specifying its type, it actually implies the most conventional type of SAPs, i.e., the anionic acrylic that comprises a copolymeric network based on the partially neutralized acrylic acid (AA) or acrylamide (AM).

Main Starting Materials

Variety of monomers, mostly acrylics, is employed to prepare SAPs. Acrylic acid (AA) and its sodium or potassium salts, and acrylamide (AM) are most often used in the industrial production of SAPs (discussed later).

The AA monomer is inhibited by methoxyhydroquinone (MHC) to prevent spontaneous polymerization during storage. In industrial production, the inhibitor is not usually removed due to some technical reasons [2]. Meanwhile, AA is converted to an undesired dimer that must be removed or minimized.

The minimization of acrylic acid dimer (DAA) in the monomer is important due to its indirect adverse effects on the final product specifications, typically soluble fraction and the residual monomer. As soon as AA is produced, diacrylic acid (β-acryloxypropionic acid) is formed spontaneously in the bulk of AA via a sluggish Michael-addition reaction [2]. Since temperature, water content, and pH have impact on the rate of DAA formation, the rate can be minimized by controlling the temperature of stored monomer and excluding the moisture [22]. Increasing water concentration has a relatively small impact on the DAA formation rate. Nevertheless, the rate roughly doubles for every 5ºC increase in temperature. For example, in an AA sample having 0.5% water, the dimerization rate is 76 and 1672 ppm/day at 20ºC and 40ºC, respectively. DAA, however, can be hydrolyzed in alkaline

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media to produce AA and β-hydroxypropionic acid (HPA). Since the latter is unable to be polymerized, it remains as part of the SAP soluble fraction. Fortunately, alkaline media used conventionally for AA neutralization with NaOH favours this hydrolytic reaction. For instance, in an 80% neutralized AA, the dimerization rate at 23ºC and 40ºC has been determined to be 125 and 770 ppm/day, respectively [2].

DAA can also be polymerized to go into the SAP network. It may be then thermally cleaved through a retro-Michael reaction in the course of heating in the drying step of the final product. As a result, free AA will be released and causes the enhancement of the level of residual monomer.

On laboratory scales, however, number of monomers such as methacrylic acid (MAA), methacrylamide (MAM), acrylonitrile (AN), 2-hydroxyethylmethacrylate (HEMA), 2-acrylamido-2-methylpropane sulphonic acid (APMS), N-vinyl pyrrolidone (NVP), vinyl sulphonic acid (VSA) and vinyl acetate (VAc) are also used.

In the modified natural-based SAPs (i.e., hybrid superabsorbents) trunk biopolymers such as cellulose, starch, chitosan, gelatin and some of their possible derivatives e.g., carboxymethyl cellulose (CMC) are also used as the modifying substrate (polysaccharide-based SAPs section).

The bifuntional compound *N,N'*-methylene bisacrylamide (MBA) is most often used as a water soluble cross-linking agent. Ethyleneglycole dimethacrylate (EGDMA), 1,1,1-trimethylolpropane triacrylate (TMPTA), and tetraalyloxy ethane (TAOE) are known examples of two-, three- and four-functional cross-linkers, respectively.

Potassium persulphate (KPS) and ammonium persulphate (APS) are water soluble thermal initiators used frequently in both solution and inverse-suspension methods of polymerization (discussed in the snap shot section of production processes). Redox pair initiators such as Fe^{2+}-H_2O_2 (Fenton reagent) and APS-sodium sulphite are also employed particularly in the solution method.

Synthetic SAPs

The greatest volume of SAPs comprises full synthetic or of petrochemical origin. They are produced from the acrylic monomers, most frequently acrylic acid (AA), its salts and acrylamide (AM). Figure 3 shows

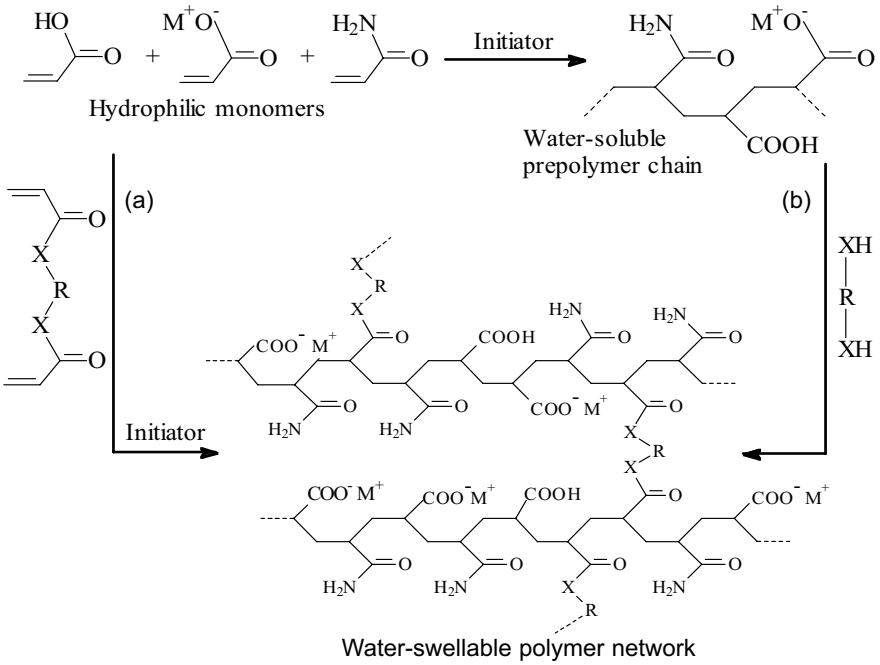


Figure 3. Chemical structures of the reactants and general pathways to prepare an acrylic SAP network: (a) Cross-linking polymerization by a polyvinylic cross-linker, (b) Cross-linking of a water-soluble prepolymer by a polyfunctional cross-linker. R is often CH_2 or another aliphatic group. M stands for the sodium or potassium cations [7]. X= O, NH.

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two general pathways to prepare acrylic SAP networks, i.e., simultaneous polymerization and crosslinking by a polyvinylic cross-linker, and cross-linking of a water-soluble prepolymer by a polyfunctional cross-linker. More discussions on the synthetic SAPs are provided in the related sections.

Polysaccharide-based SAPs

Although the majority of the superabsorbents are nowadays manufactured from synthetic polymers (essentially acrylics) due to their superior price-to-efficiency balance [2,5,9], the worlds firm decision for environmental protection potentially support the ideas of partially/totally replacing the synthetics by "greener" alternatives [17].

Carbohydrate polymers (polysaccharides) are the cheapest and most abundant, available, and renewable organic materials. Chitin, cellulose, starch, and natural gums (such as xanthan, guar and alginates) are some of the most important polysaccharides.

Generally, the reported reactions for preparing the polysaccharide-based SAPs are held in two main groups; (a) graft copolymerization of suitable vinyl monomer(s) on polysaccharide in the presence of a cross-linker, and (b) direct cross-linking of polysaccharide.

In graft copolymerization, generally a polysaccharide enters reaction with initiator by either of two separate ways. First, the neighbouring OHs on the saccharide units and the initiator (commonly Ce^{4+}) interact to form redox pair-based complexes. These complexes are subsequently dissociated to produce carbon radicals on the polysaccharide substrate via homogeneous cleavage of the saccharide C-C bonds. These free radicals initiate the graft polymerization of the vinyl monomers and cross-linker on the substrate.

In the second way of initiation, an initiator such as persulphate may abstract hydrogen radicals from the OHs of the polysaccharide to produce the initiating radicals on the polysaccharide backbone. Due to employing a thermal initiator, this reaction is more affected by temperature compared to previous method.

The earliest commercial SAPs were produced from starch and AN monomer by the first mentioned method without employing a cross-linker. The starch-*g*-PAN copolymer (SPAN) was then treated in

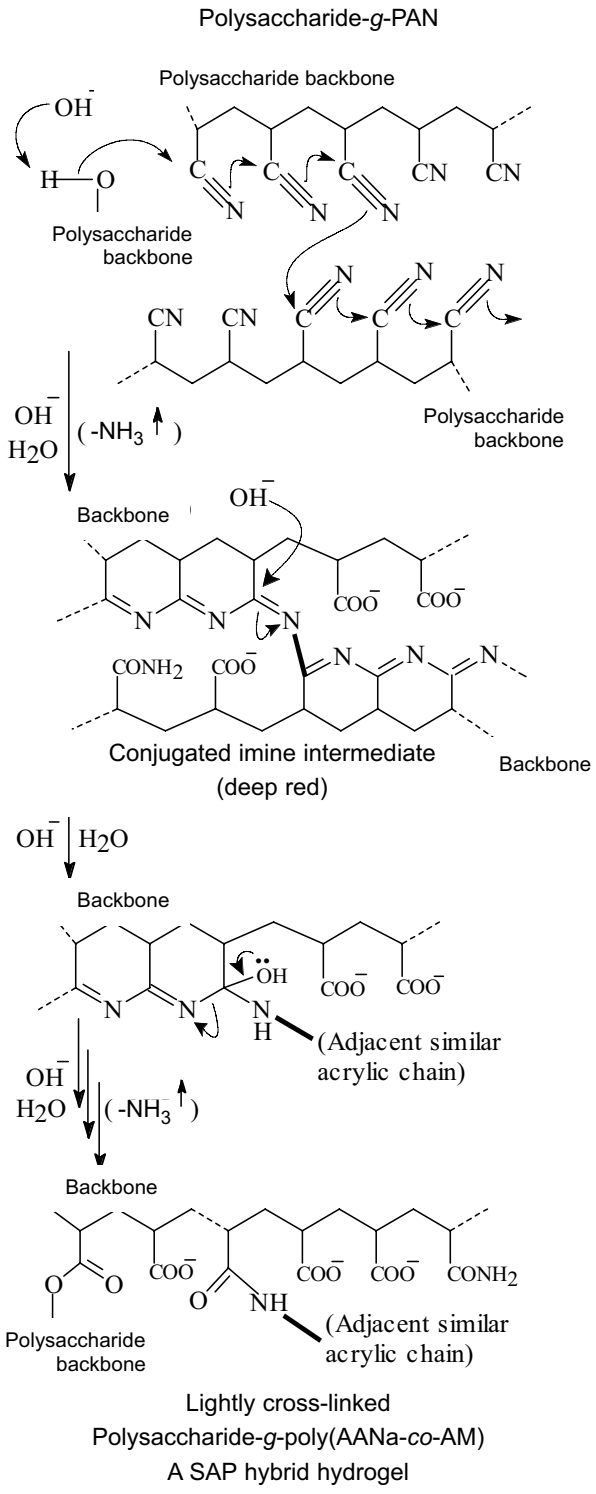


Figure 4. The mechanism of in-situ cross-linking during the alkaline hydrolysis of polysacchride-g-PAN copolymer to yield superabsorbing hybrid material.

alkaline medium to produce a hybrid SAP, hydrolyzed SPAN (H-SPAN) while an in-situ cross-linking

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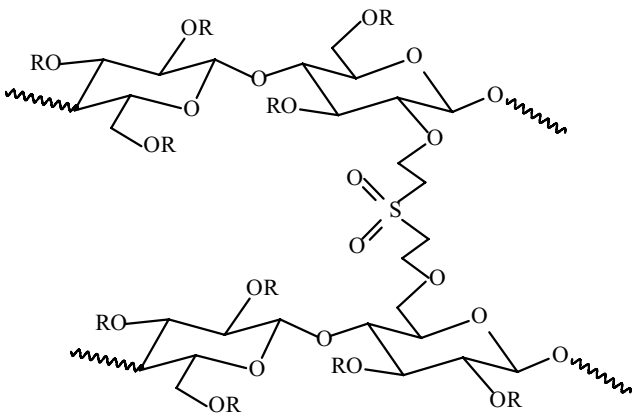


Figure 5. Typical cellulose-based SAP prepared via direct cross-linking of sodium carboxymethyl cellulose (CMC; R= H, COO^-Na^+) or hydroxyethyl cellulose (HEC; R= H, CH_2CH_2OH) [24].

occurred simultaneously. This fascinating approach (Figure 4) has been employed to convert various polysaccharides into SAP hydrogel hybrids [23].

In the method direct cross-linking of polysaccharides, polyvinylic compounds (e.g., divinyl sulphone, DVS) or polyfunctional compounds (e.g., glycerol, epichlorohydrine and glyoxal) are often employed [13,23]. $POCl_3$ is also used for the cross-linking. Figure 5 exhibits the structure of valuable CMC- and hydroxyethyl cellulose (HEC)-based SAPs prepared by Saninno et al. [24]. Most recently, they have also synthesized fully natural SAP hydrogels via cross-linking of the cellulosics by citric acid [25].

Poly(amino acid)-based SAPs

Dissimilar to polysaccharide-based hydrogels, relatively fewer works have been reported on the natural-based SAP hydrogels comprising polypeptides as the main or part of their structure. Proteins from soybean, fish, and collagen-based proteins are the most frequently used hetero-polypeptides for preparation of proteinaceous super-swelling hydrogels.

The most important research programme of the protein-based SAPs has been conducted by Damodaran et al. [26-35] working in the Department of Food Science, University of Wisconsin, Madison, USA. They converted soy and fish proteins to SAP through modification by ethylenediamine tetraacetic dianhydride (EDTAD) in the first stage. EDTAD has low toxicity because the only reactive group introduced into the network is the carboxyl group, and lysyl residues of the protein that can be modified with EDTAD in a relatively fast reaction. They often used the soy protein isolate (SPI) for the modification. The modified product was prepared by extraction of defatted soy flour with water at pH 8 at a meat-to-water ratio of 1:10 [26].

In the second stage, the remaining amino groups of the hydrophilized protein are lightly cross-linked by glutaraldehyde to yield a hydrogel network with superabsorbing properties. The SAP was capable of imbibing 80-300 g of deionized-water/g of dry gel after centrifugating at 214 g, depending on the extent of modification, protein structure, cross-link density, protein concentration during the second step, gel particle size, and environmental conditions such as pH, ionic strength, and temperature [26].

The EDTAD-modified soy protein SAPs are reported to be highly pH sensitive. It also exhibits reversible swelling-deswelling behaviour when the swollen gel is alternatively exposed to 0.15 m NaCl, and deionized water [26,32].

Some patents have also been disclosed, investigating extensively on the preparation and properties of the SAPs based on the soy protein isolate [32,33]. The inventors have specified that similar approaches can be used on other proteins such as leaf (alfalfa) protein, microbial and animal proteins and those recovered from food-processing wastes.

Following the introduction of a large number of hydrophilic groups into fish protein (FP) concentrate by modification with EDTAD, the proteins are reported to be cross-linked by sulphhydryl-disulphide interchange reaction between the endogenous sulphhydryl groups (-SH) and -S-S- bonds to produce a SAP network [28]. The swelling capacity of a 76% EDTAD-modified FP is reported to be 540 g/g at 214 g, assumed to be dependent on pH and ionic strength of the swelling media, similar to what observed for EDTAD-modified SPI hydrogels [26,27,32,34]. When glutaraldehyde (GA) was employed as a cross-linker, the SAP swelling ability was diminished to 150-200 g/g, whereas the gel rigidity was enhanced. Therefore, these SAPs are preferred to be used for water absorption under pressure in real applications, such as diapers.

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Proteins can also be modified by either polysaccharides or synthetics to produce hybrid hydrogels with super-swelling properties. For instance, the researchers have studied the water swelling property of binary polymer networks (frequently as interpenetrated polymer networks, IPNs) of modified proteins with some water-soluble, hydrophilic, biodegradable, and non-toxic polymers, e.g., modified soy protein, gelatin, sodium carboxymethyl cellulose (CMC), poly(ethylene glycol) (PEG), poly(vinyl alcohol), guar gum, chitosan, and carboxymethyl chitosan [30, 35-40].

Collagen-based proteins including gelatin and hydrolyzed collagen (H-collagen; very low molecular weight products of collagen hydrolysis) have been used for preparing SAP materials. For example, gelatin-*g*-poly (NaAA-*co*-AM) hydrogel has been synthesized through simultaneous cross-linking and graft polymerization of AA/AM mixtures onto gelatin [41]. The hybrid hydrogels in 0.15 mol salt solutions show appreciable swelling capacity (e.g., in NaCl 38 g/g, and in $CaCl_2$ 12 g/g). The SAP hydrogels exhibit high sensitivity to pH, thus swelling changes may be observed in a wide range of pH 1-13.

H-collagen was also graft copolymerized with AA [42] , binary mixtures of AA and AM [43], AM and AMPS [44], AA and AMPS [45,46], AM and methacrylic acid (MAA) [47], and AA and hydroxyethyl acrylate (HEA) [48] for preparation of SAP hybrid materials.

Homo-poly(amino acid)s of poly(aspartic acid)s, poly(*L*-lysine) and poly(γ-glutamic acid)s have also been employed to prepare SAP materials. In 1999, Rohm and Haas Company's researchers reported lightly cross-linked high MW sodium polyaspartates with superabsorbing, pH- and electrolyte-responsiveness properties [49]. They used ethylene glycol diglycidylether (EGDGE) as a cross-linker. Polyethylene glycol diglycidylether (PEG-diepoxide) with different MWs has also been employed to synthesize biodegradable poly(aspartic acid) hydrogels with super-swelling behaviour [50]. To enhance the swelling capacity, several hydrophilic polymers (i.e., starch, ethyl cellulose, carrageenan, PAM, β-cyclodextrin, and CMC) were incorporated into the hydrogels (after or before the hydrolysis step) to attain modified SAP composites [51].

Super-swelling hydrogels based on poly(γ-glutamic acid), PGA, has been prepared by cross-linking reactions via both irradiation [52-54] and chemical approaches [55-61]. Similar to PGA, highly swollen hydrogels based on *L*-lysine homopolymer have been also prepared simply by γ-irradiation of their aqueous solutions [52-54,62].

SAPs PROPERTIES DETERMINATION FACTORS

SAP Technical Features

The functional features of an ideal SAP material can be listed as follows [8]:

- The highest absorption capacity (maximum equilibrium swelling) in saline
- Desired rate of absorption (preferred particle size and porosity) depending on the application requirement
- The highest absorbency under load (AUL)
- The lowest soluble content and residual monomer
- The lowest price
- The highest durability and stability in the swelling environment and during the storage
- The highest biodegradability without formation of toxic species following the degradation
- pH-neutrality after swelling in water
- Colourlessness, odourlessness, and absolute non-toxicity
- Photostability
- Re-wetting capability (if required)

The SAP has to be able to give back the imbibed solution or to maintain it; depending on the application requirement (e.g., in agricultural or hygienic applications).

Obviously, it is impossible that a SAP sample would simultaneously fulfil all the above mentioned required features. In fact, the synthetic components for achieving the maximum level of some of these features will lead to inefficiency of the rest. Therefore, in practice, the production reaction variables must be optimized such that an appropriate balance between the properties is achieved. For example, a hygienic SAP must possess the highest absorption rate, the lowest re-wetting and the lowest residual monomer. In contrary, for an agricultural SAP the

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Table 2. Effect of the main synthetic (internal, structural) factors affecting SAP material properties [8][a].

Variation in synthetic factor[b]	Absorption capacity	Absorption rate	Swollen gel strength or AUL	Soluble fraction
Increase in crosslinker concentration	-	-	+	-
Increase in initator concentration	+	-	-	+
Increase in monomer concentration	-	+	-	+
Increase in reaction temperature	+	-	-	+
Increase in particles porosity	×[c]	+	-	-+
Surface cross-linking	-	-+	+	-+

(a) + = increasing, - = decreasing, +- = varied, depending on the reagents and/or techniques employed. (b) Each factor is considered under a constant value of the rest factors. (c) Some authors have reported absorption enhancement, however, no absorption rise has to be logically observed if more accurate methods are employed for swelling measurement, e.g., centrifuge method.

absorption rate is not much necessary; instead it must acquire higher AUL and lowest sensitivity to salinity.

Reaction Variables

According to the voluminous research on the acrylic anionic SAP literature [2-6,8,10,14,18,41-48] the most important reaction variables affecting the final properties are as follows:

(a) Cross-linker type and concentration
(b) Initiator type and concentration
(c) Monomer(s) type and concentration
(d) Type, size, and amount of inorganic particles incorporated (if any)
(e) Polymerization method
(f) Polymerization temperature
(g) Amount and type of the surfactant used
(h) Stirrer/reactor geometry and rate of stirring
(i) Porosity generating method or the amount and type of the porogen (if used)
(j) Drying; its method, temperature, and time
(k) Post-treatments such as surface cross-linking to enhance the swollen gel strength

Each of the above mentioned variables has its own individual effects on the SAP properties. However, to optimize a process, a set of variables having the most special effects on the desired SAP product should be taken into consideration.

Effect of "Synthetic Parameters" on Properties

Employing fixed type of reactants, the acrylic SAP properties are affected by the main synthetic factors abstracted in Table 2 [8]. Many researchers have studied the effects of the preparative reaction variables on the SAP characteristics. These table contents have been actually extracted from numerous published works [2-6, 63-86].

Additionally in recent years, researchers have partially focused on SAP composites [69,78,87-91] and nanocomposites [92-94] to improve particularly the mechanical and thermal properties of the hydrogels.

Effect of "Environmental Parameters" on Properties

The SAP particle physical specifications (e.g., size and porosity) as well as the swelling media also greatly affect their properties. These physical and environmental factors, particularly for acrylic anionic SAPs, have been studied widely by many researchers [2-6, 63-94]. Table 3 summarizes the results of plenty published works on the conventional SAPs properties [8].

PRODUCTION PROCESSES: A SNAP SHOT

Acrylic acid (AA) and its sodium or potassium salts, and acrylamide (AM) are most frequently used in the SAP industrial production. AM, a white powder, is pure enough to be often used without purification. AA, a colourless liquid with vinegar odour, however, has a different story due to its ability to convert into its dimer (sub-section main starting materials). In this regard, the DAA level must be minimized to prevent the final product deficiencies, e.g., yield reduction, loss of soluble fraction, residual monomers, etc. Due to the potential problems originating from the inherent nature of AA to dimerize over time, manufactur-

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In spite of the SAP attractiveness, there are some drawbacks seeming to be worth noting. First of all, the researchers do not use a unified standard for swelling measurement in their works, a problem that makes the comparison of hydrogels more or less impossible.

Another drawback in this field in general is an absence of sol fraction data in nearly all reports involving the SAP synthesis. Considering this fact that hygiene occupies the largest market for SAP and diapers making up 83% of the worldwide market applications for superabsorbing hydrogels, the necessity of producing new kind of SAPs with high gel content (minimum extractable or soluble fraction) seems more tenable. Thus, there is now a need to develop new hydrogels with minimized sol fraction and residual monomer; characteristics that usually are neglected by the academic researchers. Another point to note is that, unlike the SAPs manufacturers, the academic researchers do not usually report saline-absorbency under load (AUL) values in the case of newly synthesized hydrogels. It should be emphasized that load-free absorbency (free-swelling) that are usually reported in research articles, is not an important factor from the practical or industrial point of view. Thus, measurement and reporting the mentioned practical data will be extremely beneficial.

Finally, considering high-cost and increasing prices of crude oil, the necessity of preparing natural-based SAPs seems more obvious. This paves the way to further developments in this area in the mid and far future ahead.

REFERENCES

1. Gel, Wikipedia, The free encyclopedia, http://en.wikipedia.org/wiki/gel, available in 28 May 2008.
2. Buchholz FL, Graham AT, *Modern Superabsorbent Polymer Technology*, Wiley-VCH, New York, Ch 1-7, 1998.
3. Brannon-Peppas L, Harland RS, *Absorbent Polymer Technology*, Elsevier, Amsterdam, Ch 1-4, 1990.
4. Andrade JD, *Hydrogels for medical and related applications, ACS Symp. Series,* **31**, American Chemical Society, Washington DC, 1, 1976.
5. Po R, Water-absorbent polymers: A patent survey, *J Macromol. Sci-Rev Macromol Chem Phys*, **C34**, 607-662, 1994.
6. Buchholz FL, Peppas NA, *Superabsorbent Polymers Science and Technology*, *ACS Symposium Series*, **573**, American Chemical society, Washington, DC, Ch 2, 7, 8, 9, 1994.
7. Omidian H, Zohuriaan-Mehr MJ, Kabiri K, Shah K, Polymer chemistry attractiveness: Synthesis and swelling studies of gluttonous hydrogels in the advanced academic laboratory, *J Polym Mater*, **21**, 281-292, 2004.
8. Zohuriaan-Mehr MJ, Super-Absorbents (in Persian), Iran Polymer Society, Tehran, 2-4, 2006.
9. Superabsorbent hydrogels, Website of the leading Iranian manufacturer of superabsorbent polymers; Rahab Resin Co., Ltd.; www.rahabresin.com, available in 10 September 2007.
10. Dayal U, Mehta SK, Choudhari MS, Jain R, Synthesis of acrylic superabsorbents, *J Macromol Sci-Rev Macromol Chem Phys*, **C39**, 507-525, 1999.
11. Superabsorbents, Website of the European Disposables and Nonwovens Association (EDANA); www.edana.org, available in 28 May 2008.
12. Mathur AM, Moorjani SK, Scranton AB, Methods for synthesis of hydrogel networks: A review, *J Macromol Sci-Rev Macromol Chem Phys*, **C36**, 405-430, 1996.
13. Kulicke W-M, Nottelmann H, Structure and swelling of some synthetic, semisynthetic, and biopolymer hydrogels, *Adv Chem Ser*, **223**, 15-44, 1989.
14. Kazanskii KS, Dubrovskii SA, Chemistry and physics of "agricultural" hydrogels, *Adv Polym Sci*, **104**, 97-140, 1992.
15. Bouranis DL, Theodoropoulos AG, Drossopoulos JB, Designing synthetic polymers as soil conditioners, *Commun Soil Sci Plant Anal*, **26**, 1455-1480, 1995.
16. Dutkiewicz JK, Superabsorbent materials from shellfish waste-A review, *J Biomed Mater Res (Appl Biomater)*, **63**, 373-381, 2002.
17. Ichikawa T, Nakajima T, Superabsorptive Polymers (from natural polysaceharides and

Archive of SID

www.SID.ir
Pet. Ex 1017 - Appendix Zohuriaan-Mehr
10 of 17

polypeptides), In: *Polymeric Materials Encyclopedia*, Salamone (Ed), CRC, Boca Raton (Florida), 8051-8059, 1996.
18. Athawale VD, Lele V, Recent trends in hydrogels based on starch-graft-acrylic acid: A review, *Starch/Starke*, **3**, 7-13, 2001.
19. Buchholz FL, Recent advances in superabsorbent polyacrylates, *Trend Polym Sci*, **2**, 277-281, 1994.
20. Chin Y-R, Al-Dayel A, Acrylic acid based superabsorbent polymer, *Process Economics Program Review No. 85-1-2*, Stanford Research Institute, SRI International, Dec. 1985.
21. Chatterjee PK, Gupta BS (Eds), *Absorbent Technology*, Elsevier, Amsterdam, ch 1-2, 2002.
22. Wampler FM, Formation of diacrylic acid during acrylic acid storage, *Plant/Operation Prog*, **7**(3), 183-189, 1988.
23. Zohuriaan-Mehr MJ, Pourjavadi A, Kurdtabar M, Salimi H, Polysaccharide-based superabsorbent hydrogels: A Review, *Carbohydr Polym*, submitted, 2008.
24. Sannino A., Esposito A., De Rosa A., Cozzolino A., Ambrosio L., Nicolais L., Biomedical application of a superabsorbent hydrogel for body water elimination in the treatment of edemas, *J Biomed Mater Res*, **67A**, 1016-1024, 2003.
25. Demitri C, Delsole R, Scalera F, Sannino A, Vasapollo G, Maffezzoli A, Nicolais L, Novel superabsorbent cellulose-based hydrogels crosslinked with citric acid, *J Appl Polym Sci*, 2008, (in press).
26. Hwang D-C, Damodaran S. Equilibrium swelling properties of a novel ethylenediamine tetraacetic dianhydride (EDTAD)-modified soy protein hydrogel. *J Appl Polym Sci*, **62**, 1285-1293, 1996.
27. Hwang D-C, Damodaran S, Chemical modification strategies for synthesis of protein-based hydrogelm, *J Agric Food Chem*, **44**, 751-758, 1996.
28. Hwang D-C, Damodaran S, Synthesis and properties of Fish protein-based hydrogel. *J Am Oil Chem Soc*, **74**, 1165-1171, 1997.
29. Rathna GVN, Damodaran S, Swelling behavior of protein-based superabsorbent hydrogels treated with ethanol, *J Appl Polym Sci*, **81**, 2190-2196, 2001.
30. Rathna GVN, Damodaran S, Effect of nonprotein polymers on water-uptake properties of fish protein-based hydrogel, *J Appl Polym Sci*, **85**, 45-51, 2002.
31. Hwang D-C, Damodaran S, Metal-chelating properties and biodegradability of an ethylenediamine tetraacetic acid dianhydride modified soy protein hydrogel, *J Appl Polym Sci*, **64**, 891-901, 1997.
32. Damodaran S, Hwang D-C, Carboxyl-modified superabsorbent protein hydrogel, *US Patents 5,847,089*, 1998.
33. Stern T, Lamas MC, Benita S, Design and characterization of protein-based microcapsules as a novel catamenial absorbent system, *Int J Pharm*, **242**, 185-190, 2002.
34. Damodaran S, Carboxyl-modified superabsorbent protein hydrogel, *US Patents 6,310,105 B1*, 2001.
35. Damodaran S, Protein-polysaccharide hybrid hydrogels, *US Patents 6,821,331 B2*, 2004.
36. Chatterji PR, Kaur H, Interpenetrating hydrogel network. 3. Properties of the gelatin-sodium carboxymethylcellulose system, *Polymer*, **33**, 2388-2391, 1992.
37. Yao KD, Yin YJ, Xu MX, Wang YF, Investigation of pH-sensitive drug delivery system of chitosan/gelatin hybrid polymer network, *Polym Int*, **38**, 77-82, 1995.
38. Fang Y-E, Cheng Q, Lu X-B, Kinetics of in-vitro release from chitosan/gelatin hybrid membranes, *J Appl Polym Sci*, **68**, 1751-1758, 1998.
39. Yao KD, Liu WG, Lin Z, Qiu XH, In situ atomic force microscopy measurement of the dynamic variation in the elastic modulus of swollen chitosan/gelatin hybrid polymer network gels in media of different pH, *Polym Int*, **48**, 794-798, 1999.
40. Chen L, Du Y, Huang R. Novel pH, ion sensitive polyampholyte gels based on carboxymethyl chitosan and gelatin, *Polym Int*, **52**, 56-61, 2003.
41. Pourjavadi A, Sadeghi M, Mahmodi Hashemi M, Hosseinzadeh H, Synthesis and absorbency of gelatin-*graft*-poly(sodium acrylate-*co*-acrylamide) superabsorbent hydrogel with salt- and pH-responsiveness properties. *e-Polymers*, No. 057:1-15 2006 (http://www.e-polymers.org).
42. Pourjavadi A, Kurdtabar M, Mahdavinia GR, Hosseinzadeh H, Synthesis and super-swelling behavior of a novel protein-based superabsorbent

Archive of SID

www.SID.ir
Pet. Ex 1017 - Appendix Zohuriaan-Mehr
11 of 17

hydrogel, *Polym Bull,* **57**, 813-824, 2006.
43. Pourjavadi A, Kurdtabar M, Collagen-based highly porous hydrogel without any porogen: synthesis and characteristics, *Eur Polym J*, **43**, 877-889, 2007.
44. Pourjavadi A., Salimi H., Kurdtabar M, Hydrolyzed collagen-based hydrogel with salt and pH-responsiveness properties, *J Appl Polym Sci*, **106**, 2371-2379, 2007.
45. Pourjavadi A, Kurdtabar M, Ghasamzadeh H, Salt- and pH-resisting collagen-based highly porous hydrogel, *Polym J*, **40**, 94-103, 2008.
46. Seidi Ghalehgah F, Optimization of novel gelatin-based superabsorbent hydrogels using Taguchi method and investigation of their swelling behavior in various conditions, M.Sc. dissertation, Chem Dept, Sharif Univ Tech, 2006.
47. Bagheri Marandi G, Biranvand F, Babapour M, Esfandiari K, Sadeh S, Kurdtabar M. Synthesis and swelling behavior of hydrolyzed collagen-*g*-poly(methacrylic acid-*co*-acrylamide) hydrogel. *J Appl Polym Sci*, 2007 (submitted).
48. Pourjavadi A, Salimi H, A new protein-based hydrogel with superabsorbing properties: Effect of monomer ratio on swelling behavior and kinetics, *Ind Eng Chem Res*, 2008, submitted.
49. Chang CJ, Swift G. Poly(aspartic acid) hydrogel, *J Macromol Sci-Pure Appl Chem*, **A36**, 963-970, 1999.
50. Min SK, Kim J-H, Chung DJ, Swelling behavior of biodegradable crosslinked gel based on poly(aspartic acid) and PEG-diepoxide, *Korea Polym J Macromol Res*, **9**, 143-149, 2001.
51. Yang J, Fang L, Tan T, Synthesis and characterization of superabsorbent hydrogels composites based on polysuccinimide, *J Appl Polym Sci*, **102**, 550-557, 2006.
52. Kunioka M, Choi HJ, Hydrolytic degradation and mechanical properties of hydrogels prepared from microbial poly(amino acid)s, *Polym Degrad Stab*, **59**, 33-37, 1998.
53. Choi HJ, Yang R, Kunioka M, Synthesis and characterization of pH-sensitive and biodegradable hydrogels prepared by γ irradiation using microbial poly(γ-glutamic acid) and poly(ε-lysine), *J Appl Polym Sci*, **58**, 807-814, 1995.
54. Kunioka M, Biodegradable water absorbent synthesized from bacterial poly(amino acid)s, *Macromol Biosci*, **4**, 324-329, 2004.
55. Gonzales D, Fan K, Sevoian M, Synthesis and swelling characterizations of a poly(gamma-glutamic acid) hydrogel, *J Polym Sci A Polym Chem*, **34**, 2019-2027, 1996.
56. Kunioka M, Furusawa K, Poly(γ-glutamic acid) hydrogel prepared from microbial poly(γ-glutamic acid) and alkanediamine with water-soluble carbodiimide, *J Appl Polym Sci*, **65**, 1889-1896, 1997.
57. Matsusaki M, Yoshida H, Akashi M, The construction of 3D-engineered tissues composed of cells and extracellular matrices by hydrogel template approach, *Biomaterials*, **28**, 2729-2737, 2007.
58. Shimokuri T, Kaneko T, Akashi M, Specific thermosensitive volume change of biopolymer gels derived from propylated poly(γ-glutamate)s, *J Polym Sci A Polym Chem*, **42**, 4492-4501, 2004.
59. Matsusaki M, Serizawa T, Kishida A, Akashi M, Novel functional biodegradable polymer. III. The construction of poly(γ-glutamic acid)-sulfonate hydrogel with fibroblast growth factor-2 activity, *J Biomed Mater Res*, **73A**, 485-491, 2005.
60. Markland P, Zhang Y, Amidon GL, Yang VC, A pH- and ionic strength-responsive polypeptide hydrogel: Synthesis, characterization and preliminary protein release studies, *J Biomed Mater Res*, **47**, 595-602, 1999.
61. Yang Z, Zhang Y, Markland P, Yang VC, Poly(glutamic acid) poly(ethylene glycol) hydrogels prepared by photoinduced polymerization: Synthesis, characterization, and preliminary release studies of protein drugs, *J Biomed Mater Res*, **62**, 14-21, 2002.
62. Kunioka M, Choi HJ, Properties of biodegradable hydrogels prepared by irradiation of microbial poly(ε-lysine) aqueous solutions, *J Appl Polym Sci*, **58**, 801-806, 1995.
63. Kabiri K, Faraji-Dana S, Zohuriaan-Mehr MJ, Novel sulfobetaine-sulfonic acid-contained superswelling hydrogels, *Polym Adv Technol*, **16**, 659-666, 2005.
64. Kabiri K, Zohuriaan-Mehr MJ, Porous superabsorbent hydrogel composites: Synthesis, morphology and swelling rate, *Macromol Mater Eng*,

Archive of SID

www.SID.ir
Pet. Ex 1017 - Appendix Zohuriaan-Mehr
12 of 17

289, 653-661 2004.
65. Kabiri K, Zohuriaan-Mehr MJ, Superabsorbent hydrogels from concentrated solution terpolymerization, Iran Polym J, **13**, 423-430, 2004.
66. Omidian, H; Hashemi, SA, Sammes PG, Meldrum I, Modified acrylic-based superabsorbent polymers. Effect of temperature and initiator concentration, *Polymer*, **39**, 3459-3466, 1998.
67. Kabiri K, Omidian H, Hashemi SA, Zohuriaan-Mehr MJ, Concise synthesis of fast-swelling superabsorbent hydrogels: Effect of initiator concentration on porosity and absorption rate, *J Polym Mater*, **20**, 17-22, 2003.
68. Kabiri K, Omidian H, Hashemi SA, Zohuriaan-Mehr MJ, Synthesis of fast-swelling superabsorbent hydrogels: Effect of crosslinker type and concentration on porosity and absorption rate, *Eur Polym J*, **39**, 1341-1348, 2003.
69. Kabiri K, Zohuriaan-Mehr MJ, Superabsorbent hydrogel composites, *Polym Adv Technol*, **14**, 438-444, 2003.
70. Kabiri K, Omidian H, Zohuriaan-Mehr MJ, Novel approach to highly porous huperabsorbent hydrogels: Synergistic effect of porogens on porosity and swelling rate, *Polym Int*, **52**, 1158-1164, 2003.
71. Omidian H, Zohuriaan-Mehr MJ, DSC studies on synthesis of superabsorbent hydrogels, *Polymer*, **43**, 269-277, 2002.
72. Kabiri K, Mirzadeh H, Zohuriaan-Mehr MJ, Undesired effects of heating on hydrogels, *J Appl Polym Sci*, 2008, accepted.
73. Ramazani-Harandi MJ, Zohuriaan-Mehr MJ, Ershad-Langroudi A, Yousefi AA, Kabiri K, Rheological determination of the swollen gel strength of the superabsorbent polymer hydrogels, *Polym Test*, **25**, 470-474, 2006.
74. Jamshidi A, Ahmad Khan Beigi F, Kabiri K, Zohuriaan-Mehr MJ, Optimized HPLC determination of residual monomer in hygienic SAP hydrogels, *Polym Test,* **24**, 825-828, 2005.
75. Zohuriaan-Mehr MJ, Motazedi Z, Kabiri K, Ershad-Langroudi A, Allahdadi I, Gum arabic-acrylic superabsorbing hydrogel hybrids: Studies on swelling rate and environmental responsiveness, *J Appl Polym Sci*, **102**, 5667-5674, 2006.
76. Mahdavinia GR, Pourjavadi A, Zohuriaan-Mehr MJ, A convenient one-step preparation of chitosan-poly(sodium acrylate-*co*-acrylamide) hydrogel hybrids with super-swelling properties, *J Appl Polym Sci*, **99**, 1615-1619, 2006.
77. Mohamadnia Z, Zohuriaan-Mehr MJ, Kabiri K, Razavi-Nouri M, Tragacanth gum-graft-polyacrylonitrile: Synthesis, characterization and hydrolysis, *J Polym Res*, **15**, 173-180, 2008.
78. Pourjavadi A, Hosseinzadeh H, Mahdavinia GR, Zohuriaan-Mehr MJ, Carrageenan-*g*-poly(sodium acrylate)/kaolin superabsorbent hydrogel composites: Synthesis, characterisation and swelling behavior, *Polym Polym Comp*, **15**, 43-51, 2007.
79. Pourjavadi A, Ghassempouri N, Zohuriaan-Mehr MJ, Hosseinzadeh H, Modified CMC. 5. Synthesis and super-swelling behavior of hydrolyzed CMC-*g*-PAN hydrogel, *J Appl Polym Sci*, **103**, 877-883, 2007.
80. Zohuriaan-Mehr MJ, Motazedi Z, Kabiri K, Ershad-Langroudi A, New superabsorbing hydrogel hybrid from arabic gum and acrylic monomers, *J Macromol Sci-Pure Appl Chem*, **42**, 1655-1666, 2005.
81. Hosseinzadeh H, Pourjavadi A, Mahdavinia GR, Zohuriaan-Mehr MJ, Modified carrageenan. 1. H-CarragPAM, a novel biopolymer-based superabsorbent hydrogel, *J Bioact Compat Polym*, **20**, 475-490, 2005.
82. Pourjavadi A, Zohuriaan-Mehr MJ, Mahdavinia GR, Modified chitosan. III. superabsorbency, salt- and pH-sensitivity of smart ampholytic hydrogels from chitosan-*g*-PAN, *Polym Adv Technol*, **15**, 173-180, 2004.
83. Mahdavinia GR, Pourjavadi A, Hosseinzadeh H, Zohuriaan MJ, Modified chitosan. 4. Superabsorbent hydrogels from poly(acrylamide-*co*-acrylic acid) grafted chitosan with salt- and pH-responsiveness properties, *Eur Polym*, **40**, 1399-1407, 2004.
84. Hosseinzadeh H, Pourjavadi A., Zohuriaan-Mehr MJ, Modified carrageenan. 2. Hydrolyzed crosslinked kappa-carrageenan-*g*-PAAm as a novel smart superabsorbent hydrogel with low salt sensitivity, *J Biomater Sci, Polym Edn*, **15**, 1499-1511 2004.
85. Zohuriaan-Mehr MJ, Pourjavadi A, Superabsorbent hydrogels from starch-*g*-PAN: Effect of some reaction variables on swelling

Archive of SID

www.SID.ir
Pet. Ex 1017 - Appendix Zohuriaan-Mehr
13 of 17

behavior, *J Polym Mater*, **20**, 113-120, 2003.
86. Pourjavadi A, Mahdavinia GR, Zohuriaan-Mehr MJ, Modified chitosan. II. H-ChitoPAN, a novel pH-responsive superbasorbent hydrogel, *J Appl Polym Sci*, **90**, 3115-3121, 2003.
87. Zheng Y, Wang A, Study of superabsorbent composites. XVIII. Preparation, characterization and property evaluation of poly(acrylic acid-*co*-acrylamide)/organomontmorillonite/sodium humate superabsorbent composites, *J Appl Polym Sci*, **108**, 211-219, 2008.
88. Zheng Y, Gao T, Wang A, Preparation, swelling and slow-release characteristics of superabsorbent composite containing sodium humate, *Ind Eng Chem Res*, **47**, 1766-1773, 2008.
89. Su X, Zhang G, Xu K, Wang J, Song C, Wang P, The effect of MMT/modified MMT on the structure and performance of the superabsorbent composite, *Polym Bull*, **60**, 69-78, 2008.
90. Pourjavadi A, Seidi F, Salimi H, Soleyman R, Grafted CMC/silica gel superabsorbent composite: synthesis and investigation of swelling behavior in various media, *J Appl Polym Sci*, **108**, 3281-3290, 2008.
91. Pourjavadi A, Ayyari M, Amini-Fazl MS, Taguchi optimized synthesis of collagen-*g*-poly(acrylic acid)/kaolin composite superabsorbent hydrogel, *Eur Polym J*, **44**, 1209-1216, 2008.
92. Kasgoz H, Durmus A, Kasgoz A, Enhanced swelling and adsorption properties of AAm-AMPSNa/clay hydrogel nanocomposites for heavy metal ion removal, *Polym Adv Tech*, **19**, 213-220, 2008.
93. Al E, Guclu G, Iyim T, Emik S, Ozgumu S, Synthesis and properties of starch-graft-acrylic acid/Na-montmorillonite superabsorbent composite hydrogels, *J Appl Polym Sci*, **109**, 16-22, 2008.
94. Qiu H, Yu J, Polyacrylate/(carboxymethylcellulose modified montmorillonite) superabsorbent nanocomposite: preparation and water absorbency, *J Appl Polym Sci*, **107**, 118-123, 2008.
95. Omidian H, Hashemi SA, Askari F, Nafisi S, Modifying acrylic-based superabsorbents. I.modification of crosslinker and comonomer nature, *J Appl Polym Sci*, **54**, 241-249, 1994.
96. Omidian H, Hashemi SA, Askari F, Nafisi S, Modifying acrylic-based superabsorbents. II. Modification of process nature *J. Appl Polym Sci*, **54**, 251-256, 1994.
97. Hunkeler D, Synthesis and characterization of high molecular weight water-soluble polymers, *Polym Int*, **27**, 23-33, 1992.
98. Watanabe N, Hosoya Y, Tamura A, Kosuge H, Characteristics of water-absorbent polymer emulsions, *Polym Int*, **30**, 525-531,1993.
99. Trijasson P, Pith T, Lambla M, Hydrophilic polyelectrolyte gels by inverse suspension, *Macromol Chem Macromol Symp*, **35/36**, 141-169, 1990.
100. Askari F, Nafisi S, Omidian H, Hashemi SA, Synthesis and characterization of acrylic-based superabsorbents *J. Appl Polym Sci*, **50**, 1851-1855, 1993.
101. Technical Brochure of Superabsorbent Polymer Research Lab., Nippon Shokubai Co., www.shokubai.co.jp, available in 15 August 2005.
102. Omidian H, Hashemi SA, Sammes PG, Meldrum, I. Modified acrylic-based superabsorbent polymers (dependence on particle size and salinity), *Polymer*, **40**, 1753-1761, 1999.
103. Ramazani-Harandi MJ, Zohuriaan-Mehr MJ, Ershad-Langroudi A, Yousefi AA, Kabiri K, On the structure-property relation in SAP gels: Effect of structural variables on AUL and rheological behavior, *Polym Eng Sci*, submitted, 2008.
104. Fanta GF, Doane WM, In: *Agricultural and Synthetic Polymers: Biodegradability and Utilization*, Glass JE, Swift G (Eds.), American Chemical Society, Washington DC, 288-303, 1990.
105. Omidian H, Hashemi, SA, Sammes PG, Meldrum I, A model for the swelling of superabsorbent polymers, *Polymer*, **39**, 6697-6704, 1998.
106. Qi X, Liu M, Chen Z, Zhang F, Study of the swelling kinetics of superabsorbent using open circuit potential measurement, *Eur Polym J*, **44**, 743-754, 2008.
107. Lu S, Duan M, Lin S, Synthesis of superabsorbent starch-graft-poly(potassium acrylate-*co*-acrylamide) and its properties, *J Appl Polym*

Archive of SID
www.SID.ir
Pet. Ex 1017 - Appendix Zohuriaan-Mehr
14 of 17

Sci, **88**, 1536-1542, 2003.
108. Chervyakova GN, Pomerantseva EG, Klyuzhin ES, Kruglyachenko MB, Determination of the gel fraction content of a superabsorbent based on acrylic acid by UV spectroscopy, *Int Polym Sci Technol*, **23**, T/87-T/88, 1996.
109. Brown L, High-performance liquid chromatographic determination of acrylic acid monomer in natural and polluted aqueous environments and polyacrylates, *Analyst*, **104**, 1165, 1979.
110. Fallahi D, Biocompatibility evaluation of hydrophilic and hydrophobic silicone rubbers, M.Sc. dissertation, Department of Biomaterials, Iran Polymer and Petrochemical Institute, 2000.
111. Natural superabsorbents, Web page for the introduction of the superabsorbent SNAP made by Lysac Technologies; www.lysac.com/lysac/english/about.html, available in 2 February 2008.
112. Das A, Kothari VK, Makhija S, Avyaya K, Development of high-absorbent light-weight sanitary napkin, *J Appl Polym Sci*, **107**, 1466-1470, 2008.
113. Kim JJ, Park K, Smart hydrogels for bioseparation, *Bioseparation*, **7**, 177-184, 1998.
114. Chen J, Park H, Park K, Synthesis of superporous hydrogels: hydrogels with fast swelling and superabsorbent properties, *J Biomed Mater Res*, **44**, 53-62 1999.
115. Omidian H, Roccaa JG, Park K, Advances in superporous hydrogels, *J Contr Rel*, **102,** 3-12, 2005.
116. Abd El-Rehim HA, Hegazy ESA, Abd El-Mohdy HL, Radiation synthesis of hydrogels to enhance sandy soils water retention and increase plant performance, *J Appl Polym Sci*, **93**, 1360-1371, 2004.
117. Bakass M, Mokhlisse A, Lallemant M, Absorption and desorption of liquid water by a superabsorbent polymer: Effect of polymer in the drying of the soil and the quality of certain plants, *J Appl Polym Sci*, **83**, 234-243, 2002.
118. Liu M, Liang R, Zhan F, Liu Z, Niu A, Preparation of superabsorbent slow release nitrogen fertilizer by inverse suspension polymerization, *Polym Int*, **56**, 729-737, 2007.
119. Bowman DC, Evans RY, Paul JL, Fertilizer salts reduce hydration of polyacryamide gels and affect physical properties of gel-amended container media, *J Amer Soc Hort Sci*, **115**, 382-386, 1990.
120. Wu L, Liu M, Liang R, Preparation and properties of a double-coated slow-release NPK compound fertilizer with superabsorbent and water-retention, *Bioresource Tech*, **99**, 547-554, 2008.
121. Wu L, Liu M, Preparation and characterization of cellulose acetate-coated compound fertilizer with controlled-release and water-retention, *Polym Adv Tech*, 2008, in press (DOI: 10.1002/pat.1034).
122. Abedi-Koupai J, Sohrab F, Evaluation the effect of superabsorbents on water retention and potential of three soils, *J Polym Sci Technol (Persian)*, **17**, 163-173, 2004.
123. Abedi-Koupai J, Asadkazemi J, Effects of a Hydrophilic Polymer on the Field Performance of an Ornamental Plant (Cupressus arizonica) under Reduced Irrigation Regimes, *Iran Polym J*, **15**, 715-725, 2006.
124. Mousavinia SM, Atapour A, Investigating the effect of polymer Superab A-200 on the irrigation water of turf grass, 3rd Specialized Training Course and Seminar on the Application of Superabsorbent Hydrogels in Agriculture, Iran Polymer and Petrochemical Institute, Tehran, Iran, Nov, 7, 2005.
125. Allahdadi I, Investigation the effect of superabsorbent hydrogels on reducing plant dry stress, 2nd Specialized Training Course and Seminar on the Application of Superabsorbent Hydrogels in Agriculture, Iran Polymer and Petrochemical Institute, Tehran, Iran, 2002.
126. Moazen Ghamsari B, Evaluation of levels of superabsorbent polymer (Superab A-200) and different levels of drought stress on growth and yield of forage corn, Faculty of Plant and Animal Sciences, M.Sc. Dissertation, University College of Aburaihan, Tehran Univ, June 2006.
127. Jafarzadeh S, Effect of superabsorbent on the efficiency of clay mulch and biological fixation of sand dunes, M.Sc. thesis, Department of Agriculture, Isfahan University of Technology, 2004.

Archive of SID

www.SID.ir
Pet. Ex 1017 - Appendix Zohuriaan-Mehr
15 of 17

128. Assadzadeh A, Investigation of the effect of superabsorbent hydrogels and low irrigation on preserving nutrients in hydroponic systems, *3rd Specialized Training Course and Seminar on the Application of Superabsorbent Hydrogels in Agriculture*, Iran Polymer and Petrochemical Institute, Tehran, Iran, Nov. 7, 2005.
129. A. Mirhejazi, Remarkable reduction of olive sapling casualty via employing superabsorbent Superab A-300, 3rd Specialized Training Course and Seminar on the Application of Superabsorbent Hydrogels in Agriculture, Iran Polymer and Petrochemical Institute, Tehran, Iran, Nov. 7, 2005.
130. Sojka1 RE, Bjorneberg1 DL, Entry1 JA, Lentz RD, Orts WJ, Polyacrylamide in Agriculture and Environmental Land Management, *Adv Agronomy*, **92** , 75-162, 2007.
131. Gao D, Heimann RB, Alexander SDB, Box-Behnken design applied to study the strengthening of aluminate concrete modified by a superabsorbent polymer/clay composite, *Adv Chem Res*, **9**, 93-97,1997.
132. Yamane H, Ideguchi T, Tokuda M, Koga H, A new ground-reducing material based on water-absorbent polymer, *Electronics and Communications in Japan*, Part 1, **77**, 68-77, 1994.
133. Kenawy E-R, Recent advances in controlled release of agrochemicals, *J Macromol Sci-Rev Macromol Chem Phys*, **C38**, 365-390, 1998.
134. Rudzinski WE, Dave AM, Vaishnav UH, Kumbar SG, Kulkarni AR, Aminabhavi TM, Hydrogels as conclolled release devices in agriculture, *Designed Monomers Polym*, **5**, 39-65, 2002.
135. Guo M, Liu M, Zhan F, Wu L, Preparation and properties of a slow release membrane-encapsulated urea fertilizer with superabsorbent and moisture preservation, *Ind Eng Chem Res*, **44**, 4206-4211, 2005.
136. Liu M, Liang R, Zhan F, Liu Z, Niu A, Synthesis of a slow-release and superabsorbent nitrogen fertilizer and its properties, *Polym Adv Technol*, **17**, 430-438, 2006.
137. Liang R, Liu M, Wu L, Controlled release NPK compound fertilizer with the function of water retention, *React Func Polym*, **67**, 769-779, 2007.
138. Guo M, Liu M, Liang R, Niu A, Granular urea-formaldehyde slow-release fertilizer with superabsorbent and moisture preservation, *J Appl Polym Sci*, **99**, 3230-3235, 2006.
139. Liu M, Liang R, Zhan F, Liu Z, Niu A, Preparation of superabsorbent slow release nitrogen fertilizer by inverse suspension polymerization, *Polym Int*, **56**, 729-737, 2007.
140. Wu L, Liu M, Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention, *Carbohydr Polym*, **72**, 240-247, 2008.
141. Levy R, Nichols MA, Miller TW, Evaluation of superabsorbent polymer-pesticide formulations for prolonged insect control, ASTM Special Technical Publication, No. 1234, 330-339, Proceedings of the 14th Symposium on Pesticide Formulations and Application Systems, Dallas, TX, Oct. 12-13, 1995.
142. Ahmadpour A, Maskoki A, Rezaie M, *Iran J Polym Sci Tech* (in Persian), Dewatering of yogurt using a permeable membrane and acrylic superabsorbent hydrogel, **20**, 551-559, 2007.
143. Mudiyanselage TK, Neckers DC, Photochromic superabsorbent polymers, *Soft Matter*, **4**, 768-774, 2008.
144. Mudiyanselage TK, Neckers DC, Highly absorbing superabsorbent polymer, *J Polym Sci A Polym Chem*, **46**, 1357-1364, 2008.
145. Cordani P, Method of modifying weather, *U.S. Patents 6,315,213*, 2001.
146. Agricultural Section, Web site of SNF Co., Agricultural Section, Technical data Sheet of Superabsorbent; www.snf-group.com/IMG/pdf/Aquasorb_E. pdf, available in 28 February 2004.
147. The Trawet *Super absorbents Catalogue*, The Trawet Corporation, San Diego, CA, 1993 (Water absorbents, www.terawet.com, available in 21 June 2003.).
148. Superabsorber, Website of Stockhausen, Inc., the manufacturer of the superabsorbent STOCKOSORB; www.stockhausen-inc.com, available in 2 April 2006.
149. Material Safty Data Sheet of the commercial

Archive of SID

www.SID.ir
Pet. Ex 1017 - Appendix Zohuriaan-Mehr
16 of 17

superabsorbents; www.hydrosource.com/web_clb/990310/msds0399.htm, available in 20 July 2006.
150. Superabsorbent Super-Hydro-Grow made by Super Absorbent Co., www.superabsorbent.com, available in 5 October 2005.
151. Horta-Sorb Superabsorbents, Website of Horticultural Alliance, Inc., www.hortsorb.com, available in 7 April 2003.
152. Stahl JD, Cameron MD, Haselbach J, Aust SD, Biodegradation of superabsorbent polymers in soil, *Environ Sci Pollut Res*, **7**, 83-88, 2000.
153. Wolter M, Wiesche C, Zadrazil F, Hey S, Haselbach J, Schnug E, Biological degradability of synthetic superabsorbent soil conditioners, *Landbauforschung Volkenrode*, **1**, 43-52, 2002.
154. Larson RJ, Bookland EA, Williams RT, Yokom KM, Saucy DA, Freeman MB, Swift G, Biodegradation of acrylic acid polymers and oligomers by mixed microbial communities in activated sludge, *J Environment Polym Degrad*, **5**, 41-48, 1997.
155. Cutie SS, Buzanowski WC, Berdasco JA, Fate of superabsorbents in the environment (analytical techniques), *J Chromatogr A*, **513**, 93-105, 1990.
156. Barvenik FW, Polyacrylamide characteristics related to soil applications, *Soil Sci*, **158**, 235-243, 1994.
157. Grula MM, Huang M-L, Sewell G, Interactions of certain polyacrylamides with soil bacteria, *Soil Sci*, **158**, 291-300, 1994.
158. Wallace A, Wallace GA, Abuzamzam AM, Effects of a polymer as soil conditioner on yields and mineral nutrition of plants, *Soil Sci*, **143**, 377-380, 1986.

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www.SID.ir
Pet. Ex 1017 - Appendix Zohuriaan-Mehr
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United States Patent [19]

Weaver et al.

[11] **3,997,484**

[45] **Dec. 14, 1976**

[54] **HIGHLY-ABSORBENT STARCH-CONTAINING POLYMERIC COMPOSITIONS**

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[73] Assignee: **The United States of America as represented by the Secretary of Agriculture**, Washington, D.C.

[22] Filed: **Sept. 8, 1975**

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Related U.S. Application Data

[62] Division of Ser. No. 456,911, April 3, 1974, Pat. No. 3,935,099.

[52] **U.S. Cl.** ..... **260/17.4 GC**; 260/17.4 R; 260/17.4 CL; 260/17.4 ST

[51] **Int. Cl.**[2] **C08L 3/00**

[58] **Field of Search** ..... 260/17.4 GC, 17.4 CL, 260/17.4 R, 17.4 ST

[56] **References Cited**

UNITED STATES PATENTS

3,288,707	11/1966	Hurwitz et al.	210/54
3,425,971	2/1969	Gugliemelli et al.	260/17.4
3,661,815	5/1972	Smith	260/17.4
3,932,322	4/1976	Duchane	260/17.4

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[57] **ABSTRACT**

Starch-containing polymer compositions are prepared which absorb amounts of water equaling up to more than 1000 times their own weight. The compositions find many applications including their incorporation into products such as disposable diapers, surgical pads and sheets, and paper towels.

15 Claims, No Drawings

HIGHLY-ABSORBENT STARCH-CONTAINING POLYMERIC COMPOSITIONS

This is a division of application Ser. No. 456,911 filed Apr. 3, 1974, and now U.S. Pat. No. 3,935,099.

BACKGROUND OF THE INVENTION

The invention relates to starch-graft copolymer compositions which absorb and retain under pressure large quantities of aqueous fluids and to their method of preparation. The invention further relates to various compositions and articles of manufacture which utilize the instant composition.

Crosslinked polymeric substances which possess the ability to absorb large quantities of fluids are known in the prior art. For example, U.S. Pat. No. 3,669,103 discloses that a variety of monomers may be polymerized to give copolymers and terpolymers which must be crosslinked in manners known in the polymer arts. One such copolymer contains carboxamide and carboxylate groups and is crosslinked by including a difunctional monomer such as N,N-methylenebisacrylamide into the polymerization solution. The crosslinking reaction is of critical importance. When the copolymers and terpolymers are not crosslinked, they are water soluble and have limited utility as absorbents.

U.S. Pat. No. 3,670,731 discloses the utility of particulate, water-insoluble, crosslinked polymeric compositions as absorbents in fabricated articles such as diapers, sanitary napkins, and the like.

It is an object of this invention to provide polymeric absorbent compositions which have the preparative ease and economic advantages inherent in starch graft copolymers and which will absorb aqueous fluids in quantities many times their own weight.

it is a further object of the invention to provide polymeric absorbent compositions which have not been subjected to normally used crosslinking compositions or procedures and yet are water-insoluble solids.

In accordance with the objects of the invention, we prepared aqueous fluid-absorbing compositions comprising water-insoluble alkali salts of saponified gelatinized-starch-polyacrylonitrile graft polymers containing gelatinized starch (GS) and saponified polyacrylonitrile (HPAN) in molar ratios of from about 1:1.5 to 1:9 GS:HPAN. The water-insoluble alkali salts of saponified gelatinized-starch-polyacrylonitrile graft polymers are further characterized as water-insoluble solids capable of absorbing in excess of 300 parts of water by weight per part of the water-insoluble solids.

Compositions comprising water-insoluble organic amine salts of the compositions described above were found to absorb aqueous fluids which contain organic components in major porportions.

Also in accordance with the objects of the invention, we discovered a method of preparing water-insoluble aqueous fluid-absorbing compositions comprising the following steps:

a. saponifying a gelatinized starch-polyacrylonitrile graft polymer (GS-PAN) in an aqueous slurry with an alkali in amounts such that the molar ratio of alkali to the acrylonitrile repeating unit of said GS-PAN is from about 0.1:1 to 7:1 to form a water-soluble saponified GS-PAN (water-soluble GS-HPAN; and

b. optionally adjusting the pH of said water-soluble GS-HPAN to about 3 followed by isolating the resulting water-insoluble acid form of GS-HPAN, and readjusting the pH of said water-insoluble acid form of GS-HPAN to from about 4 to 12 to reform said water-soluble GS-HPAN; and

c. drying said water-soluble GS-HPAN to a moisture level of from about 1 to 15% water by weight.

Incorporation of the instant compositions in disposable soft goods such as diapers, hospital bed pads, surgical pads and sheets, catamenial devices, and the like would greatly increase the fluid-absorbing capacity of the articles. Such increased absorbency of the disposable soft goods is important from both an economic and an ecological standpoint, since the higher absorbency permits the use of a smaller quantity of material to be disposed of by incineration or by discharge into sewage systems. The use of smaller quantities of GS-HPAN also decreases the amount of the synthetic polymers used in the application of the invention. Acrylonitrile is a petrochemical, and its decreased consumption increases the amount of petroleum that can be diverted to more urgently needed products. The instant compositions are also useful in agricultural applications for increasing water-holding capacity of soils which promotes more efficient germination of seeds and plant growth.

When the instant composition were applied as coatings onto substrates such as seeds, clay, starch, fibers, paper, or the like, a large increase in the water-holding capacity of the substrate was realized.

The organic amine salts of the invention, which absorb large amounts of aqueous-organic fluids, are useful in the formulation of jellied fuels, paint removers, and other formulations where it is desirable to have an organic solvent, containing a minimum amount of water, in an essentially solid form.

DETAILED DESCRIPTION OF THE INVENTION

In prior art methods of producing water-absorbing compositions, it was assumed that water-soluble products had to be rendered insoluble by crosslinking by the polymers, by saponifying in an aqueous-alcoholic medium, or by adjusting the pH so that the product was in an insoluble acid form. We were surprised, therefore, when we discovered a water-insoluble composition was formed by simply drying water-soluble saponified starch-polyacrylonitrile graft polymer containing starch that had been gelatinized prior to graft polymerization. We were further surprized when we found that the instant products had water absorptive capabilites which were from three to over 10 times greater than the best prior art starch graft compositions. The term "water-soluble composition" is herein defined to include apparently soluble or highly dispersed compositions.

Water-absorbing alkali salts of saponified starch-polyacrylonitrile graft polymers are disclosed in U.S. Pat. No. 3,661,815. Both the method of preparation and the resulting products disclosed therein differ from the method and compositions of the instant invention in several critical areas. It is specifically stated, for instance, in U.S. Pat. No. 3,661,815 that "carrying out the saponification in an alcohol-containing medium is an essential feature of (the) invention." Absorptive values in Table VII of U.S. Pat. No. 3,661,815 show that saponification in an alcohol-free medium results in a product having water-absorptive properties which are inferior to the product saponified in an alcohol-containing medium. It is also disclosed in U.S. Pat. No. 3,661,815 that pretreating starch in an aqueous slurry

at 60° C. before grafting was beneficial to the product while pretreatment of starch at 65° C. was detrimental, and that "tapioca and potato starch required lower pretreatment temperatures, because of their lower gelatinization temperatures."

In contrast to the teachings disclosed in U.S. Pat. No. 3,661,815, we have found that in the instant method the presence of alcohol in the saponification medium is not only unnecessary, its use results in final products having significantly lower absorptive capabilities. Two portions of GS-PAN were saponified in the presence of alcohol and in the absence of alcohol in accordance with Examples 24–26 of U.S. Pat. No. 3,661,815, and the products, which were dried in vacuo at 110° C. for 16 hr., were tested for water and synthetic urine absorptivity. Aqueous-alcohol-KOH saponification resulted in a product which absorbed 31 g./g. (i.e., grams substance absorbed per gram absorbent composition) synthetic urine and 220 g./g. water. The aqueous-KOH saponification product absorbed 53 g./g. synthetic urine and 800 g./g. water. The reason that the aqueous-alcohol-KOH saponified product prepared in accordance with Examples 24–26, U.S. Pat. No. 3,661,815 (supra), had a higher absorptive value that is shown in Table VII, U.S. Pat. No. 3,661,815, for similar products is believed to lie in the fact that our starting material was GS-PAN (i.e., a starch-polyacrylonitrile graft polymer prepared from starch which had been pretreated in aqueous slurry at temperatures above the gelatinization temperature of the starch).

It is well known that starch in the granule state is insoluble in water at ambient temperatures. It is also known that when a water suspension of unmodified starch granules is heated the granules first slowly and reversibly take up water with limited swelling and then, at a definite temperature, typically about 70° C., the granules undergo irreversibly a sudden rapid swelling. As the temperature is increased beyond about 70° C., more starch molecules diffuse from the granules until, at a temperature range of about 80° to 100° C., the starch appears to become soluble. It is an essential and critical feature of the present invention that the graft copolymerization of acrylonitrile be carried out on starch that has been pretreated by methods known to those skilled in the art so as to render it soluble. We prefer to solubilize the starch by heating an aqueous suspension of starch to about 70° to 100° C. and holding the suspension at such temperatures for about 15 min. or longer.

We are aware, also, that U.S. Pat. No. 3,425,971 (cited as a reference in U.S. Pat. No. 3,661,815) discloses water-soluble alkali salts of (nongelatinized) starch-polyacrylonitrile graft polymers and the insoluble acid form therof which is resolubilized by adjusting the pH with alkali. The alkali salt products are used as thickeners and as such must be water soluble or completely water dispersible. In U.S. Pat. No. 3,425,971 (supra) as in U.S. Pat. No. 3,661,815 (supra), there is no teaching that simply gelatinizing the starch before graft polymerizing and drying the alkali salt graft polymer after saponification would give an insoluble product with such surprisingly different properties.

Starch-polyacrylonitrile graft copolymers are well known. Fanta, *Block and Graft Copolymerization*, R. J. Ceresa, ed., John Wiley and Sons, 1973, Chapter 1, has recently reviewed the various methods for making starch graft copolymers and the influence of such variables as type of initiator used, type of pretreatment of starch, kinds of polymerization media employed, amounts of monomer used, and the like on starch copolymer composition. The preferred monomer used to prepare the instant compositions is acrylonitrile (AN), but it is herein understood that methacrylonitrile (MAN) is equivalent to the acrylonitrile monomer specified in the claims. It is contemplated that, with a minimum of experimentation, those skilled in the art will find other monomers suitable for use in accordance with the invention and that monomers so found are also considered herein to be equivalent to acrylonitrile and methacrylonitrile. Preferred molar ratios of gelatinized starch to monomer range from about 1:1.5 to 1:9.

The preferred polymerization initiator is the ceric ammonium nitrate-nitric acid system used in the examples. However, other suitable initiator systems will be known to those skilled in the art (cf. Fanta, supra).

Saponification of GS-PAN is accomplished with an alkali defined herein as being the hydroxide of an alkali metal, preferably Li^+, Na^+, or K^+, or of NH_4^+. It is an essential feature of the instant invention that the saponification step be carried out in a manner such that a water-soluble product be obtained. Preferably, GS-PAN is contacted with an aqueous solution of alkali for from 1 to 3 hr. at a temperature of about 90°. Saponification apparently takes place only on the -PAN moiety of GS-PAN, converting nitrile groups to carboxamide and carboxylate groups to form the -HPAN moiety. During saponification, GS-PAN dissolves and forms a highly viscous solution of dispersion of GS-HPAN. Water-soluble GS-HPAN compositions were obtained from saponifications in which the molar ratio of alkali to the polyacrylonitrile repeating unit (i.e., alkali:AN) ranged from 0.1:1 to 7.2:1. Alkali:AN molar ratios of from 0.6:1 to 7.2:1 are preferred.

Compositions in accordance with the invention are prepared directly from the saponification reaction mixture without previous isolation of water-soluble GS-HPAN. However, higher absorptivities are obtained from GA-HPAN compositions which are purified before drying.

Isolation of water-soluble GS-HPAN is readily accomplished after completion of the saponification step by adjusting the pH of the reaction mixture by any suitable means to about 3, thereby precipitating the water-insoluble acid form of GS-HPAN. The water-insoluble precipitate is then isolated, washed, suspended in water, and the pH readjusted by any suitable means to a pH of from about 4 to 12, thereby reforming water-soluble GS-HPAN. Alternatively, the water-insoluble absorbent form of GS-HPAN can be prepared by packing a column with the acid form of GS-HPAN and allowing gaseous NH_3 to pass up the column for a period of time sufficient to form the ammonium salt.

The absorbent form of the polymer is prepared by simply drying the solution or dispersion obtained from the saponification step. Surprisingly, when a solution or dispersion containing the water-soluble GS-HPAN is cast into a film and subsequently dried by known routing methods including oven drying, drum drying, and air drying, the resulting dry films are insoluble and absorb up to about 300 times their weight in water forming clear, cohesive, self-supporting gel sheets. The dried films, which preferably contain from 1 to 15% moisture, can be ground or milled to give flakes or powders which have greatly increased surface areas over the films. The water-insoluble character of the product is retained by the flakes and the powders, and

both forms display highly rapid uptake of fluids. The amount of fluid uptake by the flakes or powders is generally similar to amount of fluid uptake observed for the parent films. The absorbent polymer can be in the form of a mat or pad. Such forms result when the soluble form of the polymer is freeze or foam dried.

As an alternative to the drying procedures described above, the viscous mixture obtained after addition of alkali is diluted with a water-miscible organic solvent such as alcohol or acetone and the precipitated product isolated in powder form by filtration and drying.

Of particular importance is the fact that the dried GS-HPAN films are insoluble in all solvents despite the fact that no crosslinking reagents were added. Treatment with boiling water, boiling 1N potassium hydroxide, and boiling 1N hydrochloric acid failed to dissolve the instant films. The exact nature by which the polymer forms the insoluble films is not clearly understood. The insolubilization apparently takes place by some unknown mechanism when water solutions are dried at temperatures as low as room temperature or lower. The extremely mild conditions under which this insolubilization takes place are unique and unexpected. The insoluble and water-swollen graft copolymer was redispersed in water by subjecting it to high mechanical shear or to sonification. Mechanical shear was accomplished in a Waring blendor and a colloid mill. Surprisingly, if shearing has not been too extensive, this dispersion yields on drying, an absorbent, insoluble film which has properties similar to the original insoluble polymer. Even dispersions which have been subjected to the highest mechanical shear will form insoluble films if they are dried at room temperature and the dried films are then allowed to stand for from about 7 to 100 days at room temperature and high humidity, or if they are dried at 160° for from about 15 to 120 min. Insolubilization of these sheared polymers is accelerated by heat and gamma irradiation.

The absorbency of a film prepared in accordance with the invention was reduced from 600 to 100 g. water per gram of polymer by 3 megarads of gamma irradiation. Such control of film swellability can be utilized in the gel entrapment of enzymes, where a large initial swelling is desirable to allow the enzyme to penetrate into the film, but subsequent use of the film requires a lower degree of swelling to keep the enzyme trapped.

The commercial value of immobilized enzymes has been the subject of many reports in recent years. One of the more frequently used immobilization techniques has been physical entrapment. Hicks et al. [Anal. Chem. 38(6): 726–730 (1966)] describe a method of entrapping enzymes such as glucose oxidase in a polyacrylamide gel. As in most procedures which entrap enzymes within synthetic polymer matrices, it was necessary for the enzyme to be present during the polymerization of the acrylamide.

Enzymes have also been entrapped in starch gels [Bouman et al., Anal. Chem. 37: 1378 (1965)]. Enzymes were dissolved into a solution of starch and the mixture worked into a slab of polyurethane foam.

Water-insoluble GS-HPAN film was treated with an aqueous solution of glucoamylase, then treated with a solution of calcium chloride. The calcium chloride shrunk the fluid-swollen film sufficiently to entrap the enzyme, which remained active through five separate and consecutive reactions with starch. The amounts of enzyme, GS-HPAN, and calcium chloride would be different for each different enzyme, depending upon the enzyme's molecular size and desired activity. Therefore, the inventive method should not be limited to any particular enzyme or to any specific ratios of enzyme to water-absorbent GS-HPAN. Since the method simply involves the absorption of a solution of the desired enzyme by the water-absorbent film, it would be easy for one skilled in the art to perform a few experiments to determine the necessary amount of all components

Any soluble mineral salt is suitable for shrinking the gel after it has absorbed the enzyme solution.

Immobilized amylase enzymes were prepared by two methods. One, an α-amylase, was covalently bonded to the instant water-absorbent compositions, and the other, a glucoamylase, was absorbed according to the method described above. It was surprising when we discovered that in neither immobilizing enzyme composition did the amylase degrade the starch moiety of the GS-HPAN, even though these enzymes are well-known degraders of starch.

The absorbent polymers of the present invention may be extended by mixing dispersions of water-soluble GS-HPAN with dispersions of inexpensive natural polymers, or their derivatives, and then drying the resulting mixtures Examples of such natural polymers are flour, guar, gelatin, starch, or dextrin.

An important application of dried water-insoluble GS-HPAN is the reduction of the water content of emulsions, suspensions, and dispersions. Milk containing 27.4% milk solids was treated with the water-absorbent composition in amounts such that the ratio of absorbent to water was about 1:100. The resulting filtrate, which was still a milk emulsion, contained 39.4% milk solids. It will be understood that milk solids include minerals, protein, and butterfat. Linseed oil-in-water emulsions containing 9.5% and 52.3% oil were concentrated to emulsions containing 12.3% and 57.9% oil, respectively, when treated with dried films of the absorbent compositions in amounts such that the ratios of absorbent to water were about 0.1:90 and 1:100, respectively. The numerous emulsions known to those skilled in the art will require varying amounts of the water-absorbent compositions of the instant invention to accomplish the desired amounts of concentration. However, optimum amounts of absorbent for each emulsion can be easily determined by a few simple trial experiments. Preferably, amounts of the instant absorbent composition to water contained in emulsions was from 0.1 to 1 part of absorbent to 100 parts of water (by weight).

Aqueous dispersions or suspensions such as sewage sludge can be beneficially treated by addition of the instant water-absorbent composition so that the use of settling ponds can be reduced or eliminated. Sewage sludge containing 3.9% solids was dewatered to the extent that the solids content was increased by 25% by the addition of 0.5 g. of absorbent to 100 ml. of sludge. When the same sewage sludge was treated with 1 part of absorbent to 100 ml. of sludge, the resulting fluid mass was too thick to pass through the 40-mesh sieve used to separate the gelled water-absorbing composition from concentrated sludge.

Although the fluid mass could be separated by other means, it is preferred that the instant compositions be added to the sludge at a rate of about 0.1 to 0.5 part absorbent per 100 ml. of water (by weight).

It was found that adding the water-absorbent composition to the sewage sludge at a rate of at least 2 parts absorbent per 100 parts water provided a crumbly-solid material which cannot be pumped but can be handled by mechanical means including shovels, scoops, end loaders, and conveyors. It can be carried in wheelbarrows and trucks, and can be dispersed on field by means of manure spreaders and the like. Theoretically, there is no upper limit to the amount of absorbent which can be combined with sewage sludge. However, for economic reasons, the preferred range of addition is from 2 to 10 parts absorbent per 100 parts water.

Thin films of water-insoluble GS-HPAN greatly increase the water-holding capacity of many substrates. Since prior art absorbent compositions require cross-linking reactions or saponifications in the presence of alcohol to make them insoluble, it would be very difficult to coat substrates with them in order to increase the water-absorptive abilities of the substrates. The instant absorptive compositions, on the other hand, can be easily obtained as coatings on any water-insoluble substrate by merely drying solution of water-soluble GS-HPAN while the solutions are in contact with the desired substrate. Examples of such substrates include silica, clay, animal litter or bedding, granular starch, cellulose fibers, cloth, and paper. The preferred amount of dry saponified starch-polyacrylonitrile is 0.5 to 3%, based on the dry weight of substrate.

Starch granules coated with water-absorbent GS-HPAN show a viscosity rise at a lower temperature than untreated starch when heated in water. Also, final viscosities after heating 90° C. are higher than that shown by untreated starch. In the manufacture of paper or mineral board, coated starches are retained better than untreated starch when added at the wet end along with a cationic retention aid.

Seeds may be coated with saponified starch-polyacrylonitrile and subsequently dried. Water content in the vicinity of the seed during germination would thus be maximized. Also, dry GS-HPAN, in powder or flake form, may be blended with soil. In an arid climate, such a blend will hold a higher percentage of water for longer periods than untreated soil. The instant compositions are also useful as soil conditioners. Silt-type soils are composed of fine particles which pack together to form almost impenetrable surfaces, increasing water runoff and greatly adding to erosion and pollution problems. Many polyelectrolyte materials have been used to aggregate soil particles so that the soil would allow water to penetrate, thereby minimizing water runoff.

Dispersions of water-soluble GS-HPAN were added to silt-loam soils in amounts of from 0.3 to 0.9 part GS-HPAN to 100 parts soil and the resulting soil allowed to dry, leaving a coating of water-absorbent compositions on the soil particles. These coated soils and uncoated control soils were then evaluated according to the soil conditioner testing method of R. M. Hedrick [J. Agr. Food Chem. 2(4): 182–185 (1954)]. Up to 96% of the soils coated with the instant compositions formed aggregates which would not pass a 20-mesh screen while 100% of untreated soil passed through 60-mesh screens.

By adding seeds to a dispersion or solution of saponified starch-polyacrylonitrile, casting and drying a film from the resulting mixture, the seeds are immobilized in a water-swellable film for use in gardening or farming.

Nutrients such as nitrates, lime, etc. can be added to the water-soluble GS-HPAN solution before casting the film, or they can be added as a solution to the seed containing water-absorbent film. Seeds thus immobilized can be planted in strips, or the film can be broken up and the seeds planted in a more conventional manner. Ground or powdered materials such as iron can be added to the slurry of seeds and water-soluble GS-HPAN before casting the seed-ladened film in order to give the immobilized seed sufficient weight to minimize its being washed away. The use of iron in the film allows handling by means of magnets.

The form of the polymer, which will absorb large quantities of aqueous-organic fluids where the organic material is the principle component, is prepared by first isolating the acid form from the saponification reaction mixture as described above and reacting it with a suitable organic amine in quantities such that the reaction mixture has a pH of from 5 to 11. The resulting thick solutions or dispersions of the organic-amine salts of GS-HPAN are then dried to yield insoluble films which will absorb organic fluids containing minimal amounts of water. Examples of suitable organic amines include primary amines such as methyl-, ethyl-, hexyl-, dodecyl-, benzyl-, chlorobenzyl-, and ethanolamines; secondary and tertiary analogs of the same; aniline; cyclohexylamine and pyridine. Other suitable amines will be known to those skilled in the art.

The following examples are intended only to further illustrate the invention which is defined by the claims.

All percentages mentioned herein are by weight unless otherwise specified.

EXAMPLES 1–8

A. Preparation of GS-HPAN

Stirred slurries consisting of 5 to 10% by weight starch in water were heated for 30 min. at the designated temperature, Table 1, and cooled under a nitrogen atmosphere to 27° C. To each stirred mixture was added 0.1 molar ceric ammonium nitrate solution in 1N nitric acid (see Table 1). After 10 min., acrylonitrile was added and the mixture stirred for 3 hr. at 35° C. The starch-polyacrylonitrile graft copolymer was isolated by filtration and dried, Table 1.

B. Preparation of water-insoluble acid form of GS-HPAN

The GS-PAN compositions from Examples 1A-8A were slurried in water and varying amounts of sodium or potassium hydroxide added, Table 2. The mixtures were stirred at 90° C. until the orange-red color, which formed on initial heating with alkali, had disappeared. The smooth, light yellow dispersions were diluted to 5% solids, cooled to room temperature, and sulfuric acid added to give a pH of 3.2. The water-insoluble acid form, which precipitated on acidification, was isolated by centrifugation and washed successively with water, 5:1 methanol-acetone, and acetone. The product was finally isolated by filtration and dried at 25° C., Table 2.

Table 1

Example	Starch variety	GS, g.	AN, g.	H_2O, ml.	Ce^{+4}, mmoles	Starch pretreat temp., °C	Reaction time, hr.	Yield, g.	GS:PAN mole ratio
1A	Corn	25.0	15.0	400	1.5	95	3	38.3	1:1.6
2A	Corn	37.4	40.0	600	1.9	55	3	60.0	1:2.4
3A	Corn	27.0	31.8	480	1.5	88	17	57.0	1:3.3
4A	Waxy sorghum	27.0	31.8	480	1.5	88	17	57.0	1:3.3
5A	Wheat	42.4	61.6	400	1.5	85	3	71.0	1:3.5
6A	Waxy corn	42.0	61.5	400	1.5	90	3	87.0	1:3.8
7A	Wheat	28.8	75.5	400	1.4	85	3	90.0	1:5.7
8A	Corn	25.5	75.0	400	1.5	95	3	97.0	1:8.6

Table 2

Example	GS-PAN (from Part A) Amount, g.	Conc. in H_2O, wt. %	Alkali	Alkali:PAN molar ratio	Reaction Temp., °C.	Reaction time. hr.	GS-HPAN water-insol., acid form Yield, g.	% N
1B	15	6.12	NaOH	1.3:1	92	3.0	—	—
2B	60	3.0	NaOH	1.3:1	90	3.0	—	—
3B	50	6.25	NaOH	1.3:1	95	3.0	37	4.2
4B	50	6.25	NaOH	1.3:1	95	1.5	41	4.3
5B	32	3.2	KOH	2.7:1	100	1.5	—	5.5
6B	33	4.4	KOH	1:1	100	2.5	32	—
7B	10	4.0	KOH	7.2:1	80	2.0	—	6.5
8B	12	4.6	NaOH	1.3:1	92	3.0	—	—

C. Preparation of water-insoluble GS-HPAN absorbent compositions

To prepare the absorbent polymer, 5 g. of the water-insoluble acid form of GS-HPAN selected from Examples 1B–8B were sifted into 500 ml. of rapidly stirred water, and high-speed stirring was continued for 30 sec. The pH of the dispersion was adjusted to 6–9 by addition of 1N potassium, sodium, or ammonium hydroxide. Some of the resulting viscous solutions were then spread on trays and dried at 25°–35° C. to yield a continuous film of absorbent polymer; others, after tray drying, were coarsely ground to a flake-like material.

Still other solutions of the water-soluble GS-HPAN compositions were drum dried using a drum temperature of about 132° C. This product was also coarsely ground.

To rapidly evaluate water absorbency of the dry, particulate products, 0.25 g. of the now water-insoluble GS-HPAN absorbent polymer was sifted into 500 ml. of distilled water and allowed to soak for 30 min. The mixture, containing swollen polymer and excess water, was then poured onto a 40-mesh sieve held in a funnel leading to a graduated cylinder. The unabsorbed water was collected and measured, and the grams of fluid absorbed per gram of dry polymer were calculated.

A similar procedure was followed to determine the absorption of an electrolyte solution simulating urine (simulated urine: 97.09% distilled water, 1.94% urea, 0.80% NaCl, 0.11% $MgSO_4.7H_2O$, 0.06% $CaCl_2$). One gram of absorber is soaked for 30 min. in 100 ml. of simulated urine, poured through a 60-mesh sieve, and the excess urine collected and measured.

The procedure used with 0.9% sodium chloride solution was identical to that used with synthetic urine.

See Table 3.

Table 3

Example	Alkali[1]	Method of drying	Absorbency of insol. GS-HPAN: Water, g./g.[2]	Synthetic urine, g./g.[2]	0.9% NaCl solution, g./g.[2]
1C	NaOH	tray	320	34	—
2C	NaOH	tray	160	30	—
2C	NaOH	drum	189	34	—
3C-1	KOH	drum	896	—	60
3C-2	KOH	tray	648	54	—
3C-3	NH_4OH	tray	725	53	—
3C-4	NaOH	tray	711	61	—
4C	KOH	drum	1000	60	—
5C	KOH	tray	1150	—	115
7C	KOH	tray	1040	—	140
8C	NaOH	tray	973	74	—
Cellulose (control)	—	—		34	—

[1]Alkali used to adjust pH of GS-HPAN.
[2]g./g. = grams of absorbed substance per gram absorbent composition.

EXAMPLE 9

Absorbents for aqueous-organic fluids are prepared by reacting saponified starch-polyacrylonitrile in the acid form with an organic amine.

Ten grams of the acid form of GS-HPAN of Example 3B were sifted into 1 liter of water, and 4 ml. of triethylamine were added to the stirred mixture. The resulting thick dispersion was spread onto a tray and allowed to dry at 25°–35° C. The resulting continuous film was then coarsely ground and tested for absorbency as

described in Examples 1–8. One gram of this polymer absorbed 48 g. of simulated urine, 80 g. of 80:20 (by volume) ethanol:water and 87 g of 40:40:20 (by volume) acetone:methanol:water.

EXAMPLE 10

A stirred slurry of 135 g. of wheat starch in 2400 ml. of water was heated for 30 min. at 85°–90° C. and then cooled under a nitrogen atmosphere to 25° C. To the stirred mixture were added 75 g. of 0.1 molar ceric ammonium nitrate solution in 1N nitric acid. After 10 min., 159 g. of flash-distilled acrylonitrile were added and the mixture stirred for 3 hr. at 35° C.

The mixture was diluted with water, sodium hydroxide was added in varied amounts, and the mixture was heated to temperatures of 95°–150° C., Table 4. An autoclave was used for temperatures over 100° C. The resulting water-soluble GS-HPAN compositions were shown by infrared analysis to be substantially the same as the composition prepared in accordance with Examples 1–8.

Table 4

Conc. of GS-PAN in water, %	NaOH:PAN mole ratio	Reaction temp., °C.	Reaction time, hr.
4.7	0.85:1	95	3.0
2.4	0.85:1	95	3.0
2.4	0.6:1	95	3.0
2.4	0.4:1	95	3.0
2.4	0.4:1	125	3.0
4.7	0.2:1	150	1.5
6.0	0.4:1	150	—
4.7	0.1:1	150	—

EXAMPLE 11

A particularly convenient method of obtaining the absorbent polymer in particulate form is to loosely pack a column with the acid from of GS-HPAN and then pass gaseous ammonia up through the column for 15 min. Infrared analysis shows conversion from the carboxyl to the carboxylate form. See Table 5.

EXAMPLE 12

The wide pH range which may be used to prepare the absorbent polymer is shown in Table 6. The water-insoluble acidic polymer of Example 3B was neutralized with potassium hydroxide to the pH's given in the table and the dispersions then dried and ground as in Example 1C.

EXAMPLE 13

The following procedure illustrates prior isolation of the starch-polyacrylonitrile graft copolymer is unnecessary.

Table 5

Acid form of GS-HPAN (Example)	Absorbency: Water per polymer, g./g.	Absorbency: Synthetic urine per polymer, g./g.	Absorbency: 0.9% NaCl solution per polymer, g./g.
3B	1300	80	—
4B	960	52	50

Table 6

pH Before drying	Absorbency: Water per polymer, g./g.	Absorbency: 0.9% NaCl solution per polymer, g./g.
4.0	450	—
4.8	820	60
6.45	960	80
7.85	920	100
11.3	580	80
12.0	340	60

A slurry of 33.2 g. of waxy corn starch in 600 ml. of distilled water was stirred and heated at 90° C. for 30 min. and then cooled to 25° C. under nitrogen. To the stirred mixture was added 18.7 g. of 0.1 molar ceric ammonium nitrate in 1N nitric acid. After the mixture was stirred for 10 min., 40 g. of acrylonitrile were added. The reaction mixture was stirred for 3 hr. at 35° C. and then heated to 90° C. A solution of 25 g. of sodium hydroxide in 600 ml. of water was added, and stirring at 90° C. was continued for 3 hour. The thick, clear dispersion was diluted to 5% solids and cooled to room temperature. The pH was adjusted to 3.2 by addition of 28g. of sulfuric acid. The acid form of GS-HPAN was separated by centrifugation, washed with 1 liter of water, and finally dewatered with 5:1 methanol:acetone and dried. The yield was 64 g.

The absorbent form of the copolymer (i.e., water-insoluble GS-HPAN) was prepared by neutralizing with potassium hydroxide, tray drying, and coarse grinding as in Examples 1–8. This composition absorbed 795 times its weight of water at 25° C. and 59 times its weight of synthetic urine.

The procedure was repeated with the exception that 37.4 g. of waxy corn starch, 80 g. of acrylonitrile, and 44 g. of NaOH (i.e., 0.75 mole NaOH per mole PAN) were used. The absorbent form, prepared as above, absorbed 1480 times it weight of water and 87 times its weight of synthetic urine.

EXAMPLE 14

The following procedure illustrates the preparation of water-insoluble GS-HPAN with no intermediate isolation steps.

Preparation of the starch-polyacrylonitrile graft copolymer and its reaction with sodium hydroxide were carried out as in Example 13 with 37.4 g. waxy corn starch, 40 g. acrylonitrile, and 25 g. NaOH. The thick, clear dispersion was diluted to 5% solids and drum dried directly without acidification using a drum temperature of 132° C. The yield was 96 g. The dry product was crushed and passed through a coarse screen. This polymer absorbed 280 times its weight of water at 25° C. and 56 times its weight of synthetic urine.

The above procedure was repeated except that the thick, clear dispersion was drum dried at 13% solids and gave a comparable product.

The above procedure was again repeated with the exception that 37.4 g. waxy corn starch, 80 g. acrylonitrile, and 36 g. NaOH (i.e., 0.6 mol. NaOH per mole PAN) were used. The absorbent form, prepared as above, absorbed 425 times it own weight of water and 50 times its weight synthetic urine.

EXAMPLE 15

The rapidity with which these polymer will absorb aqueous fluids is shown in Table 7 for the absorbent composition of Example 3C-2 which was tray dried.

EXAMPLE 16

As an estimate of the absorbency of these polymers under pressure, the compositions of Example 15 containing 648 g./g. water and 54 g./g. urine was centrifuged at 45 and 180 × gravity. It is apparent from Table 8 that this polymer loses only a small percentage of its absorbed fluid under pressure, as compared with cellulose.

EXAMPLE 17

The useful absorptive properties of these polymers are not confined only to synthetic electrolyte solutions or to water.

The composition of Example 3C-2 absorbed 40 times its weight of pork liver blood, 100 times its weight of human urine, more than 300 times its weight of water at 75° C., and more than 300 times its weight of water at 0° C.

EXAMPLE 18

A 2-cm. square of absorbent polymer film, prepared from the tray-dried product of Example 3C-2 weighed 0.03 g. and had a thickness of 0.009 cm. When placed in a tray of distilled water, the film imbibed water immediately, and after 10 min. had swelled to an 11.5-cm. square weighing 9.2 g., which is an absorbence of 300 g./g. When the pH was adjusted to 2.3 with hydrochloric acid, the film shank back to a 2-cm. square and showed rubberlike elasticity. When the surrounding liquid was replaced first with potassium hydroxide solution (pH 11), then with distilled water, and finally with hydrochloric acid solution (pH 2.3), the respective dimensions of the squares were 7.5, 12, and 2 cm. This cycling of expansion and shrinkage with pH adjustment was repeated three times. Each time the dimensional changes were the same, and apparently the film will undergo extensions and contractions repeatedly.

Table 7

Time, sec.	Absorbency: Water per polymer, g./g.	Absorbency: Synthetic urine per polymer, g./g.
30	365	—
60	410	39
180	538	—
300	570	46
600	616	49
1800	648	54
3600	—	54

Table 8

	Fluid per polymer, g./g.		
	No pressure	45 X g.	180 X g.
Cellulose fibers			
Water	40	2.1	1.05
Synthetic urine	32	1.8	1.0
Polymer of Example 15			
Water	648	409	—
Synthetic urine	54	40	37

EXAMPLE 19

Another useful form of the absorbent copolymer is the sponge-like mat which is obtained when the viscous mixture of Example 4B, after addition of alkali to pH 6–9, is freeze dried. Such a freeze-dried product absorbed more than 400 times its weight in water.

EXAMPLE 20

The following examples show that efficient absorbents for aqueous fluids may be prepared by mixing water-soluble GS-HPAN with inexpensive extenders and drying the resulting mixtures.

Five-gram samples of the water-insoluble acid form of GS-HPAN of Example 3B were sifted into 500 ml. of water and the pH adjusted to 7-9 with potassium hydroxide solution. Dispersions of 5 g. of the extenders in 500 ml. of water were prepared separately. Heat was applied to the extender dispersions when necessary to obtain a smooth dispersion. The two dispersions were mixed and the final dispersion either spread onto a tray and allowed to dry at 25°–35° C. in a forced air oven, or drum dried at about 130°. The resulting continuous film was coarsely ground, Table 9.

EXAMPLE 21

A thinned dispersion is obtained by subjecting dispersions of water-soluble GS-HPAN to high shear conditions, such as sonification, colloid milling, or Waring blending. Excessive shearing will drastically reduce the viscosity of an aqueous dispersion.

Table 9

Extender	Ratio of GS-HPAN to extender	Method of drying	Absorbency: Water per absorbent, g./g.	Absorbency: Synthetic urine per absorbent, g./g.
Flour	50:50	drum	334	32
Guar	50:50	drum	373	38
Acid-modified flour	33:67	drum	370	22
Acid-modified flour	50:50	drum	386	28
Guar	50:50	tray	448	53
Gelatin	42:58	tray	458	34
Hydroxyethyl flour	50:50	tray	444	40
Control	100:0	tray	648	54
Control	100:0	drum	896	60

A 1-liter 1% dispersion of water-soluble GS-HPAN from Example 3C-2 was sonified at 20 kHz for about 1 hr. which reduced the viscosity of the dispersion from

30,000 cp. to 30 cp. Films prepared by drying the 30-cp. solution at room temperature are soluble and will dissolve in water giving a viscosity near 30 cp.

The soluble films were irradiated with gamma rays from a Cobalt 60 source for a period of time sufficient to obtain total radiation dosages of from 0 to 4 megarads, which resulted in products which were water insoluble and highly absorbent, Table 10.

Table 10

Radiation dose, megarad	Absorbency of ground film, water per polymer, g./g.
0	none (polymer is sol.)
1	570
2	245
3	165
4	125

Saponified starch-polyacrylonitrile can thus be applied to a substrate in the from of a nonviscous aqueous solution and then converted to the absorber form after drying.

EXAMPLE 22

Soluble films were prepared in the manner described in Example 21 and converted to the insoluble, highly absorbent form by heating in a vacuum oven at 160° C. for from 0 to 150 min., Table 11.

Table 11

Time at 160° C., min.	Absorbency of ground film, water per polymer g./g.
0	none (polymer is sol.)
30	2000
60	1200
90	700
120	400
150	240

EXAMPLE 23

Soluble films were prepared in the manner described in Example 21 and converted to the insoluble, highly absorbent form by merely standing at normal room temperature (25° C.) at a range of relative humidities. After 105 days at room temperature and 43% relative humidity, 90% of the film was still soluble while 10% was converted to an insoluble gel. After 7 days at room temperature and 93% relative humidity, over 70% of the film was an insoluble gel which absorbed 600 g. water per gram of polymer. After 100 days at room temperature and 93% relative humidity, over 90% of the film was an insoluble gel which absorbed 400 g. water per gram of polymer.

EXAMPLE 24

If the insoluble, highly absorbent form GS-HPAN is allowed to swell in water and the swollen polymer subjected to mechanical shear, smooth dispersions are obtained which, on further shearing, are converted to low viscosity solutions.

One part, by weight, of polymer film, prepared from the product of Example 3C-4, was swollen in 99 parts of water and then a 10-ml. sample was subjected to sonification at 20 kHz for 5 min. until a clear solution was obtained with a viscosity of 30 cp. On drying at room temperature, a film was obtained which behaved the same as that of Example 21. This film was converted to the insoluble, highly absorbent form by the methods described in Example 21, 22 or 23.

EXAMPLE 25

Various substrates were slurried in 1% by weight dispersions of water-soluble GS-HPAN prepared as described in Example 3C-4 prior to drying.

The mixtures were dried at 25° to 75° C. in a forced air oven and slurried in 2.5 g. of water per gram of absorbent-coated substrate. The volume of supernatant was measured after the mixture had settled and was subtracted from the original volume to give the volume of water absorbed, Table 12.

EXAMPLE 26

A thin film of GS-HPAN may be dried down onto cellulose or paper to greatly increase its water-holding capacity.

A 1% GS-HPAN dispersion was prepared as described in Example 25. This dispersion (Brookfield viscosity: 2980 c.p.s.) was treated for a total of 12 min. in a Branson Sonifier set at maximum output of ultrasound. This treatment reduced the Brookfield viscosity to 80 c.p.s. and thus gave a dispersion which more rapidly penetrated the substrate. Circles of Whatman No. 1 filter paper were soaked for 30 sec. in the dispersion, the excess dispersion was removed by passing through rolls, and the filter papers were dried at 25° C. in a forced air oven. Water-insoluble (GS-HPAN) content of the dried papers was 1.66%. Papers containing water-insoluble GS-HPAN absorbed 3.27 times their weight of deionized water, as compared with 2.55 for untreated papers.

Table 12

Substrate	% Water-soluble GS-HPAN on substrate, by wt.	Drying temp., ° C.	Absorption, ml. water/g. substrate: Substrate with absorbent	Absorption, ml. water/g. substrate: Substrate with no absorbent
Celite	3.0	25	2.5	1.1[1]
Cat litter	1.0	75	2.0	—
	2.0	75	2.5	1.2
Wheat starch	0.5	25	1.8	1.1
	1.0	25	2.1	1.1
	2.0	25	2.5	1.1

[1]Approximate value due to incomplete settling.

EXAMPLE 27

Finely divided inorganic substrates coated with a thin film of GS-HPAN are not only good absorbents for animal wastes but also help reduce the accompanying objectionable odors.

A portion of cattle feedlot waste, obtained from a soluble fraction by freeze drying, was dissolved in water

to give a 1% solution. Twenty-five milliliters of the resulting waste solution were absorbed into 10 g. of the GS-HPAN treated celite of Example 25. After the mixture had stood in a stoppered bottle for several days, microorganism growth was observed, and the highly objectionable odor was no longer evident. Only a mild, musty odor of mold remained.

EXAMPLE 28

When the water-insoluble GS-HPAN coated starches prepared in Example 25 are heated in water, they show a viscosity rise at a lower temperature than untreated starch. Also, final viscosities after heating at 90° C. are higher than those shown by untreated starch.

These properties are shown by heating 8% by weight water dispersions in a Brabender Amylograph at 75 r.p.m. using a 350-g. cartridge and a heating rate of 1.5° C. per minute. Mixtures were heated from 25° to 90° C. over a 43-min. period, held at 90° C. for 17 min., and then cooled back to 25° over a 43-min. period. Results are shown in Table 13.

EXAMPLE 29

The absorbent polymer films act as metal ion-exchangers.

Table 13

% H-SPAN on starch	Mixture shows measurable viscosity: Minutes	Temp., ° C.	Viscosity at 90° C., Brabender units	Viscosity at end of run, 25° C., Brabender units
0.0 (control)	36	79	550	2280
0.5	25	62	950	2930
1.0	22	58	1600	2980
2.0	20	55	2480	3930

A 20.5-mg. sample of dry film prepared as described in Example 3C-2 was placed into 100 ml. of tap water for 10 min., after which the unabsorbed water was removed and reserved. The water-soaked film was then placed in a second 100 ml. volume of tap water for 1 hr., after which the water was again removed and reserved. This procedure was repeated once more leaving the film to soak for 3 hr. The reserved water and the film were analyzed for K^+ and Mg^+ by atomic absorption. The water lost 0.068 mmoles of Mg^{+2} and gained 0.066 mmoles of K^+.

EXAMPLE 30

This example shows the utility of absorbent polymers prepared in accordance with the invention for concentrating of dewatering aqueous emulsions or dispersions.

Portions of the dried absorbent product of Example 3C-2 were added as ground flakes or as film to various emulsions which were then stirred and allowed to stand at 25° C. The mixtures were then poured through a 40-mesh sieve, the filtrate collected, and the percent solids determined, Table 14.

Table 14

Emulsion or dispersion: Description	% Solids	Amount	GS-HPAN: Wt., g.	Form	Standing time, min.	% Solids in filtrate
Milk, 2% butterfat	27.4	100 ml.	1.0	flakes	60	39.4
Sewage sludge	3.9	50 ml.	1.0	flakes	—	—[1]
Sewage sludge	3.9	100 ml.	1.0	flakes	40	—[2]
Sewage sludge	3.9	100 ml.	0.5	film	45	4.8
Oil in water	52.3[3]	100 g.	0.5	film	30	57.9[3]
Oil in water	9.5[3]	100 g.	0.1	film	30	12.3[3]

[1]Became a crumbly solid on addition of GS-HPAN.
[2]Was too thick to filter.
[3]Content of linseed oil.

EXAMPLE 31

Films of GS-HPAN serve as insoluble supports for enzymes, and enzymes are readily covalently bonded to the support.

A 0.25-g. sample of tray-dried film prepared as described in Example 3C-2 was added to 10 ml. of a 5% solution of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide and 5 ml. of stock H.T-1000 α-amylase solution, prepared by making a 10% solution and then filtering. The film was allowed to swell for 30 min. and 10 ml. of 1% calcium chloride solution were added. The film, which shrank considerably, was transferred to fresh calcium chloride solution and finally to distilled water. Gradual swelling of the film was observed on standing in water for 1 wk. Water was finally decanted off, and the film reshrunk with 1% calcium chloride.

Enzyme activity was tested by reacting the film, containing the bound enzyme, with a 1% starch solution in 1% calcium chloride. The film was placed in a Petri dish and 10 ml. of the starch solution added. Incubation was for 1 hr. at 40° C., and iodine solution was used to test for unreacted starch. The solution was then tested for reducing sugar by the ferricyanide procedure.

The film was then washed with 1% calcium chloride solution, and the procedure was repeated with a fresh starch solution. The procedure was performed a total of three times, and the results are shown in Table 15.

Table 15

Trial	Starch-iodine color	Reducing sugar, (as glucose), mg. per 100 ml.
1	colorless	114
2	colorless	121
3	slight blue	78

EXAMPLE 32

Enzymes may be rendered insoluble by entrapment in swollen water-insoluble films of GS-HPAN. A 0.25-

g. sample of tray-dried film, prepared as described in Example 3C-2, was swollen in 10 ml. of water containing glucoamylase enzyme having approximately 160 glucoamylase units. The film absorbed all of the solution. A 10-ml. portion of 1% calcium chloride solution was added to shrink the film, and the resulting film was then washed several times to remove untrapped enzyme.

Activity of the film was tested by placing it in a Petri dish and adding 5 ml. of a 1% starch solution in 1% calcium chloride at pH 6.5. Five different starch solutions were used consecutively, and after incubation, solutions were tested for reducing sugar by the ferricyanide procedure, Table 16.

Table 16

Trial	Reducing sugar, (as glucose), mg. per 100 ml.
1	288
2	214
4	340
5	520

EXAMPLE 33

Addition of the absorbent polymer to soil decreases water loss due to evaporation.

Three grams of water-insoluble GS-HPAN, prepared as described in Example 3C-2, were blended with 300 g. of white sand in a small container (weight: 17 g.) and five bean seeds were planted. Similar plantings were made in sand containing 3.0 g., 1.5 g., 0.75 g., and 0 g. of absorbent polymer. Water was added to each container to bring the total weight to 400 g. Containers were allowed to stand at room temperature overnight, weighed to determine water content, and water was added on the 2nd, 5th, 6th, 7th, and 9th days to bring the total weight to 400 g. Percentages of the original water remaining after standing are shown in Table 17. A high percentage of all the bean seeds germinated.

Table 17

Day	Days standing without adding water	% Original water remaining Grams absorbent polymer per 300 g. sand 0	0.75	1.5	3.0
1	0	100	100	100	100
2	1	63	68	70	70
5	3	0	11	10	9
6	1	65	67	65	64
7	1	60	65	69	68
8	1	63	66	70	70
9	2	26	46	49	47
12	3	10	29	28	29

EXAMPLE 34

When dispersions of water-soluble GS-HPAN are added to soil, they act as soil conditioners to stabilize small dirt clods against disintegration in heavy rains, and thus minimize excessive soil packing and the resulting problems of water runoff.

One hundred grams of Miami silt loam were wetted with a combination of 1 ml. of 1% calcium acetate and 30 ml. of a 3% dispersion of water-soluble GS-HPAN, prepared as described in Example 25. Using a method for evaluating soil conditioners described by R. M. Hedrick [J. Agr. Food Chem. 2: 182 (1954)], the wet cake was pressed through a screen with 4.76-mm. openings, and the resulting crumbs were dried in a forced air oven at 60° C. Forty grams of the dry crumb were placed on a 20-mesh sieve which was then agitated gently in water for 30 min. At the end of this time, over 96% of the crumb was retained on the sieve, as compared to 0% for a control crumb which was prepared in the absence of polymer.

When the experiment was repeated with 30 ml. of a 0.09% dispersion of water-soluble GS-HPAN, 20% of the crumbs was retained on the 40-mesh screen. The remainder passed through.

EXAMPLE 35

When seeds are slurried in a dispersion of water-soluble GS-HPAN and the resulting slurry spread in a tray and allowed to dry, a continuous film of insoluble GS-HPAN containing entrapped seeds is obtained. This system is ideally suited to hydroponic gardening, since addition of an aqueous nutrient solution to the film yields a highly swollen gel containing entrapped and completely immobilized seeds.

A 1% saponified starch-polyacrylonitrile dispersion was prepared from the product of Example 3B by adding potassium hydroxide to pH 6–9. Marigold seeds were added, and the resulting dispersion was spread onto a tray and allowed to dry at room temperature. A hydroponic nutrient mixture was prepared from the following components: potassium nitrate (16.49%), ammonium sulfate (4.80%, potassium sulfate (42.22%, calcium dehydrogen phosphate (14.44%, calcium sulfate (16.06%), magnesium sulfate (5.98%). One tablespoon of this mixture was dissolved in 1 gal. of water, and the resulting solution was added to the film containing the entrapped seeds. Swelling of the film was observed, and the seeds germinated.

This experiment was repeated with petunia seeds, and germination of the seeds was again observed.

We claim:

1. Aqueous fluid-absorbing compositions comprising water-insoluble alkali salts of aqueous alkali saponified gelatinized-starch-polyacrylonitrile graft polymers containing gelatinized starch (GS) and saponified polyacrylonitrile (HPAN) in molar ratios of from about 1:1.5 to 1:9 GS:HPAN, said water-insoluble alkali salts of aqueous alkali saponified gelatinized-starch-polyacrylonitrile graft polymers being further characterized as water-insoluble solids capable of absorbing in excess of 300 parts of water by weight per part of said water-insoluble solids.

2. Aqueous fluid-absorbing compositions as described in claim **1** wherein the insoluble alkali salts of aqueous alkali saponified gelatinized-starch-polyacrylonitrile graft polymers are further characterized as water-insoluble solids capable of absorbing from about 300 to 1500 parts by weight per part of said water-insoluble solids.

3. Aqueous fluid-absorbing compositions as described in claim **1** wherein the gelatinized starch contained therein is wheat starch, corn starch, waxy corn starch, or waxy sorghum starch.

4. A method of preparing water-insoluble aqueous fluid-absorbing compositions comprising the following steps:

a. saponifying a gelatinized-starch-polyacrylonitrile graft polymer (GS-PAN) in an aqueous slurry with an alkali in amounts such that the molar ratio of alkali to the acrylonitrile repeating unit of said GS-PAN is from about 0.1:1 to 7:1 to form a water-soluble saponified GS-PAN (water-soluble GS-HPAN); and

b. optionally adjusting the pH of said water-soluble GS-HPAN to about 3, followed by isolating the resulting water-insoluble acid form of GS-HPAN, and readjusting the pH of said water-insoluble acid form of GS-HPAN to from about 4 to 12 to reform said water-soluble GS-HPAN; and

c. drying said water-soluble GS-HPAN to a moisture level of from about 1 to 15% water by weight.

5. A method of preparing water-insoluble aqueous fluid-absorbing compositions as described in claim **4** wherein the molar ratio of alkali to the acrylonitrile repeating unit of said GS-PAN is from about 0.6:1 to 7:1.

6. A method of preparing water-insoluble aqueous fluid-absorbing compositions as described in claim **4** wherein the GS-PAN is prepared by the method comprising the steps of:

a. gelatinizing starch (GS) in an aqueous suspension at a temperature of from 80° to 100° C. for at least 15 min.; and

b. graft polymerizing the gelatinized starch resulting from step (a) with acrylonitrile (AN) or methacrylonitrile (MAN) in amounts such that the molar ratio of GS to AN or MAN is from about 1:1.5 to 1:9, said graft polymerizing taking place in the presence of a suitable polymerization initiator.

7. A method of preparing water-insoluble aqueous fluid-absorbing compositions as described in claim **6** wherein the starch is wheat starch, corn starch, waxy corn starch, or waxy sorghum starch.

8. A method of preparing insoluble aqueous-organic fluid-absorbing compositions comprising the steps of:

a. saponifying a gelatinized-starch-polyacrylonitrile graft polymer (GS-PAN) in an aqueous slurry with an alkali in amounts such that the molar ratio of alkali to acrylonitrile repeating units of said GS-PAN is from about 0.1:1 to 7:1 to form a water-soluble saponified GS-PAN (water-soluble GS-HPAN);

b. adjusting the pH of said water-soluble GS-HPAN to about 3, followed by isolating the resulting water-insoluble acid form of GS-HPAN;

c. reacting said water-insoluble acid form of GS-HPAN in an aqueous slurry with an organic amine in amounts such that the pH of the reaction mixture is from 5 to 11; and

d. drying the product of step (c) to a moisture content of about 1 to 15% water by weight.

9. A method of preparing insoluble aqueous-organic fluid-absorbing compositions as described in claim **8** wherein the organic amine is methyl-, ethyl-, hexyl-, dodecyl-, benzyl-, chlorobenzyl-, or ethanolamine, secondary or tertiary analogs of the same, aniline, cyclohexylamine, or pyridine.

10. A method of preparing a low viscosity aqueous dispersion of a water-soluble saponified gelatinized-starch-polyacrylonitrile graft polymer capable of forming a water-insoluble aqueous, fluid-absorbing composition comprising the steps of:

a. saponifying a gelatinized-starch-polyacrylonitrile graft polymer (GS-PAN) in an aqueous slurry with an alkali in amounts such that the molar ratio of alkali to the acrylonitrile repeating unit of said GS-PAN is from about 0.0:1 to 7:1 to form a water-soluble saponified GS-PAN (water-soluble GS-HPAN); and

b. optionally adjusting the pH of said water-soluble GS-HPAN to about 3, followed by isolating the resulting water-insoluble acid form of GS-HPAN, and readjusting the pH of said water-insoluble acid form of GS-HPAN to form about 4 to 12 to reform said water-soluble GS-HPAN; and

c. sonifying a 1% by weight aqueous dispersion of said water-soluble GS-HPAN at a sonifying frequency and for a time sufficient to reduce the viscosity of said dispersion to about 30 cp.

11. A method of preparing water-insoluble aqueous fluid-absorbing compositions comprising drying a low viscosity aqueous dispersion of a water-soluble saponified gelatinized-starch-polyacrylonitrile graft polymer prepared as described in claim **10** at a temperature of about 160° C. for from about 15 to 120 min.

12. A method of preparing water-insoluble aqueous fluid-absorbing compositions comprising drying a low viscosity aqueous dispersion of a water-soluble saponified gelatinized-starch-polyacrylonitrile graft polymer prepared as described in claim **10** at a temperature of about 25° C. for from about 7 days in a humid atmosphere having about 90% relative humidity to about 100 days in a humid atmosphere having from 43 to 90% relative humidity.

13. A method of increasing the water absorbency of water-insoluble substrates comprising the steps of:

a. saponifying a gelatinized-starch-polyacrylonitrile graft polymer (GS-PAN) in an aqueous slurry with an alkali in amounts such that the molar ratio of alkali to the acrylonitrile repeating unit of said GS-PAN is from about 0.1:1 to 7:1 to form a water-soluble saponified GS-PAN (water-soluble GS-HPAN); and

b. optionally adjusting the pH of said water-soluble GS-HPAN to about 3, followed by isolating the resulting water-insoluble acid form of GS-HPAN, and readjusting the pH of said water-insoluble acid form of GS-HPAN to from about 4 to 12 to reform said water-soluble GS-HPAN; and

c. mixing said water-soluble GS-HPAN in an aqueous slurry of a water-insoluble substrate; and

d. drying the mixture resulting from step (c) to a moisture content of 1 to 15% water by weight.

14. A method of increasing the water absorbency of water-insoluble substrates as described in claim **13** wherein the water-insoluble substrate is diatomaceous silica, clay, animal litter or bedding, granular starch, cellulose fibers, paper, or cloth.

15. Water-absorbent substrates prepared as described in claim **14.**

* * * * *

United States Patent [19]

Flesher et al.

[11] **Patent Number: 4,506,062**

[45] **Date of Patent: Mar. 19, 1985**

[54] **INVERSE SUSPENSION POLYMERIZATION PROCESS**

[75] Inventors: **Peter Flesher; Adrian S. Allen,** both of Bradford, England

[73] Assignee: **Allied Colloids Limited,** Bradford, England

[21] Appl. No.: **519,610**

[22] Filed: **Aug. 2, 1983**

[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **526/211;** 526/219; 526/222; 526/225; 526/209; 526/213; 526/216; 526/220

[58] **Field of Search** 526/211, 193, 219, 222, 526/225, 201

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,772,310	11/1956	Morris	526/217
3,484,375	12/1969	Guziak	526/193
3,763,120	10/1973	Atkins	526/201
3,857,824	12/1974	Atkins	526/217
4,166,152	8/1979	Baker et al.	526/201

FOREIGN PATENT DOCUMENTS

0004062	6/1979	European Pat. Off.	526/193
5778937	5/1972	Japan	526/193
50-98990	8/1975	Japan	526/211
56-135501	10/1981	Japan	526/201
57-74308	5/1982	Japan	526/201
58-52302	3/1983	Japan	526/209
1133328	11/1968	United Kingdom	526/201
1482515	8/1977	United Kingdom	526/211

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Assistant Examiner—Peter F. Kulkosky
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[57] **ABSTRACT**

A reverse phase suspension polymerization process conducted using an ionic polymerizable material and a polymerization stabilizer of opposite ionic or potentially ionic charge is modified by including also a water soluble, substantially oil insoluble, ionic non-polymerizable compound having the same charge type as the polymerizable material and having at least one alkyl group containing at least 6 carbon atoms.

9 Claims, No Drawings

INVERSE SUSPENSION POLYMERIZATION PROCESS

It is known to make a dispersion of aqueous particles of water soluble polymer in a non-aqueous liquid by forming a dispersion in the non-aqueous liquid of droplets of aqueous monomer in the presence of emulsifier and/or stabiliser and then polymerising the monomer. This is called reverse phase polymerisation. If the polymerisation occurs primarily within the monomer droplets the polymerisation is called a reverse phase suspension polymerisation. If monomer migrates from the droplets into micelles of emulsifier in the non-aqueous liquid and polymerises in the micelles then the process is a reverse phase emulsion polymerisation process. Early disclosures of such processes are to be found in, for instance, U.S. Pat. Nos. 2,982,749 and 3,284,393.

This invention is concerned particularly with problems that arise during reverse phase suspension polymerisation. This is normally conducted using a polymeric suspension stabiliser, for instance, a copolymer of hydrophilic and hydrophobic groups and which is soluble or dispersible in the non-aqueous liquid and is substantially insoluble and non-dispersible in water, for instance, as described in British Patent Specification No. 1,482,515. A small amount of an oil soluble surfactant may be included to facilitate the formation or the maintenance of the suspension.

It is well known that certain problems of reproducability arise when the monomer includes ionic monomer, for instance, when co-monomer solutions of acrylamide and quaternary ammonium derivatives or inorganic acid salts of dimethylaminoethyl acrylate or methacrylate and comonomer solutions of acrylamide and acrylic acid or its sodium or ammonium salts are subjected to reverse phase suspension polymerisation. In particular it can be difficult to obtain reproducibly particles having the desired spherical shape and having a narrow size distribution. Irregular particle shape and wide particle size distribution are undesirable for a number of reasons. Spherical and uniform particle size is then particularly desirable in order to avoid settlement of the larger particles and variation in the viscosity of the final dispersions. If the dispersion contains a large amount of particularly fine particles then it will have a much higher viscosity than would otherwise be the case, and this can be very undesirable. If the particle size range is particularly wide then there is increased risk of coagulation occurring during polymerisation or during subsequent treatment of the resultant dispersion.

It has been our object to devise a process that permits closer control of the particle shape and size distribution.

A reverse phase suspension polymerisation process according to the invention is one in which an aqueous solution of polymerisable material is dispersed as droplets in a water immiscible liquid containing a suspension polymerisation stabiliser and the polymerisable material is polymerised in the droplets to form a dispersion in the non-aqueous liquid of aqueous polymer droplets and in which the stabiliser is ionic or potentially ionic, the polymerisable material comprises polymerisable material that is ionic with a charge type opposite to that of the stabiliser and the dispersion of the said aqueous solution of polymerisable material into the water immiscible liquid is conducted in the presence of a water soluble, substantially oil insoluble, ionic, non-polymerisable compound having the same charge type as the ionic polymerisable material and containing at least one alkyl group of at least 6 carbon atoms.

We have surprisingly found that the inclusion of these defined water soluble polar, ionic, organic compounds prior to droplet formation gives greatly improved control over particle size distribution and over particle shape and eliminates or minimises the risk of aggregation or coagulation compared to the use of suspension polymerisation stabilisers alone.

It might have been expected that combination of the ionic (or potentially ionic) polymerisation stabiliser with the oppositely charged ionic additive would result in less efficient stabilisation, perhaps due to neutralisation of the charges in the stabiliser. It is also surprising that these particular water soluble ionic additives give improved results in the defined water-in-oil system since some of them are often used to promote the formation and stabilisation of oil-in-water dispersions.

It seems that the surprising results obtainable in the invention may be interpreted as being due to the formation of a stable interionic complex that is a more effective polymerisation stabiliser than the conventional stabiliser used alone. This complex, if it exists, presumably is a complex between the water soluble ionic additive and the conventional polymerisation stabiliser and is presumably formed at the interface of the aqueous particles, initially of monomer but eventually of polymer gel. However, we do not wish to be bound by theory.

The invention is of particular value in the production of high molecular weight, water soluble homopolymers of quaternary ammonium derivatives or inorganic acid salts of dialkylaminoalkyl-acrylates or -methacrylates, dialkylaminoalkyl-acrylamides, their copolymers with acrylamide, and homopolymers of acrylic acid and its sodium or ammonium salts and their copolymers with acrylamide. The polymerisable material that is used for forming the aqueous solution is therefore preferably the monomer or blend of monomers necessary for forming such polymers and in particular the ionic polymerisable material is preferably an inorganic salt or quaternary ammonium salt of a dialkylaminoalkyl-acrylate or is acrylic acid. Other known anionic or cationic monomers of ethylenically unsaturated compounds may be used.

The continuous phase for these suspension polymerisations is a liquid which is immiscible with the aqueous monomer and may include aliphatic or aromatic hydrocarbons, chlorinated hydrocarbons, higher alkyl glceride esters or any suitable liquid or liquid mixture known in the art. The preferred continuous phase is a liquid aliphatic hydrocarbon or mixture of aliphatic hydrocarbons. However, other additional liquids may be used at some stage of the process to provide benficial properties particularly to dispersions of small polymer particles in liquids.

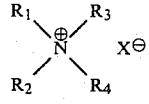
The reverse phase suspension polymerisation stabiliser is required to prevent or minimise the agglomeration of particles during the course of polymerisation. Suitable materials are well known and include copolymers of hydrophobic monomers with hydrophilic monomers which are soluble or dispersible in liquids of low polarity. The preferred stabilisers are either completely soluble or form fine dispersions in the continuous phase but are substantially insoluble in the monomer solution and do not form micelles in the continuous phase. These are typified by copolymers of alkyl acrylates or methacrylates with acrylic or methacrylic acid and copolymers

of alkyl acrylates or methacrylates with dimalkyl amino alkyl-(generally dimethyl aminoethyl-)acrylate methacrylate or quaternary ammonium or acid salt derivatives of these amino monomers. The most suitable of these are copolymers of alkyl methacrylates, where the alkyl group is a linear hydrocarbon of 12–18 carbon atoms, with methacrylic acid or trimethyl-β-methacryloxyethyl-ammonium chloride and terpolymers with methyl methacrylate and hydroxyethylacrylate. Suitable materials are described in British Patent Specification No. 1,482,515.

The amount of suspension polymerisation stabiliser used is dependent on the size range of polymer particles required because at least a mono-layer adsorbed at the interface between the aqueous polymer particle and the continuous phase is required to minimise the degree of agglomeration and coagulation during polymerisation. As the polymer particle size is decreased, the interfacial area is increased and therefore a higher concentration of stabiliser is required. Generally, for the production of large particles (in the size range 50 to 1000 microns) the amount of stabiliser used is from 0.01 to 0.5%, preferably 0.03 to 0.2%, on weight of the aqueous polymer particles. For small particles in the size range 0.2 to 5 microns 0.05 to 10%, preferably 0.5 to 5%, based on the weight of aqueous polymer particles is used. The particle size is selected within the preferred range of 0.2 to 1000 microns by appropriate choice of the degree of agitation, and is also dependent on the stabiliser and other materials used.

The choice of stabiliser used is dependent on the particular homo-polymer or copolymer being manufactured. The stabilisers for polymers containing acrylic acid or its sodium salt are cationic and those for polymers containing dimethylaminoethyl-acrylate or its salts or quaternary ammonium derivatives are anionic.

When the monomer is cationic the ionic additive should also be cationic and suitable additives are compounds of the formula



where

R_1=C_6–C_{18} alkyl and C_{8-18} alkyl substituted benzyl

R_2=H, CH_3, benzyl or, if R_1 is C_6–C_{12} alkyl, C_2–C_{12} alkyl

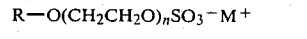
R_3 and R_4=H, CH_3, benzyl or $(CH_2CH_2O)_nCH_2CH_2OH$ where n=0–15

x is an anion derived from quaternisation or salt formation, for example, chloride, bromide, sulphate, methosulphate, ethosulphate, acetate and phosphate.

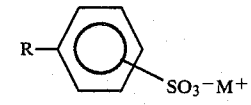
R_1 preferably contains at least 10 carbon atoms and generally should contain at least 12 carbon atoms.

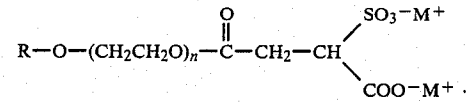
Preferred materials are triamylmethyl-ammonium methosulphate, decyl dimethyl-ammonium methosulphate, coco-trimethyl-ammonium chloride, 1-hydroxyethyl 1-methyl 2-dodecyl imidazolinium chloride and caprylamidopropyl trimethylammonium methosulphate.

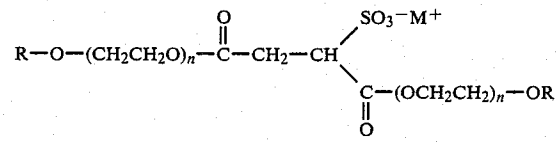
When the monomer is anionic, suitable anionic additives for use in the invention are compounds of the formulae

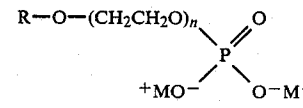


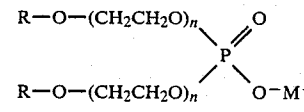
-continued











where

R=C_6–C_{18} alkyl or alkyl substituted benzene

n=0–15

M=Na, K, Li, NH_4 or a lower aliphatic amine or hydroxyethyl amine.

Particularly preferred compounds are sodium 2-ethylhexyl sulphate, sodium isodecyl sulphate, sodium lauryl sulphate and disodium dodecyl sulphosuccinate.

Any polar ionic organic compound which is soluble in the aqueous monomer but insoluble in the continuous phase, in combination with a counterionic suspension polymerisation stabiliser and which promotes the formation of uniform shaped spherical polymer particles with a narrow particle size distribution and does not cause inversion or destabilisation of the phases prior to or during polymerisation, can be used.

The amount of the polar ionic organic compound used depends on the chemical type, the polymer particle size range being produced and the amount and type of counterionic suspension polymerisation stabiliser used. Generally, the amount used will lie within the range 0.003% to 0.1% preferably 0.005 to 0.05% by weight of aqueous monomer for particle sizes in the range 50 to 1000 microns in diameter where from 0.01% to 0.5% by weight on weight of aqueous monomer of suspension polymerisation stabiliser is used, and within the range of 0.02% to 5.0% preferably 0.2 to 2% by weight on weight of aqueous monomer for particle sizes in the range 0.2 to 5 microns in diameter where from 0.05% to 10% by weight of aqueous monomer of suspension polymerisation stabiliser is used. The ratio by weight of stabiliser:ionic additive is often in the range 1:0.03 to 1, but preferably is above 1:0.08.

Preferably the amount of polar ionic organic additive is such that it does not neutralise all the charges on the suspension stabiliser, since if too much of the ionic organic additive is included there is a danger of phase reversal or coagulation. Experimentation will show the

desired proportion of ionic additive:stabiliser. Generally, the amount of ionic additive is such as to neutralise from 20 to 95%, most preferably 40 to 80% of the ionic groups of the stabiliser. However, when the additive and the monomer are anionic it is possible to obtain satisfactory results with greater amounts of the additive, for instance in amounts greater than the amounts required to neutralise all the ionic groups of the stabiliser. Thus, satisfactory results are obtained, without coagulation, when the amount of sodium lauryl sulphate or other anionic additive is a large excess over the stoichiometric amount required to neutralise the ionic groups of the stabiliser.

We find generally that the ionic additives having chain lengths of 12 carbon atoms or more are preferred in many instances but that additives having shorter chain lengths are suitable in some processes, especially when the suspension has a relatively high concentration of ionic monomer. For instance, when the polymerisable material is 70% sodium acrylate and 30% acrylamide satisfactory results are achievable with ionic additives having alkyl chain lengths as low as 8 carbon atoms or even as low as 6 carbon atoms, whilst when the amount of sodium acrylate is reduced to 40% it is desirable to increase the chain length in the alkyl group of the additive, for instance to 10, and preferably to 12 carbon atoms or more.

The water soluble polar ionic compound must not polymerise and must be substantially insoluble in the non-aqueous continuous phase. If it was substantially soluble in that phase there would be a tendency for micelles to form and for a reverse phase emulsion polymerisation to occur. This is known to cause the formation of very small polymer particles, for instance below 0.2 microns.

The kinetics of the polymerisation process of the invention are typical of solution or suspension polymerisations and are characterised by the fact that the polymer particle size distribution and shape are totally dependent upon the initial size range and shape of the droplets. This is in contrast to emulsion polymerisation kinetics where the size range is independent of initial droplet size. Emulsion polymerisation kinetics results in the production of a product in the form of an emulsion having a viscosity which is liable to be very much higher than the viscosities obtained in the invention even when the suspension contains a high polymer concentration.

The ionic additive is preferably included in the aqueous solution of polymerisable material before that is dispersed into the water immiscible liquid. However, it may sometimes be possible to introduce the additive to the non-aqueous phase separately from the aqueous solution, for instance prior to or simultaneously with the dispersion of the aqueous solution into the non-aqueous phase.

Polymerisation of the monomer solution droplets may be effected by any of the techniques commonly used to polymerise water soluble ethylenic unsaturated monomers such as the use of free radical yielding initiators in the absence of oxygen. Typical are redox couples such as potassium bromate with sulphur dioxide, tert-butyl hydroperoxide with ferrous complexes of oligoethylene oligoamines and thermal initiators such as potassium persulphate, 2,2'-azobis(2-amidinopropane) hydrochloride or 2,2'-azobiscyanoualeric acid. The preferred free radical yielding initiators are those which are soluble in the aqueous monomer solution.

Photoinitiation, X-ray or γ-ray initiation procedures may also be acceptable techniques for producing radicals in the droplets.

The process is generally conducted in the absence of emulsifying agent.

By the process described in this invention large polymer particles of narrow particle size distribution within the range 50 to 1000 microns in diameter but preferably 100 to 500 microns in diameter having a regular spherical shape can be made. The polymer gel particles so formed can be dehydrated by azeotropic evaporation followed by any suitable solid-liquid separation process, such as filtration, to yield substantially dry, dust free polymer beads which have outstanding physical properties. These can be readily dissolved in water by adding the beads to agitated water to give solutions of polymer.

Smaller regular spherical polymer particles can be made by the described process having narrow particle size distributions within the range 0.2 to 5 microns in diameter but preferably 0.2 to 2 microns in diameter. Polymer gel particles of this size are not generally isolated as solids due to their tendency to easily form dust clouds, their tendency to form agglomerates on contact with water and their very low bulk densities. It is more useful for such polymer gel particles to be formulated as free flowing liquid dispersions in non-aqueous liquid. Such liquid dispersions of gel particles can be prepared by the techniques described in this invention containing up to 40% polymer on a dry basis by weight. Additionally the dispersions may be azeotropically dehydrated to give liquid dispersions in oil containing up to 70% dry polymer by weight. The low viscosity and high active polymer content of these dispersions render them most economic and easy to use. In all azeotropic evaporation processes for the dehydration of polymer gel particles there is a great risk of coagulation and agglomeration of the particles taking place. An important feature of the invention is that the combination of water soluble polar organic compound with the water insoluble suspension stabiliser imparts improved stability of the suspension during azeotropic evaporation of the water content and prevents the coagulation and agglomeration of the polymer particles.

The described dispersions of either hydrated or dehydrated polymer may be rapidly converted to aqueous polymer solutions by addition of the dispersion to water with appropriate agitation. Additionally, suitable oil in water emulsifiers may be added to the dispersions to render the continuous phase more readily dispersible in water thereby more easily releasing the polymer particles into the water to form an aqueous polymer solution.

EXAMPLE 1

An aqueous monomer solution comprising acrylamide (46.8 grams), trimethyl-β-acryloxyethylammonium chloride (80.3 gms), tetrasodium ethylenediaminetetraacetate (0.03 gms), potassium bromate (0.032 gms) and water (81.2 gms) was prepared and the pH of the solution adjusted to 4.0.

A non-aqueous continuous phase was prepared comprising Shell SBP11 (300 gms) and a 1:3 molar ratio copolymer of ceto-stearyl methacrylate and methacrylic acid as stabiliser (0.02 gms).

The continuous phase was transferred to a 700 ml capacity resin pot and deoxygenated by bubbling nitrogen gas through the liquid via a gas diffusion tube whilst

stirring with a small bladed propeller type stirrer at 1000 r.p.m.

The monomer solution was then added to the agitated continuous phase and allowed to disperse for 3 minutes during which time the temperature of the suspension was adjusted to 25° C. The suspension was then initiated by introducing a solution of SO_2 in SBP11 (6.5 mls of 1% wt./vol. solution).

When the exothermic reaction was completed, water was azeotroped off the suspension under reduced pressure at 80° to 90° C. The resulting suspension of polymer beads was cooled to 25° C. filtered and the beads finally dried using a fluid bed drier for 30 minutes at 80° C.

The polymer beads produced had a particle size distribution ranging from 200 microns to 2500 microns and more than 70% of the particles were grossly misshapen oblate spheroids.

EXAMPLE 2

The same recipe and procedure used in Example 1 was used except coco-trimethylammonium methosulphate (0.02 gms) was added to the monomer solution prior to suspension in the hydrocarbon continuous phase.

The polymer beads produced had a particle size distribution ranging from 200 microns to 750 microns and less than 5% of the particles were misshapen showing a very marked improvement in properties compared to beads produced in the absence of coco-trimethylammonium methosulphate as given in Example 1.

EXAMPLE 3

An aqueous monomer solution comprising acrylamide (98 gms), trimethyl-β-acryloxyethylammonium chloride (70 gms), penta-sodium diethylenetriamine pentaacetate (0.2 gms) and water (212 gms) were prepared and the pH of the solution adjusted to 4.8.

A non-aqueous continuous phase comprising Solvent Pale 60 oil (115.6 gms), Shell SBP11 (150 gms) and a 2:1 molar ratio copolymer of ceto-stearyl methacrylate and methacrylic acid as stabiliser (11.4 gms) was prepared.

The suspension was produced by adding the aqueous monomer solution to the hydrocarbon continuous phase with high shear mixing using a Silverson type L2R laboratory mixer. Mixing was continued for 15 minutes and then the temperature of the suspension was adjusted to 20° C.

The suspension was transferred to a 700 ml resin pot and deoxygenated using nitrogen gas flowing at 200 mls per minute through a gas distribution tube immersed in the suspension. The nitrogen flow was continued for 30 minutes with the suspension agitated throughout using a four blade propeller type stirrer revolving at 1000 r.p.m. Tertiary-butyl hydroperoxide was then added (0.00255 gms) followed by sodium sulphite (0.002 gms) dissolved in water (6 gms) added continuously over a period of 40 minutes to effect polymerisation.

The resulting polymer gel suspension was then distilled under reduced pressure up to a temperature of 95° C. to remove water and volatile hydrocarbons to prepare a dispersion of polymer in oil containing 0.8% by weight of water and 54.8% by weight of polymer on a dry basis.

EXAMPLES 4–10

Polymer dispersions were prepared by the method given in Example 3 using various amounts of stabiliser in the continuous phase and various amounts of coco-trimethylammonium methosulphate (CTMAM) added to the aqueous monomer solution prior to dispersion.

Example No.	Weight of Stabiliser used (gms)	Wt. of CTMAM used (gms)
4	11.4	0.38
5	11.4	0.95
6	11.4	1.90
7	11.4	3.80
8	5.7	1.71
9	3.8	0.76
10	0	3.80

Polymer dispersions were obtained in Examples 4–9. No polymer dispersion was obtained for Example 10 since in the absence of stabiliser an oil in aqueous monomer solution dispersion was formed which on polymerisation formed a gel with droplets of oil dispersed therein.

EXAMPLE 11

Samples of the dispersions from Examples 3–9 were centrifuged at 1,250 g for 30 minutes as an accelerated settlement test and the degree of settlement determined by weighing the sediment.

Example No.	Concentration of Stabiliser (% on weight of aqueous monomer droplets)	Concentration of CTMAM (% on weight of aqueous monomer droplets)	Solids separated on centrifuge (% of total solids)
3	3	0	66.2
4	3	0.1	61.0
5	3	0.25	47.0
6	3	0.5	33.0
7	3	1.0	18.0
8	1.5	0.45	47.4
9	1.0	0.20	57.6

EXAMPLE 12

Samples of the dispersions from Examples 3–9 were examined under an electron microscope and particle size range assessed and particle shape observed.

Particle size ranges of dispersions prepared with both stabiliser and CTMAM were narrower than the dispersion prepared with stabiliser alone which contained a large proportion of both large and small particles.

EXAMPLE 13

Viscosities at 20° C. at the polymer dispersions from Examples 3–9 were obtained from samples both prior to and after distillation using a Brookfield RVT Viscometer at 20 rpm. These were compared to viscosities of products made by emulsion polymerisation as in U.S. Pat. No. 3,284,393 using the same recipe and procedure given in Example 3 except various amounts (recorded as % based on weight of an aqueous monomer) of Span 80 (Sorbitan monooleate, an oil soluble low HLB water-in-oil emulsifier) were incorporated in the oil phase prior to dispersion of the aqueous monomer solution. An amount of Solvent Pale 60 oil corresponding to the amount of Span 80 used was substracted from that used in Example 3 to maintain the same concentration of polymer on a dry basis as that in the dispersion of Examples 3 to 9.

	Before Distillation		After Distillation	
	Solids Content (%)	Viscosity (cps)	Solids Content (%)	Viscosity (cps)
Dispersion				
Example 3	25.6	25	54.8	80
Example 4	25.6	25	54.7	80
Example 5	25.6	27	54.3	84
Example 6	25.6	32	54.6	104
Example 7	25.6	40	54.8	128
Example 8	25.6	30	54.3	82
Example 9	25.6	25	54.5	80
Emulsion (amount of Span 80)				
5	25.6	125	50.0	175
7	25.6	1363	50.0	2025
9	25.6	2000	50.0	2875
12	25.6	4500	50.0	4400
15	25.6	5600	50.0	5575

The high viscosity obtained by emulsion polymerisation is undesirable.

EXAMPLE 14

An aqueous monomer solution comprising acrylamide (82.4 gms), sodium acrylate (35.2 gms), pentasodium diethylenetriamine pentaacetate (0.45 gms) and water (166.1 gms) was prepared and the pH of the solution adjusted to 7.0.

A non-aqueous continuous phase comprising Solvent Pale 60 oil (115.4 gms), Shell SBP11 (107.3 gms) and a 6:1 molar ratio copolymer of ceto-stearyl methacrylate and trimethyl-β-methacryloxy-ethylammonium methosulphate as stabiliser (13.2 gms) was prepared.

The suspension was produced by the same method given in Example 3 and was polymerised by adding tertiarybutyl hydroperoxide (0.007 gms) followed by sulphur dioxide (0.005 gms) dissolved in Shell SBP11 (6 mls) added continuously over a period of 20 minutes. The resulting polymer gel suspension was then distilled in the same manner as that of Example 3.

EXAMPLE 15

A polymer dispersion was prepared by the method given in Example 14 but sodium lauryl sulphate (SLS) (5.7 gms) was dissolved in the aqueous monomer solution prior to formation of the suspension.

EXAMPLE 16

Samples of the dispersions from Examples 14 and 15 were centrifuged at 1,250 g for 30 minutes and the degree of settlement determined by weighing the sediment.

Example No.	Concentration of stabiliser (% on wt. of aqueous monomer droplets)	Concentration of SLS (% on weight of aqueous monomer solution)	Solids separated (% of total solids)
14	3.0	0	93.7
15	3.0	2.0	17.0

EXAMPLE 17

Acrylamide/sodium acrylate copolymer dispersions were prepared according to the method given in Example 14 but various water soluble anionic surfactants were added to the aqueous monomer solution prior to formation of the suspension. The concentration at each anionic compound added was 2% by weight on weight of aqueous monomer solution. The distilled dispersions and dilutions of them with SBP11 were centrifuged at 1250 g for 30 minutes to determine their settlement stability.

	Dispersion at 50% solids in Pale Oil 60 (PO60)		Dispersion at 40% solids in 67/33 PO60/SBP11 w/w		Dispersion at 25% solids in 33/67 PO60/SBP11 w/w	
Additive	% Settlement	Viscosity (cps)	% Settlement	Viscosity (cps)	% Settlement	Viscosity (cps)
None	7.8	395	25.4	75	118.6	11
A	10.9	275	15.7	70	106.5	10
B	5.2	335	15.1	75	109.9	11
C	4.2	195	11.2	75	103.7	9
D	2.5	375	4.4	80	64.2	11
E	2.5	290	9.5	75	98.6	10
F	8.6	280	17.7	75	108	10
G	7.5	300	12.2	75	100.4	10

A — lauryl ether (4 moles ethylene oxide) sulphate sodium salt
B — di-octyl sulphosuccinate sodium salt.
C — dodecyl benzene sulphonic acid sodium salt.
D — sesqui-phosphate ester of 2 mole ethoxylated tridecanol sodium salt.
E — di-hexyl sulphosuccinate sodium salt.
F — sodium octanoate.
G — 50/50 w/w blend of sodium 2-ethylhexyl sulphate and sodium methyl isobutyl carbinol sulphate.

EXAMPLE 18

Acrylamide/trimethyl-B-acryloxyethammonium chloride copolymer dispersions were prepared by the method given in Example 3 using various water soluble cationic surfactants as additives to the aqueous monomer solution prior to formation of the suspension. The distilled dispersions and dilutions of them with SBP11 were centrifuged at 1,250 g for 30 minutes to determine their settlement stability.

Additive	Concentration of additive % on weight of aqueous monomer solution	Dispersion at 50% solids in Pale Oil 60 (PO60)		40% solids in 67/33 - PO60/ SBP11 w/w		Dispersion at 25% solids in 33/67 -PO60/ SBP11 w/w	
		% Settlement	Viscosity (cps)	% Settlement	Viscosity (cps)	% Settlement	Viscosity (cps)
None	—	7.4	245	52.9	60	138.4	10
H	0.5	3.8	395	21.1	75	118.1	10
I	0.5	3.4	465	25.1	80	123.7	10
J	0.5			24.1	80		
	1.0			13.3	85		
K	1			16.9	80		
L	1			16.8	80		
M	0.5			29.6	75		
N	0.5	6.0	180	42.7	40	120.1	10
O	1.0	5.6	395	30.7	70	133.8	10

-continued

Additive	Concentration of additive % on weight of aqueous monomer solution	Dispersion at 50% solids in Pale Oil 60 (PO60) % Settlement	Viscosity (cps)	40% solids in 67/33 - PO60/ SBP11 w/w % Settlement	Viscosity (cps)	Dispersion at 25% solids in 33/67 -PO60/ SBP11 w/w % Settlement	Viscosity (cps)
P	0.6	8.6	320	18.9	55	88.7	10

H — Octyl trimethylammonium chloride
I — Decyl trimethylammonium chloride
J — Dodecyl trimethylammonium chloride
K — Hexadecyl trimethylammonium chloride
L — Octadecyl trimethylammonium chloride
M — Di-dodecyl dimethylammonium chloride
N — Dodecyl benzyl trimethyl ammonium chloride
O — 15 mole ethoxylate of tallow amine quaternised with benzyl chloride
P — Coco- dimethyl amine hydrochloride

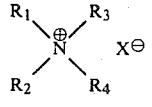
Viscosity is affected by factors other than the ionic additive and does not affect settlement stability. The meaningful results therefore are those where the systems have been diluted sufficiently for the effect of variations in viscosity to be small or minimal. Examples 17 and 18 thus show that additives D,E, J and P are particularly effective and that all the additives give a useful improvement.

We claim:

1. A reverse phase suspension polymerisation process in which an aqueous solution of polymerisable material is dispersed as droplets in a water immiscible liquid containing a suspension polymerisation stabiliser and the polymerisable material is polymerised in the droplets to form a dispersion in the non-aqueous liquid of aqueous polymer droplets and in which the stabilizer is ionic or potentially ionic, the polymerisable material comprises polymerisable material that is ionic having a charge type opposite to that of the stabiliser; characterised in that the dispersion of the said aqueous solution of polymerisable material into the water immiscible liquid is conducted in the presence of a water soluble, substantially oil insoluble, non-polymerisable polar ionic organic compound, which is cationic or anionic having the same charge type as the polymerisable material and having at least one alkyl group containing at least 6 carbon atoms, said polar organic compound being added to the aqueous solution of polymerisable material prior to droplet formation, and said suspension stabiliser is a copolymer of hydrophilic and hydrophobic monomers.

2. A process according to claim **1**, in which the said polar organic compound is a cationic compound containing an alkyl group of at least 6 carbon atoms and is present in an amount insufficient to neutralise the ionic groups of the stabiliser.

3. A process according to claim **1**, in which the said polar organic compound is a compound of the formula



where

R_1 = C_6-C_{18} alkyl and C_{8-18} alkyl substituted benzyl

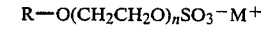
R_2 = H, CH_3, benzyl or, if R_1 is C_6-C_{12} alkyl, C_2-C_{12} alkyl

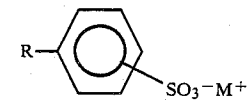
R_3 and R_4 = H, CH_3, benzyl or $(CH_2CH_2O)_nCH_2CH_2OH$ where n = 0-15

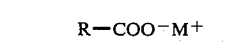
x is an anion derived from quaternisation or salt formation.

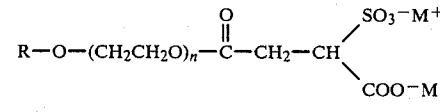
4. A process according to claim **1**, in which the said polar organic compound is selected from dodecyltrimethylammonium chloride, coco-dimethylamine hydrochloride and coco-trimethyl-ammonium chloride, and the polymerisable material is cationic.

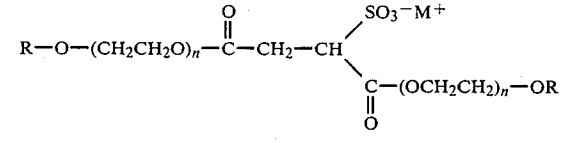
5. A process according to claim **1**, in which the said polar organic compound is a compound selected from compounds of the formulae

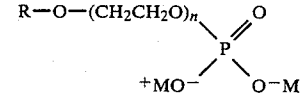


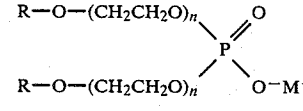












where

R = C_6-C_{18} alkyl or alkyl substituted benzene

n = 0-15

M = Na, K, Li, NH_4 or a lower aliphatic amine or hydroxyethyl amine.

6. A process according to claim **1**, in which the said polar organic compound is selected from sodium 2-ethylhexyl sulphate, sodium isodecyl sulphate, sodium lauryl sulphate and disodium dodecyl sulphosuccinate, sesquiphosphate esters of ethoxylated tridecanol sodium salts and di-hexyl sulphosuccinate sodium salt.

7. A process according to claim 1, in which the ionic polymerisable material is selected from quaternary ammonium and inorganic salts of dialkylaminoethylacrylates, dialkylaminoethyl-methacrylates, and acrylic acid.

8. A process according to claim 1 comprising the subsequent step of removing water from the droplets by subjecting the dispersion to azeotropic distillation.

9. A process according to claim 1, in which the suspension stabiliser is a copolymer of an alkyl acrylate or methacrylate with either acrylic or methacrylic acid or a dialkylamino-alkyl-acrylate, methacrylate or quaternary ammonium or inorganic salt thereof.

* * * * *

US008596255B2

(12) **United States Patent**
Meggs

(10) **Patent No.: US 8,596,255 B2**
(45) **Date of Patent: Dec. 3, 2013**

(54) **SUPER ABSORBENT POLYMER PROJECTILE LAUNCHING DEVICE**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 78 days.

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USPC **124/65**; 124/45; 124/56

(58) **Field of Classification Search**
USPC 124/1, 17, 63, 79, 16, 56, 45
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

71,162	A	11/1867	Hall	
1,202,227	A *	10/1916	Sandifur	474/81
3,408,997	A *	11/1968	De Ruymbecke et al.	124/27
3,472,218	A *	10/1969	Mers	124/67
3,631,555	A *	1/1972	Hurst et al.	15/3.5
4,834,059	A *	5/1989	Moorhouse et al.	124/67
5,285,765	A *	2/1994	Lee	124/50
5,415,151	A	5/1995	Fusi et al.	
5,622,159	A *	4/1997	Liu et al.	124/66
5,697,179	A *	12/1997	Vanmoor	42/87
6,386,293	B1	5/2002	Bartlett	
7,004,813	B2	2/2006	Zuloff	
2004/0104533	A1 *	6/2004	Larson et al.	273/404
2004/0212151	A1 *	10/2004	Peiten et al.	273/404
2009/0145412	A1	6/2009	Barish	
2010/0059237	A1 *	3/2010	Cordani	169/54
2011/0271940	A1 *	11/2011	Meggs et al.	124/56
2011/0271941	A1 *	11/2011	Meggs	124/65
2012/0152221	A1 *	6/2012	Meggs	124/41.1

FOREIGN PATENT DOCUMENTS

EP	2 253 375	A1	11/2010
GB	316645		8/1929

OTHER PUBLICATIONS

International Search Report and Written Opinion for Corresponding PCT Application No. PCT/US2011066307 dated Apr. 24, 2012.
International Search Report and Written Opinion for Corresponding PCT Application No. PCT/US2011/035801 dated Oct. 19, 2011.

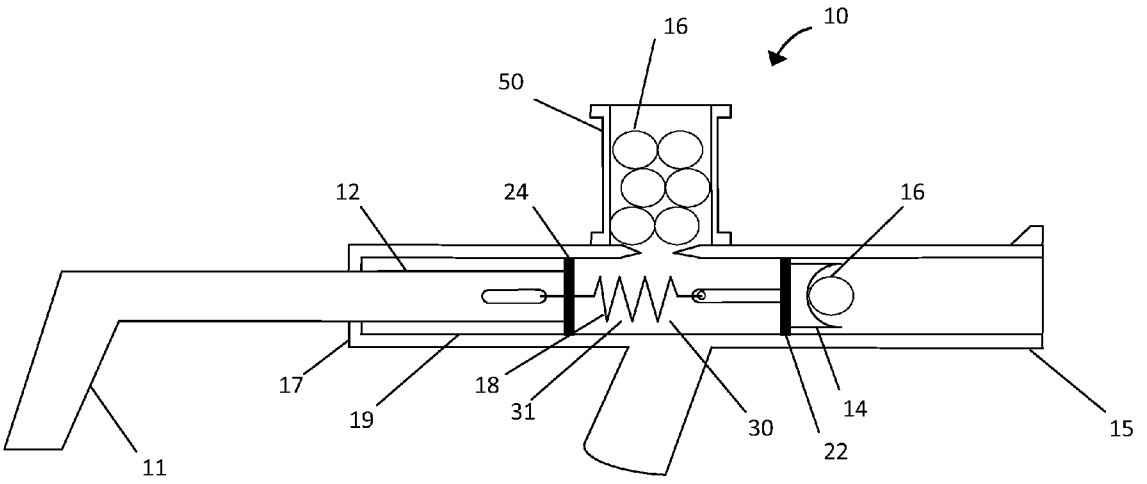
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(57) **ABSTRACT**

A device for projecting a soft-projectile made from a super absorbent polymer, the device comprising a holder designed for containing the soft-projectile made from a super absorbent polymer; and a firing mechanism operatively arranged to accelerate the holder from a firing position.

20 Claims, 13 Drawing Sheets



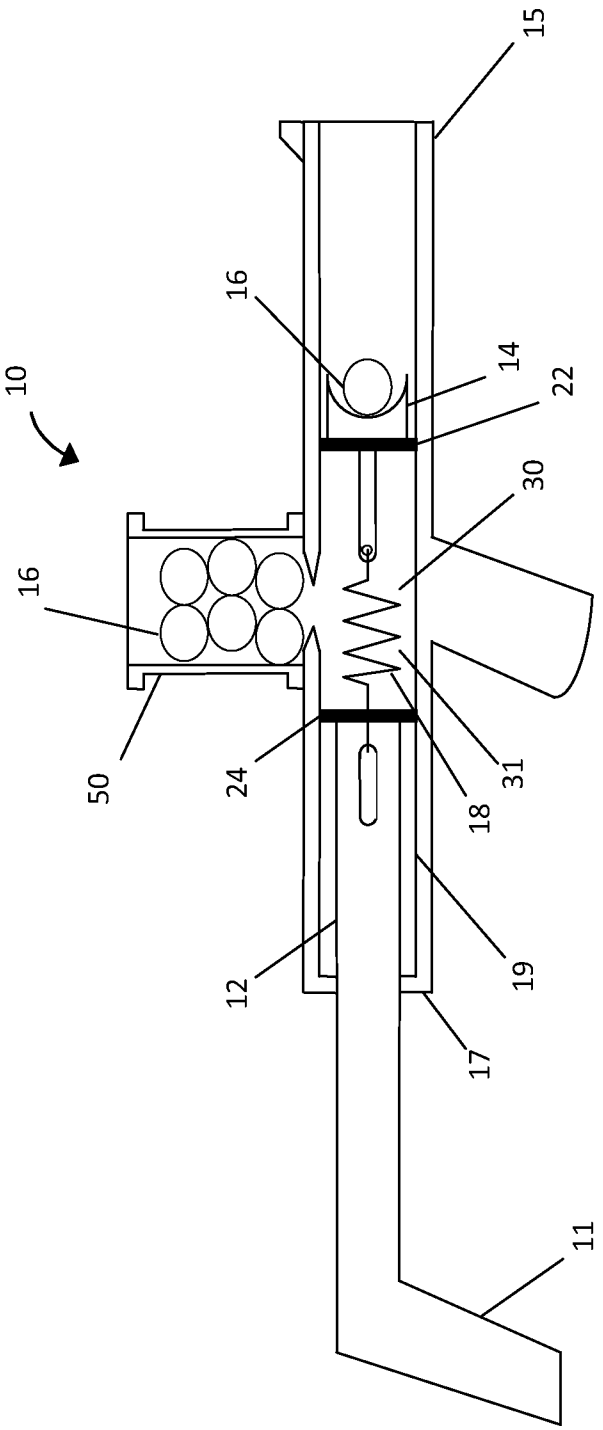


FIG. 1

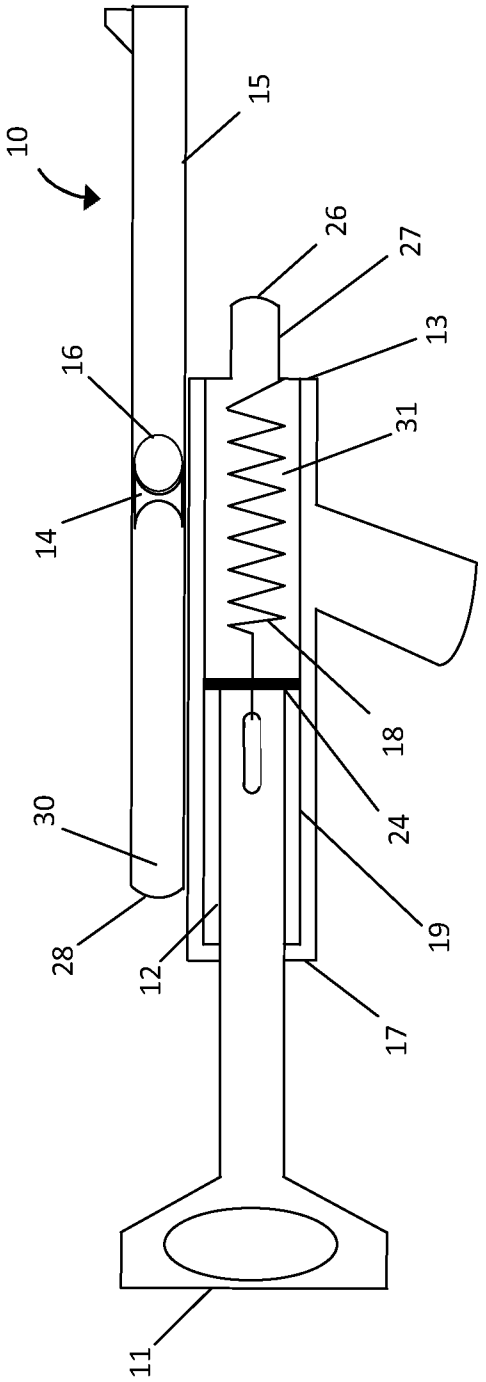


FIG. 2

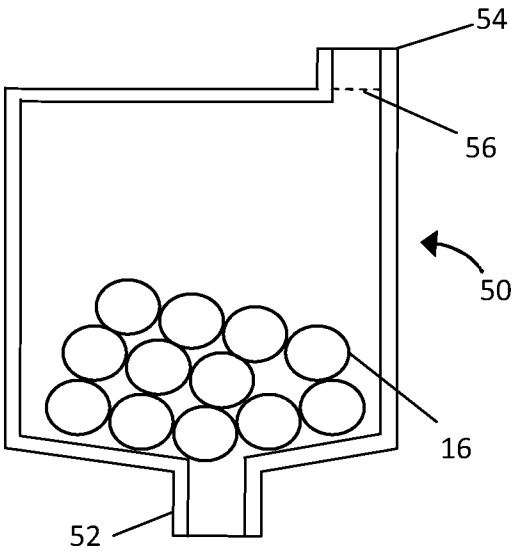


FIG. 3

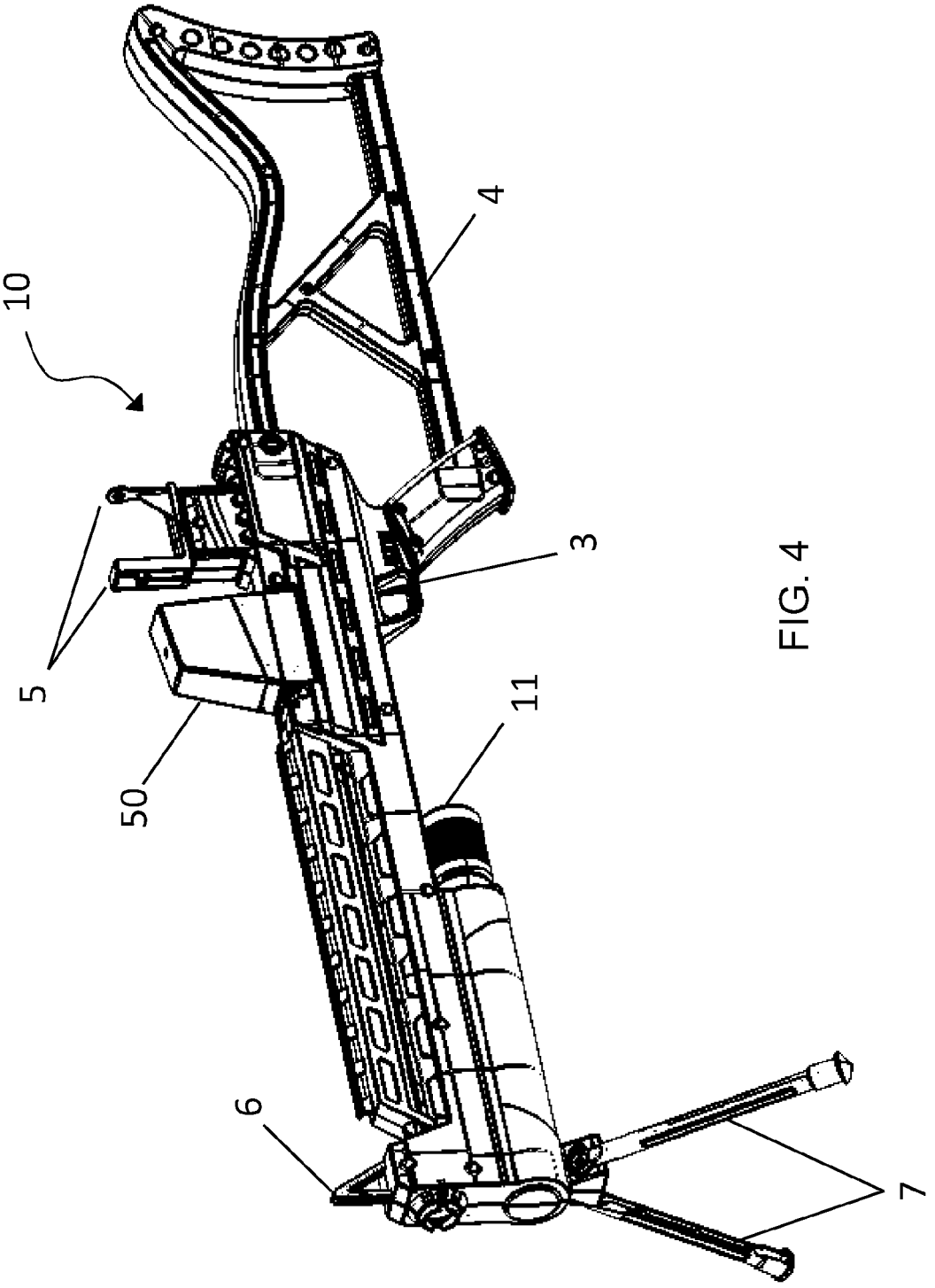


FIG. 4

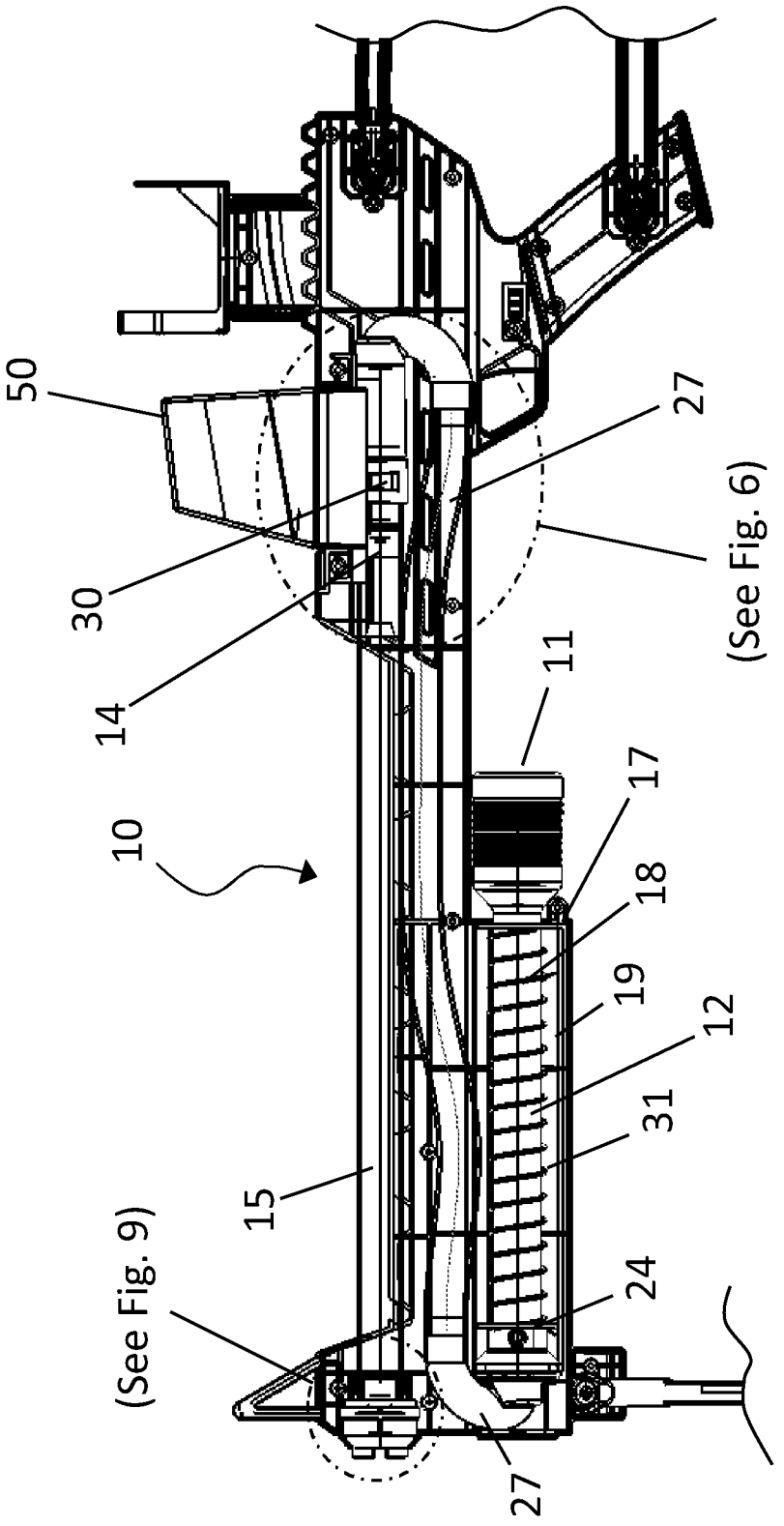


FIG. 5

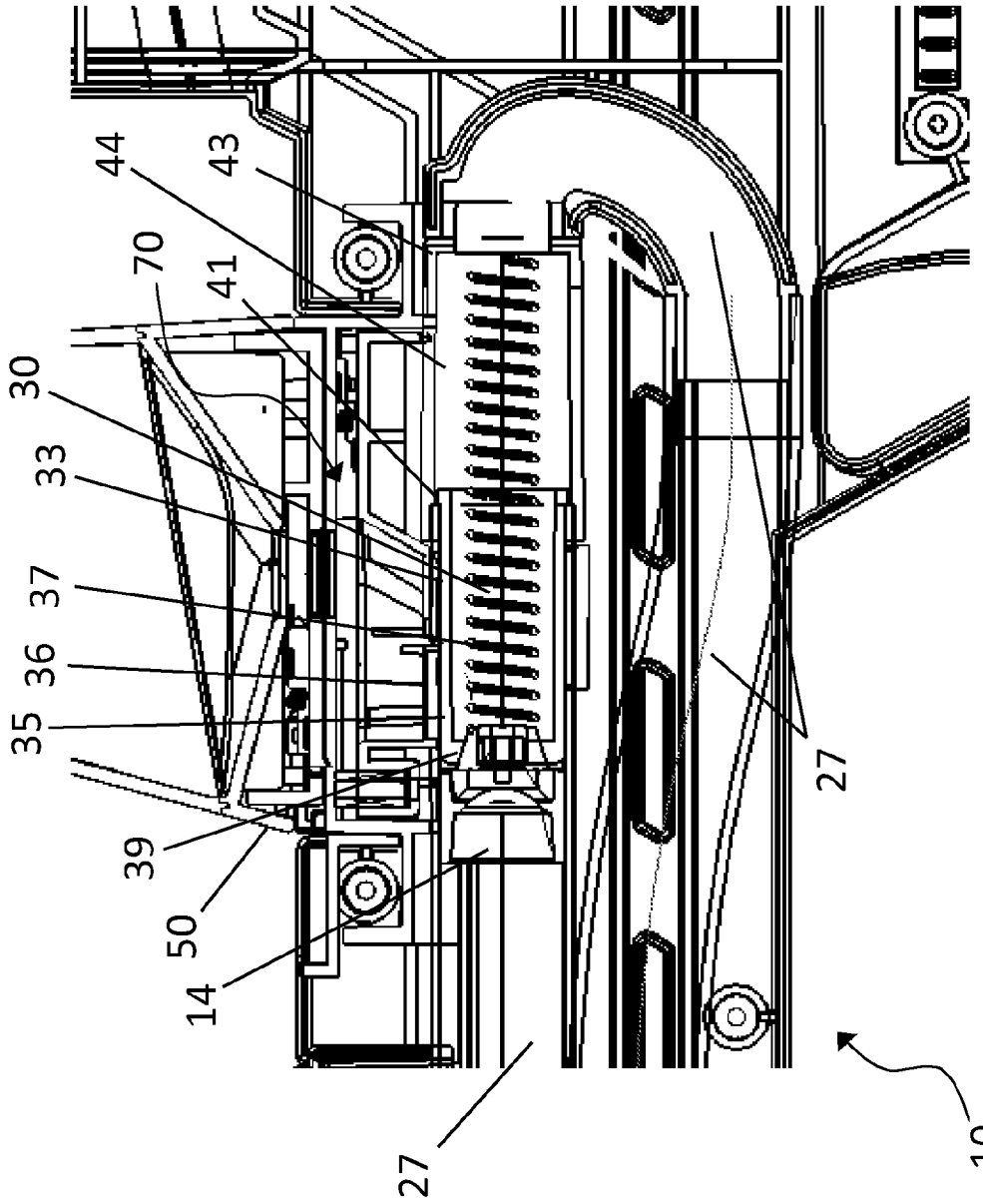


FIG. 6

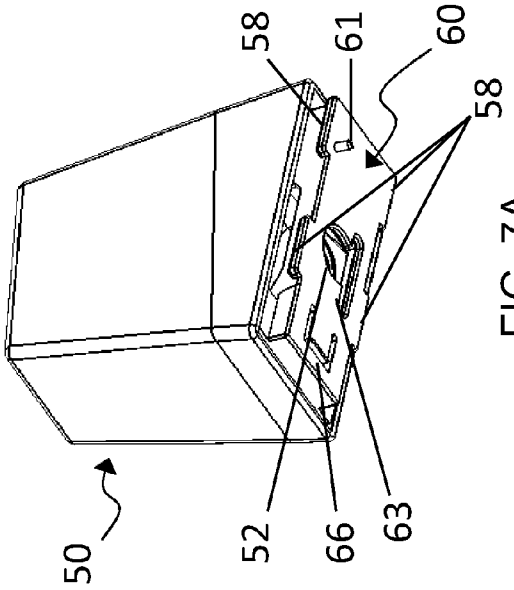


FIG. 7A

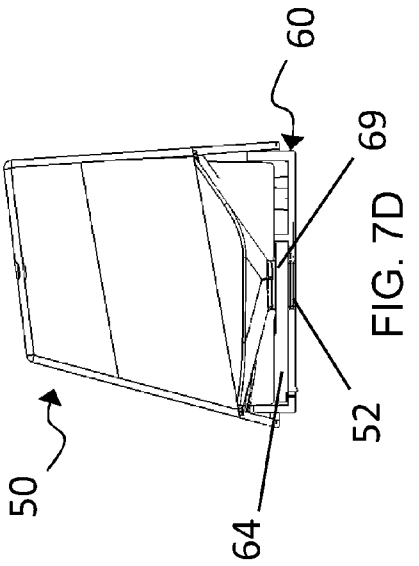


FIG. 7D

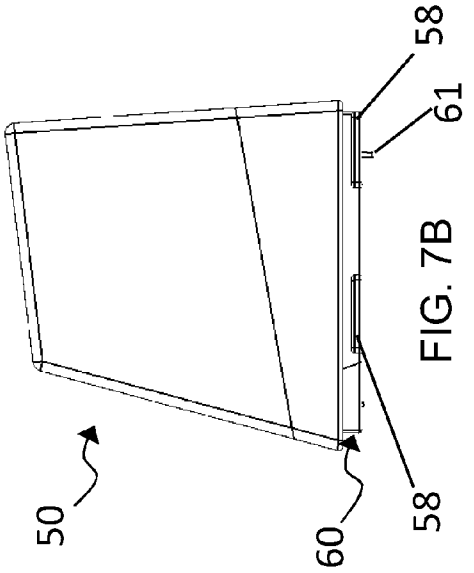


FIG. 7B

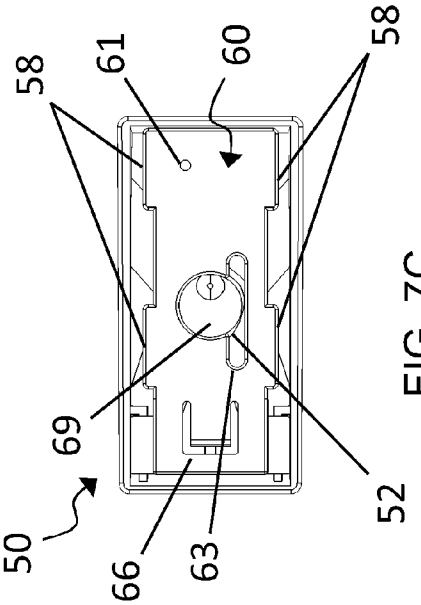


FIG. 7C

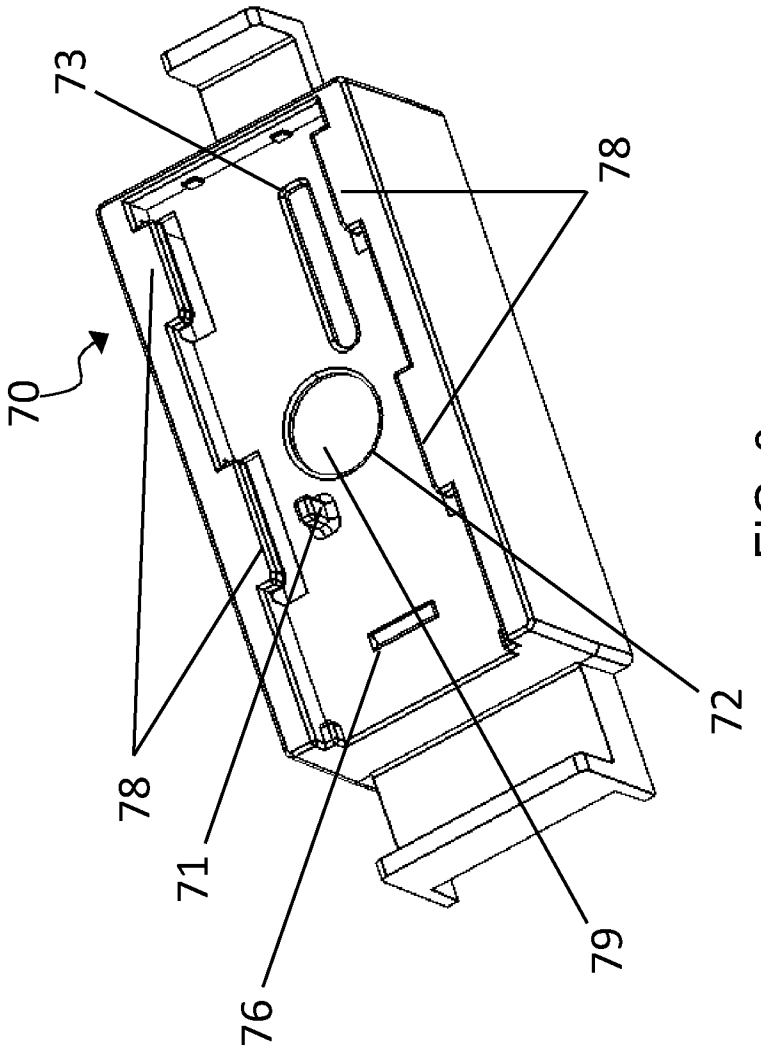


FIG. 8

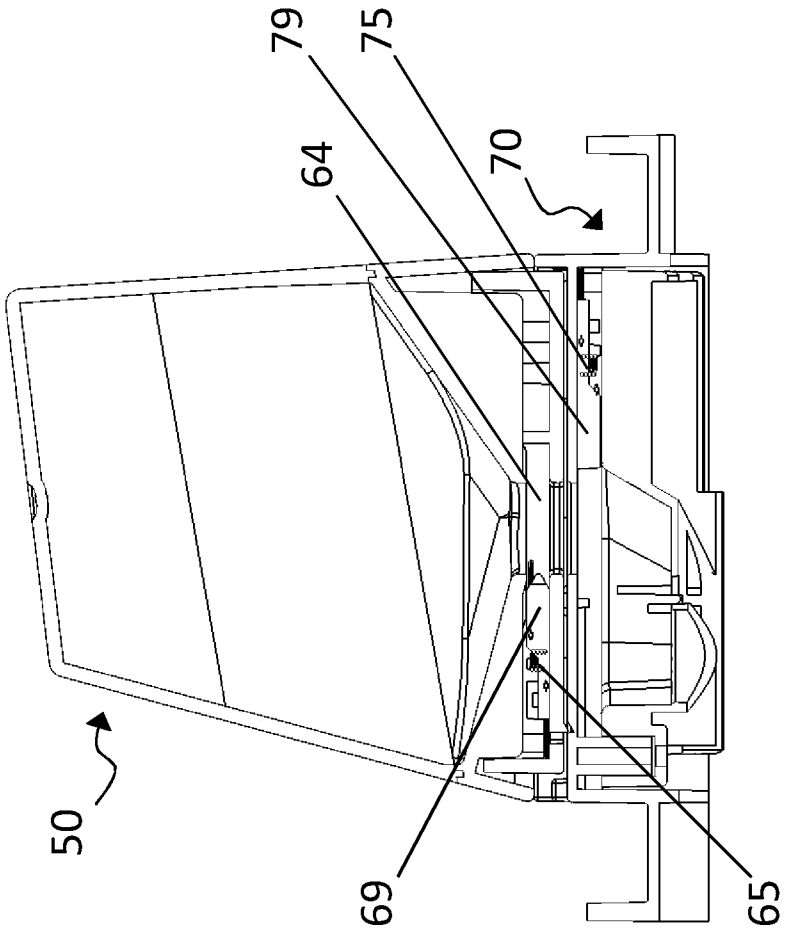


FIG. 9

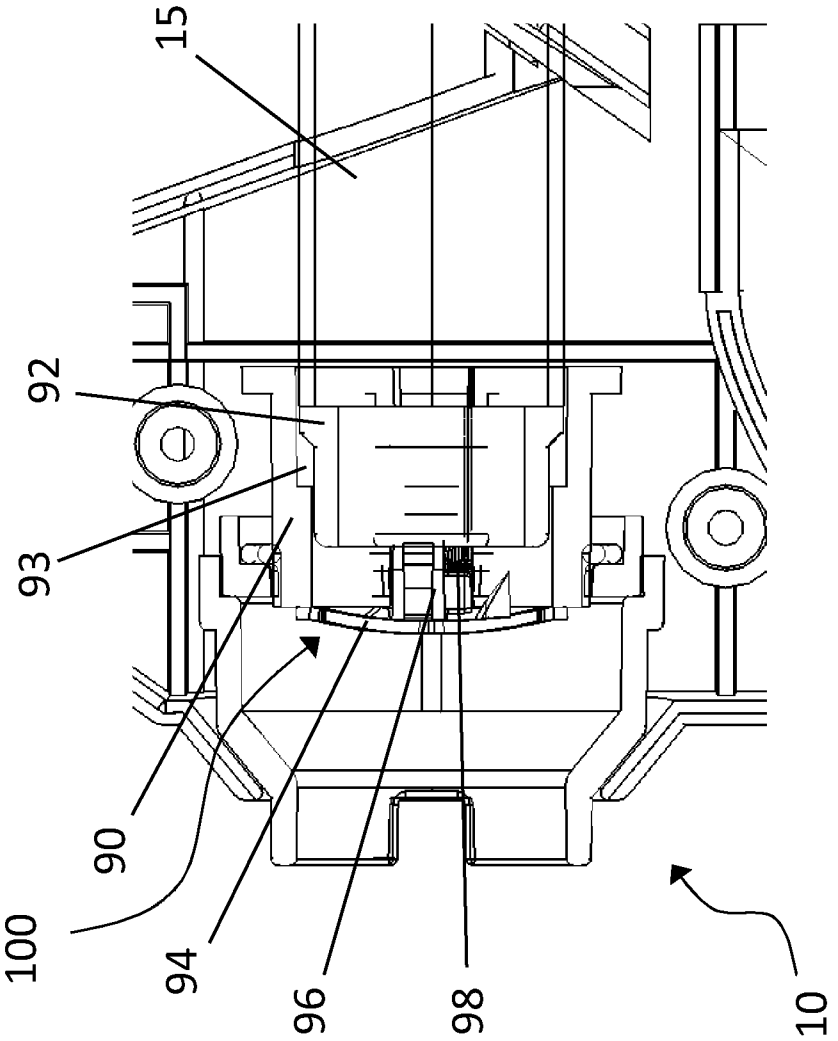


FIG. 10

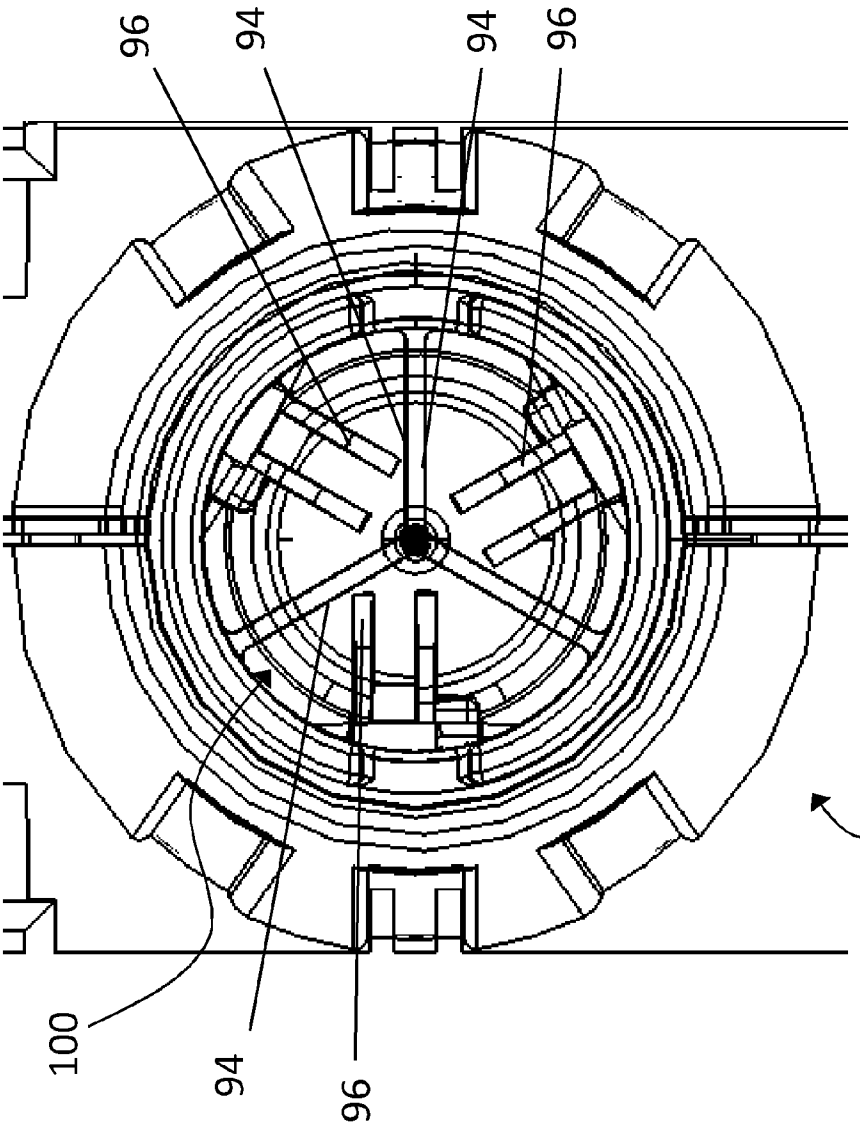


FIG. 11

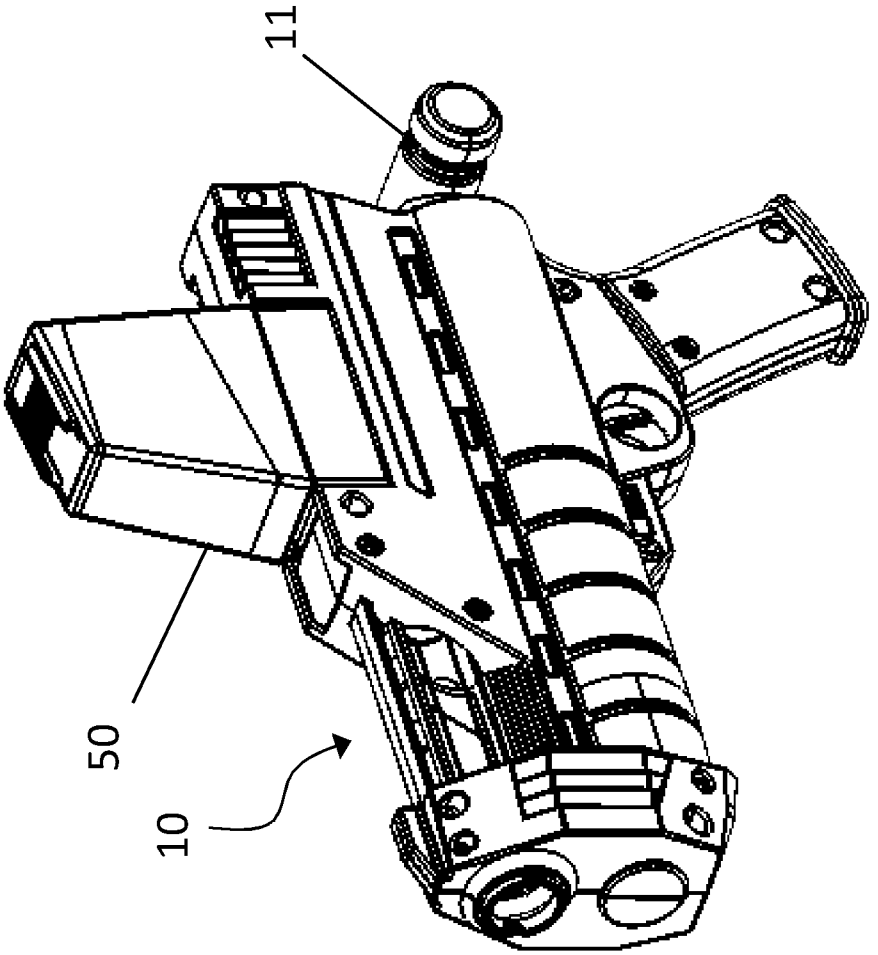


FIG. 12

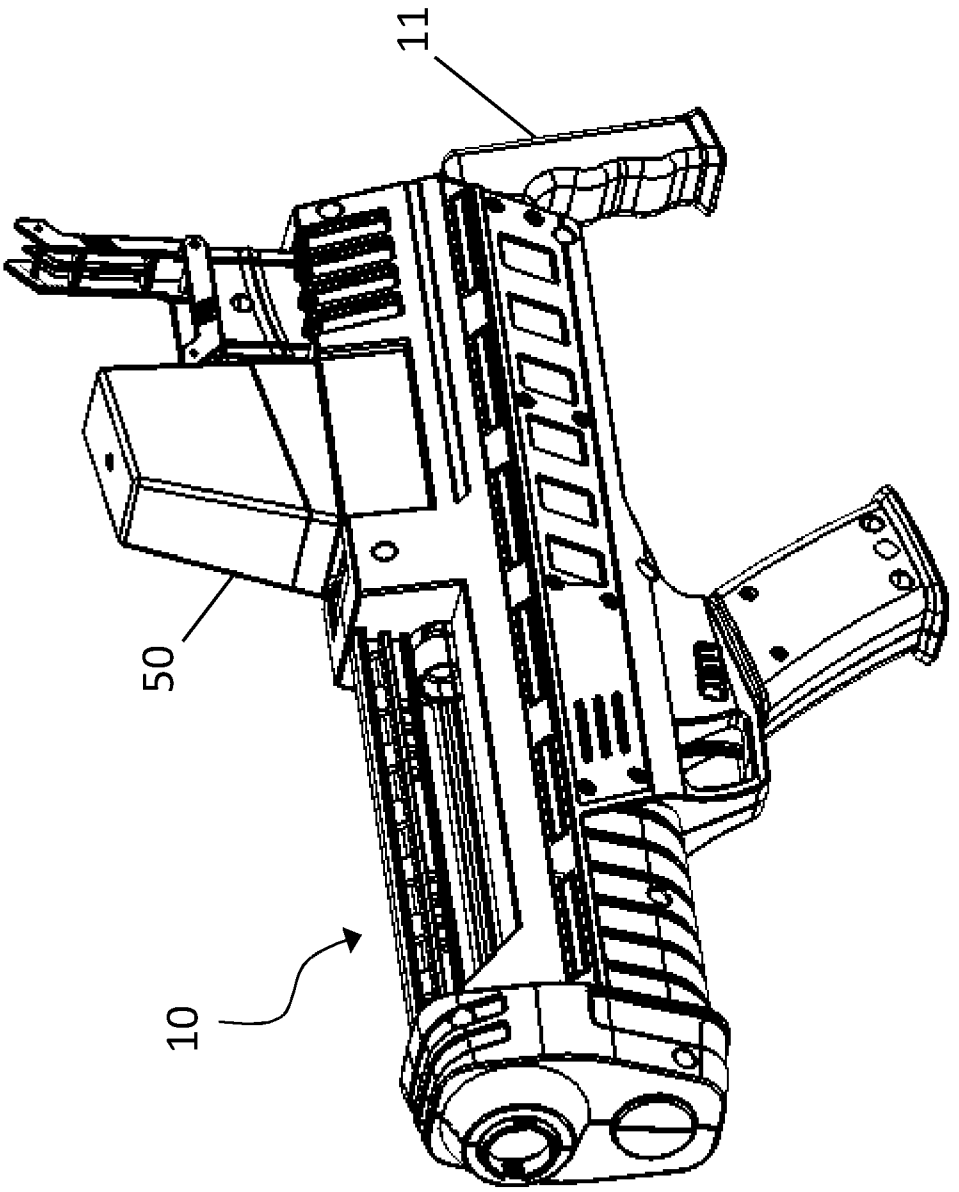


FIG. 13

SUPER ABSORBENT POLYMER PROJECTILE LAUNCHING DEVICE

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part and claims the benefit of U.S. patent application Ser. No. 12/777,134, filed May 10, 2010 now U.S. Pat. No. 8,371,282, which is hereby incorporated by reference.

FIELD

The present patent document relates to soft-projectile launching devices, such as projectile toys. More particularly, the present patent document relates to soft-projectile launching devices that launch super absorbent polymer projectiles and related devices and methods.

BACKGROUND

Children have a variety of different types of projectile launching toys available to them. For example, HASBRO® makes an entire line of NERF® weaponry that fire NERF® projectiles. NERF® is a trademarked term well known in the toy industry and is associated with soft foam-like material. Other than weaponry, NERF® is also commonly associated with sports balls such as footballs, basketballs, and others. Over the years, a large number of NERF® foam-based weaponry products have been developed, including various blasters that launch various types of NERF® projectiles including darts, rockets, and balls.

NERF® foam is a spongy cellular material produced by the reaction of polyester with a diisocyanate. The polyester resin reacts with the diisocyanate while CO_2 is simultaneously released by another reaction. The CO_2 gas creates open pockets within the polyurethane that give the NERF® foam its soft and light properties.

One reason the NERF® foam and other foam based projectile toys have became so popular has been due to the soft and light properties of the foam material. For example, NERF® balls were originally marketed as the "world's first official indoor ball." These same soft and light properties also make NERF® and other foams a great material for projectiles. Projectiles made from NERF® and other similar foams can be formed into balls and darts and fired from toy weaponry with little risk of injury. To this end, HASBRO® and other toy manufacturers have created numerous toy weaponry lines that shoot foam based projectiles including the N-Strike® line of toys.

Although NERF® and other foam like materials can be used to make toy weaponry projectiles that are relatively safe to project or launch, the properties of NERF® and other foam like materials have some significant drawbacks when used as projectiles for projectile launching toys. Because foam based materials such as NERF® foam are light, they are highly susceptible to air forces when trying to project them through the air in free flight as occurs when fired from toy weaponry. The soft, light properties of foam and NERF® type products are due to their low density. The low density of foam based projectiles decreases the momentum of the projectiles, which in turn increases the effect of air resistance, drag, and other motion retarding forces. This causes foam based projectiles to rapidly slow after initial firing and easily curve off line.

There are also small projectile systems for gaming and professional training purposes. These include paint ball guns and airsoft guns, but these systems are for adult use only due to the energy imparted to the projectile and the ability of the projectile to do serious harm.

SUMMARY OF THE INVENTION

One object of the present patent document is to provide an alternative soft-projectile launching system to those presently on the market. To this end, in one embodiment, a projectile launching device is provided that launches projectiles made from super absorbent polymers. The projectile launching device comprises: a holder designed for containing the soft-projectile made from a super absorbent polymer; and a firing mechanism operatively arranged to accelerate the holder from a firing position.

In another embodiment the holder of the soft-projectile launching system is slideably contained by the device. In another embodiment, the holder for a soft-projectile translates between the firing position and a launch point for the soft-projectile. In yet another embodiment the soft-projectile launching system further comprises a barrel having an interior in communication with the firing position wherein the holder for a soft-projectile translates down the barrel such that a soft-projectile launches from the barrel with little or no contact with the interior of the barrel.

In one embodiment, the soft-projectile launching system may have a firing mechanism incapable of storing energy independent of the user. Yet in other embodiments, the launching system may store energy. The soft-projectile launching systems of the present patent document may use air pressure, springs, rubber bands or any other suitable firing mechanism to launch the soft-projectile.

In another aspect of the present patent document, ammunition for a soft-projectile projection device is provided. The ammunition according to one embodiment comprises a plurality of projectiles made from a super absorbent polymer. The projectiles may be contained in a magazine. The projectiles may be hydrated or dehydrated.

In one embodiment, the projectiles have a diameter of less than 10 millimeters when hydrated. In yet another embodiment, the projectiles have a diameter of more than about 4 mm and less than about 9 mm when hydrated.

In another aspect of the present patent document, a magazine for a device for projecting soft-projectiles is provided. The magazine according to one embodiment comprises: a container having an interior volume having at least one opening wherein the container is configured to operatively mate with a device for projecting soft-projectiles and a plurality of projectiles made from a super absorbent polymer contained within the interior volume. The projectiles in the magazine may be hydrated or dehydrated and the magazine may include an inlet opening configured to only allow dehydrated projectiles to pass through into the magazine.

In one embodiment, the magazine further comprises a locking mechanism that prevents an outlet opening from opening unless the magazine is mated with a corresponding projection device.

In yet another aspect, a method of producing soft-projectiles is provided. The method comprises the steps of: placing a plurality of pieces of a super absorbent polymer in a liquid; allowing time for the plurality of pieces of a super absorbent polymer to absorb the liquid; and placing the plurality of pieces of a super absorbent polymer in a magazine.

In yet another aspect, a kit for making a plurality of soft-projectiles from a super absorbent polymer is provided. In one embodiment, the kit comprises: a predetermined quantity of dehydrated projectiles stored in a container, the dehydrated

projectiles comprising a super absorbent polymer; instructions for adding the dehydrated projectiles into an interior chamber of a magazine and hydrating the dehydrated projectiles in the interior chamber of the magazine. The container may, for example, comprise a sealed pouch or other low cost, disposable container.

In another embodiment, an adaptation mechanism for a projectile toy comprises: a soft-projectile holder adapted to hold a soft-projectile made from a super absorbent polymer; and an attachment mechanism connected to the soft-projectile holder wherein the attachment mechanism is designed to mate to a firing mechanism of the projectile toy.

In addition to the embodiments described above, a method of play is provided. In one embodiment, the method of play comprises launching a super absorbent polymer projectile from a projectile launcher. The launcher may come in any form including a toy weapon or a gun.

In some embodiments described herein including embodiments of the method of play, the soft-projectile made from a super absorbent polymer may be adapted for use with the firing mechanism of the projection device. In some embodiments, for example, the super absorbent polymer may have a relatively high cross-link density. The durability of the super absorbent polymer may, for example, be increased to prevent substantial damage to the soft-projectile during the launching step. In other embodiments the cross-link density of the super absorbent polymer may be set so that it is sufficient to keep the soft-projectile from breaking apart during the launching step.

Various embodiments and methods may also use various types of firing mechanisms, including firing mechanisms that use direct impact or indirect impact. For example, in some embodiments the projectile launcher comprises a firing mechanism that directly applies a force to the super absorbent polymer and in other embodiments the firing mechanism indirectly applies force to the super absorbent polymer. Further, in certain embodiments and methods, the firing mechanism stores energy independent of the user. In other embodiments, the firing mechanism is incapable of storing energy independent of the user.

In one embodiment of the method of play, the projectile launcher does not include a holder for the super absorbent polymer projectile to help transfer energy of a firing mechanism of the projectile launcher into motion of the super absorbent polymer projectile.

In yet another embodiment, the method of play further comprises loading the super absorbent polymer projectile into the projectile launcher from a magazine.

In another embodiment, a launching system is provided; the launching system comprises a projectile launcher for launching ammunition made from a super absorbent polymer and ammunition made from a super absorbent polymer that is adapted to be launched from the projectile launcher. In various embodiments of the projectile launching system, the projectile launcher is embodied by the various embodiments of a projection device described herein. Similarly, in various embodiments of the projectile launching system, the ammunition made from a super absorbent is embodied by the various embodiments of soft-projectiles described herein.

The super absorbent polymer projectile launching toys and/or weaponry described herein may increase the user experience as compared to foam-based projectile toys, yet they remain safe for children to use. Further aspects, objects, desirable features, and advantages of the devices and methods disclosed herein will be better understood from the detailed description and drawings that follow in which various embodiments are illustrated by way of example. It is to be expressly understood, however, that the drawings are for the purpose of illustration only and are not intended as a definition of the limits of the claimed invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** illustrates a cross section of one embodiment of a projectile launching toy designed for use with a plurality of projectiles made from a super absorbent polymer.

FIG. **2** illustrates a cross section of one embodiment of a projectile launching toy designed for use with a projectile made from a super absorbent polymer.

FIG. **3** illustrates a cross section of a projectile magazine for use with a projectile launching toy such as that shown in FIG. **1**.

FIG. **4** illustrates a perspective view of one embodiment of a projection device designed to be used with soft projectiles.

FIG. **5** illustrates a side view of the projection device shown in FIG. **4** with its casing removed so as to expose the inner components.

FIG. **6** enlarged cross-sectional view of the portion of the firing mechanism encircled in FIG. **5**.

FIG. **7**A illustrates a perspective view of a magazine for use with a projectile launching device.

FIG. **7**B illustrates a side view of the magazine of FIG. **7**A.

FIG. **7**C illustrates a bottom view of the magazine of FIG. **7**A.

FIG. **7**D illustrates a cross-sectional side view of the magazine of FIG. **7**A.

FIG. **8** illustrates a corresponding mating component for the magazine of FIG. **7**A.

FIG. **9** illustrates a cross-sectional view of a magazine mated to a corresponding locking device.

FIG. **10** illustrates an enlarged cross-sectional view of a safety mechanism encircled in FIG. **5** and provided to prevent foreign objects from entering the barrel while still allowing soft projectiles to exit.

FIG. **11** illustrates a view down the barrel of a projection device including the safety mechanism of FIG. **10**.

FIG. **12** illustrates a hand gun embodiment of a projection device designed to launch a soft-projectile.

FIG. **13** illustrates another embodiment of a projection device designed to launch a soft-projectile.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The term "magazine" is used herein to refer to any container that holds super absorbent polymer projectiles for a projectile toy gun or other projectile weaponry. The magazine could be of any shape size or volume and have any number of openings as long as it holds super absorbent polymer projectiles in a useable manner for a corresponding super absorbent polymer projectile launching device.

Super absorbent polymers (SAP's) were first invented by the United States Department of Agriculture (USDA) in the 1960's and are commonly used in personal disposable hygiene products such as diapers, protective underwear, and sanitary napkins. SAP's are polymers that can absorb an extremely large amount of liquid relative to their own mass. SAP's absorb aqueous solutions through hydrogen bonding with water molecules.

The present patent document discloses and teaches projectile launching devices, such as toys, amateur guns and weaponry that use projectiles formed from a super absorbent polymer (SAP). As a result, the projectiles launched by the devices of the present patent document are soft-projectiles. Further, once hydrated, the unique properties that SAP's exhibit give

the soft-projectiles several advantages over current projectile materials such as paint balls, plastics, and foams. For example, hydrated SAP projectiles can maintain their shape under modest pressure. The ability of SAP projectiles to maintain their shape allows them to be projected with a reasonable force and velocity without breaking apart. However, under excessive pressure, hydrated SAP projectiles will break down and lose their shape. Because SAP projectiles break down under excessive pressure, the force at impact is spread over a much wider surface area, thus reducing the likelihood of injury.

SAP projectiles can also be designed to break down at different pressures based on their composition. This allows them to be tailored to have specific qualities as soft-projectiles. The total absorbency and swelling capacity of a SAP varies depending on the degree of cross-linking within the polymer. The lower the density of the cross-linking the higher the absorbent capacity of the SAP. Thus, low density cross-linked SAP's generally have a higher absorbent capacity and swell to a larger degree than more highly cross-linked SAP's. Low density cross-linked SAP's also have a softer and more cohesive gel formation. High cross-link density polymers exhibit lower absorbent capacity and swell. The gel strength is firmer and can maintain particle shape even under higher pressures.

Consequently, by using a SAP with a higher cross-link density, a soft-projectile can be made to fly farther and faster without breaking apart and have a stronger impact. In contrast, soft-projectiles made from a SAP with a lower cross-link density will break apart more easily and have a much softer impact. Depending on the level of safety required, different SAP's with different cross-link densities may be used. For example, SAP's can be constructed that would be considered "highly compliant" by industry standards.

Soft-projectiles made from a SAP are preferably round but may be of other shapes as well, including, for example, dart shapes, cylinder shapes, bullet shapes, oval, square, rectangular or any other shape. Round is a preferable shape not only because it has fairly good ballistic characteristics but because SAP's are easily formed in round shapes.

Soft-projectiles made from a SAP can be any size. Preferably, however, the soft-projectiles made from a SAP are between about 3 millimeters (mm) and about 15 mm in diameter when hydrated and more preferably between about 5 mm and 8 mm in diameter when hydrated. Typically, the soft-projectiles are about 1 mm or less when the SAP forming the projectile is dehydrated.

Larger soft-projectiles made from a SAP are possible. For example, rounds having a diameter of 30 mm have been created. However, there is approximately a 20% tolerance on the final diameter of the hydrated SAP soft-projectiles and therefore, the larger rounds are more difficult to make consistently uniform in diameter.

The SAP projectiles may be colorless to prevent any staining upon impact. Alternatively, soft-projectiles made from a SAP may also have additives added during the formulation of the SAP or during hydration that will create a temporary or indelible signature upon hitting a target. For example, soft-projectiles made from a SAP may be colored by adding a die to the SAP or the aqueous solution during the hydrating process. Depending on the die employed, the resulting signature may be of any desired color. Further, the employed die compound may be visible under normal lighting conditions or only under an ultra violet black light. Other additives may also be used including those that give the soft-projectiles a tracer effect such as glow-in-the-dark additives or other materials with luminescent properties.

Soft-projectiles made from water absorbing polymers, classified as hydrogels, will absorb aqueous solutions through hydrogen bonding with the water molecule. A SAP's ability to absorb water is a factor of the ionic concentration of an aqueous solution. Consequently, soft-projectiles made from a SAP are preferably grown in water with a PH of 7. More preferably soft-projectiles made from a SAP are grown in distilled water, where they may absorb 500 times their weight, and from 30-60 times their dehydrated volume.

FIG. **1** illustrates a cross section of one embodiment of a projection device **10**, which in the present embodiment is a projectile launching toy, designed for use with soft-projectile **16**. The soft-projectiles of the present patent document are formed from a super absorbent polymer. As shown in FIG. **1**, projection device **10** is in the general form of a gun. However, in other embodiments, projection device **10** can have shapes and designs of other devices. For example, projection device **10** can be a bow, crossbow, sling shot, hand gun, machine gun, futuristic weapon, catapult, or shaped as any other type of weaponry. Projection device **10** can be made of a number of suitable materials including metals, rubbers and plastics; however, injection molded plastic is a preferred construction material.

Projection device **10** has firing mechanism with a firing position **30**. The firing position **30** is where the soft-projectile **16** is positioned just prior to being fired or launched from the projection device **10**. The firing mechanism of the embodiment shown in FIG. **1** is based on air pressure, which is created in air compression chamber **31**. However, the firing mechanism of the projection device **10** may be based on any of the known ways of firing or launching projectiles or ammunition from a projection device. For example, springs or rubber bands can be stretched and released to launch the projectile from the projection device **10**. These springs or rubber bands may further use a mechanical advantage to increase the velocity of the projectile as it is launched. As an example, compound bows use a system of levers or pulleys to make the transfer of energy from the spring of the bow to the projectile more efficient. In addition to springs and rubber bands, air pressure can be used, as in the embodiment illustrated in FIG. **1**. Air pressure can be created in a number of ways including, for example, from a plunger operated by the user, from a cartridge containing compressed gas (such as the CO_2 cartridges used with paint ball guns), from air that has been pumped into an internal chamber and then released, or from an explosion in a chamber.

In addition, various techniques of launching a projectile may also be combined. For example, the embodiment shown in FIG. **1** uses the combination of a spring and air pressure. The components of FIG. **1** will now be further described with respect to the use of projection device **10** to launch a soft-projectile **16** made from a SAP.

To begin the process of firing a soft-projectile **16** made from a SAP with the device shown in FIG. **1**, a user pulls back on the handle **11** which retracts the plunger **12** out of the aft end **17** of a plunger cylinder **19**. The plunger **12** is attached to spring **18**. As the spring **18** is stretched, air is sucked into an air compression chamber **31** located between plunger seal **24** and air seal **22**. Air seal **22** abuts against a stop (not shown) just behind the firing position **30** to prevent air seal **22** from following the plunger **12** past a certain point as it is drawn back. Consequently, the spring **18** is stretched. When the user releases the handle **12**, the spring **18** quickly pulls the plunger **12** back inside the plunger cylinder **19**. This creates a rapid increase in air pressure in the air compression chamber **31** between plunger seal **24** and air seal **22**. Consequently, air seal **22** is propelled rapidly through barrel **15** towards the

distal end of barrel **15** and simultaneously accelerates the holder **14** for a soft-projectile and the soft-projectile **16**. The soft-projectile **16** is launched from the projection device **10** on a free trajectory and the air seal **22** and soft-projectile holder **14** are retained within the barrel **15** of projection device **10**.

In the embodiment of the projection device **10** shown in FIG. **1**, the air seal **22** and the soft-projectile holder **14** are retained via their connection to the spring **18**. However, the soft-projectile holder **14** and air seal **22** may be retained by other means. For example, a stop (not shown) may be installed inside of barrel **15** to prevent air seal **22** or soft-projectile holder **14** from escaping but allow the soft-projectile **16** to pass freely. Preferably, the stop is located adjacent the barrel exit to maximize the distance over which the soft-projectile **16** is carried in the holder **14** before exiting the barrel.

Once the soft-projectile **16** made from a SAP has been launched, the plunger **12** and plunger seal **24** have been pulled inside the plunger cylinder **19** to the extent possible. In this position, the plunger seal **24** is located just behind the firing position **30**. When the user wants to fire another round, the user pulls back on the handle **11**. As the plunger **12** is retracted, air seal **22** and soft-projectile holder **14** are drawn behind the magazine or feed hopper **50**. Once the air seal **22** and the soft-projectile holder **14** are positioned behind the magazine or feed hopper **50**, another soft-projectile made from a SAP **16** can fall into the firing position **30**.

Toy guns and weaponry are typically classified into two different categories: 1) devices that can transfer stored energy into the projectile; and 2) devices that are incapable of storing energy independent of the user. The projection device **10** embodied in FIG. **1** is of the latter type. However, the device in FIG. **1** could be easily modified to store energy. For example, a one way valve could be added in combination with a trigger mechanism to prevent air seal **22** and soft-projectile holder **14** from advancing. The plunger **12** could be used to pump additional pressure into the air compression chamber **31** behind air seal **22**. The user would then pull the trigger to release the pressure that has built up from multiple pumps of the plunger **12**.

FIG. **2** illustrates a cross section of another embodiment of a projection device **10** designed for use with soft-projectiles **16** made from a super absorbent polymer. Projection device **10** of the present embodiment is a projectile launching toy. In the device **10** shown in FIG. **2**, the smaller diameter tube **27** is wrapped back around to the back of the projection device **10** and laid on top of the projection device **10** so that tube portions **26** and **28** are continuously connected. In the embodiment in FIG. **2**, the volume in front of plunger seal **24** transitions from plunger cylinder **19**, which has a comparatively large diameter, to a tube **27**, which has a smaller diameter than plunger cylinder **19**. The change in the diameter of the air compression chamber **31** from the plunger cylinder **19**, which comprises a tube of a relatively larger diameter, to a smaller diameter tube **27** will cause, during use of the device, a rapid increase in the velocity of the air flow in correlation with the conservation of energy and Bernoulli's principle. Consequently, the rapid air flow is forced down the length of the smaller diameter tube **27** until it escapes out the front of the projection device **10**. As the air rushes down the smaller diameter tube **27** the soft-projectile holder **14**, which fits with an air seal inside the smaller diameter tube **27**, is rapidly accelerated with the air, carrying the soft-projectile **16** made from a SAP and launching it out of the projection device **10**.

Although the embodiments illustrated in the present patent document include a smaller diameter tube **27**, other embodiments may include a tube of any diameter including a tube of larger diameter. As explained above, it is preferable to use a tube with a smaller diameter than the diameter of the air compression chamber **31** to take advantage of the Bernoulli principle. However, using a tube with a smaller diameter is not a requirement. In addition, the barrel **15** may be considered part of the smaller diameter tube **27** or as a separate component connected to the smaller diameter tube **27**.

Unlike the embodiment of FIG. **1**, the soft-projectile holder **14** is not retained by the spring. In the embodiment of FIG. **2**, the soft-projectile holder **14** is slideably contained by the barrel **15**, but is not otherwise attached. The soft-projectile holder **14** acts as a free sliding piston that may operate independently of the plunger **12**. A stop near the end of the barrel **15** and a stop near tube position **30** retains the soft-projectile holder **14** within a desired operating region of the barrel **15**. The stop near the end of the barrel **15** should be designed to retain the soft-projectile holder **14** without interfering with the launching of the soft-projectile **16** made from a SAP.

FIG. **2** illustrates a device **10** having a smaller tube **27** that wraps from a position relatively near the distal or front end **13** of plunger cylinder **19** back to a position relatively near the proximal or back end **17** of plunger cylinder **19** and then extends down the length of the plunger cylinder **19**. This is not required and the smaller tube could simply extend straight away from distal end **13**. However, by wrapping the tube as shown in FIG. **2**, the more rigid structure of the plunger cylinder can be used to help stiffen the tube **27**.

The soft-projectile holder **14** is preferably designed to minimize, or even prevent altogether, the contact of the soft-projectile **16** with the barrel **15** as the soft-projectile **16** travels down the barrel **15**. Although soft-projectile holder **14** is not a requirement, minimizing the contact between the soft-projectile **16** and the barrel **15** is preferable. The soft-projectile **16** will tend to retain its shape, especially if the cross-link density is high. However, if the soft-projectile **16** is nicked, scratched, or damaged by the barrel as it accelerates, it may disintegrate prior to exiting the barrel **15**, especially if the cross-link density is low. If the soft-projectile **16** disintegrates prior to exiting the barrel **15**, the soft-projectile **16** will not fly accurately or the correct distance. Consequently, the design of the soft-projectile holder **14** should take care to encase enough of the soft-projectile **16** to prevent it from touching the sides of the barrel **15** as it travels. The soft-projectile holder **14** is preferably cup shaped in a form that mates with the exterior surface of the soft-projectiles **16** to be employed with the device. However, the soft-projectile holder **14** may be bucket shaped, crescent shape, or any other shape that helps prevent or suitably minimize the contact between the soft-projectile **16** and the barrel **15**.

In addition to preventing contact between the soft-projectile **16** and the barrel **15** during launch, the soft-projectile holder **14** also helps transfer the energy of the firing mechanism into the motion of the soft-projectile **16**. In addition, if shaped similar to soft-projectile **16**, the soft-projectile holder **14** helps distribute the force generated by the firing mechanism evenly over the soft-projectile **16** and therefore, helps prevent the soft-projectile **16** from breaking during launch. Consequently, a holder **14** that mates more appropriately with the shape of the outside surface of the soft-projectile **16** is preferable. Furthermore, the soft-projectile holder **14** may help center the soft-projectile **16** and keep the soft-projectile **16** centered as it travels down the barrel **15**. To this end, a soft-projectile holder **14** in the shape of a hemisphere may be used with round soft-projectiles **16**. The hemispherically shaped holder **14** may have a diameter slightly larger than the soft-projectile **16** to not only help prevent contact with the

interior of the barrel **15**, but also to accommodate variations in the diameters of soft-projectiles **16**.

Although the embodiments of FIGS. **1** and **2** illustrate a device **10** using a spring and air pressure, and preferably a combination of a spring and air pressure is used, projection device **10** can use a catapult system, sling shot, bow style or any other type of acceleration system to launch the soft-projectile **16**. As another example, projection device **10** can accelerate the soft-projectile or soft-projectile holder by an accelerating mass, like the hammer of a gun, impacting the soft-projectile or soft-projectile holder. Furthermore, these devices can all be set up to work with stored energy or work with only energy provided by a user without departing from the embodiments of the present patent document.

FIG. **3** illustrates a cross section of a magazine **50** for use with a projectile device **10**, such as the projectile launching toy shown in FIG. **1**. Magazine **50** can be of any shape or size and is intended to contain the soft-projectiles **16** made from a SAP. Magazine **50** can be made of metal, glass, plastic, rubber, or any other suitable material. Preferably magazine **50** is constructed of injected molded plastic. Magazine **50** may be reusable and refillable or designed for a single use and disposable. Magazine **50** can be loaded with already hydrated soft-projectiles **16** made from a SAP. Alternatively, magazine **50** can be loaded with dehydrated soft-projectiles **16** made from a SAP. If dehydrated soft-projectiles are used, water or another aqueous solution is added to the magazine **50** to hydrate the soft-projectiles **16** made from a SAP. Magazine **50** is preferably sealable to prevent water or moisture from the soft-projectiles **16** from leaking out.

Magazine **50** has a first opening **52** designed to mate with a projection device **10**. Preferably the first opening **52** of magazine **50** includes a locking mechanism, such as a trap door, that blocks the first opening when the magazine **50** is not mated to a corresponding projection device **10**. The locking mechanism provides a safety mechanism that prevents foreign objects from being loaded into the magazine **50** and launched by the projection device **10**. The locking mechanism can be a keying system, child safety device, or other locking mechanism that prevents foreign objects from being loaded into the magazine.

The opening on the projection device **10** that mates with the magazine preferably has a corresponding locking mechanism to complement the locking mechanism on the magazine **50**. Consequently, soft-projectiles **16** may only be loaded into the projection device **10** from the magazine **50**. Similar to the locking mechanism that prevents foreign objects being loaded into the magazine **50**, the corresponding locking mechanism on the opening in the projection device prevents foreign objects from being loaded directly into the projection device **10** and then launched.

As shown in FIG. **3**, the magazine **50** may have a second opening **54** for refilling the magazine with soft-projectiles **16** made from a SAP into the magazine. The second opening **54** may be large enough to allow hydrated soft-projectiles **16** to be loaded directly into the magazine. In such a case, the interface between the magazine **50** and the projection device **10** should be designed to prevent foreign objects from being loaded from the magazine **50** into the projection device **10** and subsequently launched.

Alternatively, the second opening **54** may further include a screen **56** designed to prevent passage of objects larger than a particular size. The dehydrated SAP pieces forming the soft-projectiles **16** may typically have a diameter of about 1 millimeter (mm) or less. In such embodiments, the screen **56** can be designed to only allow objects of approximately 1 mm or less in diameter to pass through. The dehydrated soft-projectiles **16** can then be loaded into the magazine **50** and water or another aqueous solution can be added and the soft-projectiles **16** can swell to their appropriate size. The screen **56** is a safety mechanism to make sure foreign objects are not loaded into the magazine **50** and then subsequently launched from the projection device **10**. Although it is recognized that foreign objects of less than 1 mm can be loaded into the magazine, objects of less than 1 mm are much less likely to cause significant damage if subsequently launched by the projection device **10** because of their reduced size and weight.

The dehydrated soft-projectiles **16** may be sold in a kit designed to refill a magazine **50**. In one embodiment, the kit comprises a pre-counted number of dehydrated rounds designed to fill up a particular magazine when hydrated. A magazine **50** preferably holds between 150 and 250 rounds and more preferably holds about 200 soft-projectiles **16**. However, the magazine **50** and the kit that fills the magazine **50**, can hold any number of soft-projectiles. For example, larger clips of approximately 500 to 1000 rounds may be used for machine guns, Gatling guns, or other rapid fire projection devices **10**. In contrast, magazines or clips of 6 to 20 rounds may be used for single shot toys and weaponry.

The kit preferably further includes instructions on how to insert the dehydrated rounds into the magazine **50** and grow the dehydrated rounds inside the magazine **50**. After purchasing a kit, a user would dump the dehydrated rounds into the magazine and follow the directions to add distilled water or another appropriate aqueous solution to hydrate the rounds and swell them into their appropriate size for launching from a projectile device **10**.

In addition to projection devices designed specifically to launch soft-projectiles **16**, embodiments of the present patent document include adaption devices to adapt existing projectile toys and weaponry to launch soft-projectiles **16**. Adaption devices attach to the firing mechanism of the existing toy or weaponry and allow the transfer of energy from the firing mechanism into kinetic motion of the SAP projectile **16** without damaging the SAP projectile **16**. Preferably, soft-projectile holders **14**, similar to those of FIGS. **1** and **2**, are retrofit to the existing toys and/or weaponry to protect the soft-projectile made from a SAP **16**. However, such holders are not required, and other methods may be used without departing from the scope of the embodiments of the present patent document.

FIG. **4** illustrates a prospective view of another embodiment of a projection device **10** designed to be used with soft projectiles, such as ammunition made from a super absorbent polymer. The projection device **10** of FIG. **4** is a projectile launching toy shaped in the form of a gun. The gun shaped projection device embodied in FIG. **4** includes a magazine **50** to hold ammunition made from a super absorbent polymer **16**. The projection device **10** of FIG. **4** further includes a handle **11** which allows the user to activate the firing mechanism of the projection device **10**. As may be seen in FIG. **4**, the handle **11** in the illustrated embodiment is positioned under barrel **15** in a shotgun style pump position on the toy gun. Generally, however, the handle **11** may be operably located in any position on the projection device **10** that allows a user to easily pull and release or pull and pump the handle **11**.

In embodiments of the projection device **10** that store and release energy, a finger trigger **3** is preferably included. Finger trigger **3** may be mechanically connected to the firing mechanism to release the stored energy when finger trigger **3** is depressed by a user. In embodiments that also include handle **11**, the user may pull the handle **11** back and lock it in

the pulled back position. The finger trigger **3** may then be depressed to release the handle **11** and activate the firing mechanism.

In addition, the projection device **10** may have a number of attachments or enhancements that increase the user's experience when playing with the projection device **10**. For example, in the case of a gun as shown in FIG. **4**, the gun may further include a stock extender **4**, a gun sight **5**, alignment sight **6**, a retractable stand **7** and any other attachments or components that would further enhance the user's experience, including improving the functionality, realism or life-like nature of the projection device **10**.

FIG. **5** illustrates a side view of the embodiment of FIG. **4** with the casing removed so as to expose the inner components of the projection device **10**. The firing mechanism of the embodiment shown in FIG. **5** is similar to the firing mechanism of the embodiment of FIG. **2**. Both embodiments include a firing mechanism based on air pressure. The air pressure of FIG. **2** and FIG. **5** is created in air compression chamber **31**. A smaller diameter tube **27** traverses through the gun and then extends substantially straight down the length of the gun to form the barrel **15** and direct the compressed air.

In the embodiment shown in FIG. **5**, the spring **18** is designed to wrap around the plunger **12**, so that spring **18** is compressed, rather than stretched as it is in the embodiment of FIG. **2**, when handle **11** is pulled by the user into the firing position. Further, by extending the plunger **12** through the center of the spring **18**, the air compression chamber **31** may include the entire volume of the plunger cylinder **19**.

In operation, a user pulls the handle **11** which draws the plunger **12** and plunger seal **24** towards the aft end **17** of the plunger cylinder **19**. As the plunger **12** is retracted through the plunger cylinder **19**, the spring **18** is compressed against the aft end **17** and air is sucked into the expanding air compression chamber **31**. When the spring **18** is fully compressed against the aft end **17**, the plunger **12** is fully retracted and the air compression chamber **31** substantially includes the entire volume of the plunger cylinder **19**.

When the user releases the handle **11**, the spring **18** rapidly expands and forces the plunger seal **24** back down the plunger cylinder **19** rapidly reducing the size of the air compression chamber **31**. Similar to the embodiment of FIG. **2**, the rapid air flow is forced down the length of the smaller diameter tube **27** and barrel **15** until it escapes out the front of the projection device **10**. As the air rushes down the smaller diameter tube **27**, the soft-projectile holder **14**, which fits with an air seal inside the barrel **15**, is rapidly accelerated with the air down the barrel, carrying the soft-projectile **16** made from a SAP and launching it out of the projection device **10**.

In a preferred embodiment, the volume enclosed by the smaller diameter tube **27** and the air compression chamber **31** between the seal of soft-projectile holder **14** and the plunger seal **24** is substantially sealed. In a preferred embodiment, the plunger cylinder **19** further includes a one-way valve that allows the plunger cylinder **19** to suck air into the air compression chamber **31**, but prevents air from escaping when the handle **11** is released and the plunger **12** is rapidly forced back into the compression chamber **31** by the expanding spring **18**.

Substantially sealing the volume between the soft-projectile holder **14** and the plunger seal **24** allows the position of the soft-projectile holder within the smaller diameter tube **27** to be manipulated by the user when pulling or releasing the handle **11**. In addition to causing the soft-projectile holder **14** to rapidly accelerate down the smaller diameter tube **27** when the user releases the handle **11**, the seal may also be used to pull the soft-projectile holder **14** into the firing position **30**. As the user pulls the handle **11** back and expands the volume of the air compression chamber **31**, air is sucked from the smaller diameter tube **27**. As the air is pulled from the smaller diameter tube **27**, the soft-projectile holder **14** is drawn back down the barrel **15** towards the firing position **30**.

Once the soft projectile holder **14** is in the firing position **30**, additional air may be sucked into the air compression chamber through a one way valve. However, a one way valve is not necessary and air may be sucked in through small imperfections in the seal between the plunger seal **24** and the seal around the soft-projectile holder **14**.

As may be seen by the embodiment shown in FIG. **5**, the smaller diameter tube **27** may be comprised of numerous tube components. Forming the smaller diameter tube **27** out of more than one piece may allow for a cheaper and more cost effective construction. Furthermore, because a portion of the smaller diameter tube **27** is required to be straight to form the barrel **15** and other portions of the small diameter tube **27** may traverse a tortuous path to conform to the inside of the gun, using different types of tube may be advantageous.

FIG. **6** illustrates an expanded cross-sectional view surrounding the firing position **30** of the projection device shown in FIG. **4**. The projection device **10** of the embodiment shown in FIG. **6** includes a magazine **50** that holds soft projectiles, such as ammunition formed from a SAP. The projection device **10** may include a loading mechanism **33** to ensure only a single soft projectile at a time is loaded from the magazine **50**. Numerous types of loading mechanisms may be used without departing from the scope of the present patent document. The loading mechanism **33** of the embodiment of FIG. **6** is explained below as an example of one type of loading mechanism that may be used.

The barrel portion **15** of the smaller diameter tube **27** has an opening **36** which provides access to the interior of the smaller diameter tube **27** directly above the firing position **30**. The opening **36** is large enough for a single soft projectile to fit through. The opening **36** allows the soft projectile to pass from the magazine **50** into the firing position **30** of the projection device **10**.

However, without the loading mechanism **33**, there would be no control over when the soft projectiles where allowed to descend into the firing position or how many soft projectiles descended into the firing position. Furthermore, without a loading mechanism **33**, soft projectiles would be able to drop into the firing position **30** behind the soft projectile holder **14**, which would potentially prevent the projection device **10** from working. The loading mechanism **33** controls the loading of soft-projectiles into the firing position and prevents unwanted loading by selectively obstructing the opening **36** in the barrel portion of the smaller diameter tube **27** directly above the firing position **30**.

The loading mechanism **33** shown in the embodiment of FIG. **6** comprises a plunger **35**, a spring **37**, and a plunger chamber **44**. The plunger **35** is a hollow cylinder that has an outer diameter slightly smaller than the inner diameter of the barrel **15**. The plunger chamber **44** is a portion of the smaller diameter tube **27** or barrel **15** just behind the firing position **30**. The plunger **35** is designed to telescope in and out of the plunger chamber **44**. The plunger is biased in its fully extended position by spring **37** and retained by an interference with the plunger chamber **44**.

The plunger **35** is positioned in the barrel **15** under the opening **36** and the magazine **50**. The plunger **35**, which is cylindrical in the present embodiment, includes a first flange **39** on the interior of its forward end and a second flange **41** on the exterior of its back end. A compression spring **37** is mounted inside the plunger **35** so that a first end abuts the first flange **39** and the second end extends back into a plunger

chamber **44**. The second end of the compression spring abuts a third flange inside the plunger chamber **44**.

In a preferred embodiment, the plunger **35** has a cylindrical design and the first, second, and third flanges have a small annular height in order to maintain the smaller diameter tube **27** and the barrel **15** substantially open to air flow.

When the user pulls the handle **11** of the projection device back in preparation for firing, a vacuum is pulled on the smaller diameter tube **27** causing the soft-projectile holder **14** to be drawn towards the back of the gun as explained above. As the soft-projectile holder **14** is pulled back by the vacuum, the soft-projectile holder **14** begins to push on the plunger **35** of the loading mechanism **33**. In turn, the plunger **35** telescopes back into the plunger chamber **44**, compresses the spring **37**, and allows the soft-projectile holder **14** to continue to be drawn backwards by the vacuum in the smaller diameter tube **27**.

In the preferred embodiment, the fully retracted position of the plunger **35** into the plunger chamber **44** is designed to be the fully compressed position of the spring **37**. In another embodiment, the plunger may interfere with a second portion of the plunger chamber **44** to restrict the retraction of the plunger **35** into the plunger chamber **44** to be where the soft-projectile holder **14** is positioned just slightly behind the opening **36** in the top of the barrel **15** (i.e., when the soft-projectile holder **14** is just behind the firing position **30**). Once the soft-projectile holder **14** is retracted to just behind the firing position **30**, the plunger **35** and/or soft-projectile holder **14** are/is no longer obstructing the opening **36** above the firing position **30** in the barrel **15** and a single soft-projectile may drop into the firing position **30** of the barrel **15**.

Preferably, the spring **37** maintains a constant bias on the plunger **35** in order to maintain the plunger in its fully extended position blocking the opening **36**. Once a vacuum is no longer being pulled on the smaller diameter tube **27** or the firing mechanism **33** has been released, the spring **37** forces the plunger **35** forward back into its steady state position blocking any additional soft-projectiles from entering the barrel **15**.

Preferably, the spring **37** has a sufficiently small spring constant to allow it to be retracted with the force generated from soft-projectile holder **14** as it is pulled back down the barrel **15** by the vacuum created when the user retracts the handle **11**. The spring constant should also be sufficiently small so that the spring does not cause the plunger **35** to force the soft-projectile holder **14** down the barrel **15** prematurely should a vacuum no longer pull the soft-projectile holder **14** backward. For example, if the user where to retract the handle **11** of the gun and then hold it for a period of time prior to releasing it, small leaks in the system may prevent the plunger **35** from continually being retracted in the plunger chamber **44**.

Preferably the compression spring **37** is also designed to bias the plunger **35** to maintain the plunger's position obstructing the opening above the firing position in the barrel **15** when a soft-projectile is not being loaded. The plunger **35** is retained in the obstructing position by the second flange **41** on the back of the plunger **35** which interferes with a flange on the inside of plunger chamber **44**.

Although the embodiment of FIGS. **4-6** illustrates a device **10** having a firing mechanism designed to use a combination of spring and air pressure projection device **10** may use any suitable type of firing mechanism. For example, the firing mechanism may rely exclusively on spring or air pressure. Alternatively, the firing mechanism may be a catapult type system, sling shot type system, bow style system or any other type of suitable acceleration system to launch the soft-projectile **16**. As another example, projection device **10** may accelerate the soft-projectile **16** or soft-projectile holder **14** by an accelerating mass, like the hammer of a gun, directly impacting the soft-projectile or soft-projectile holder. Furthermore, the embodiment of FIGS. **4-6** may all be set up to work with stored energy or work with only energy provided by a user without departing from the scope of the present patent document.

In the soft-projectile **16**, either through pneumatic force or mechanical impact, it is preferable to modify the durability of the soft-projectile to allow the soft-projectile to withstand the direct force of the firing mechanism. To this end, the properties of the soft-projectile may be modified to further adapt it to work with a direct force firing mechanism. For example and as explained above, the gel hardness of SAPs may be modified by changing their cross-link density. Thus, the projectiles **16** made from a SAP may be made harder to work with a direct force firing mechanism by increasing their cross-link density.

FIGS. **7A-7D** shows various views of a magazine **50**. The magazine **50** embodied in FIGS. **7A-7D** includes a locking mechanism **60** to prevent access to the interior of the magazine **50** except when the magazine **50** is mated to a projection device **10** or some other mating device designed to allow such access. For example, one such additional device may be a container designed to refill the magazine with additional hydrated rounds of SAP ammunition.

FIG. **7A** illustrates a perspective view of a magazine **50**. FIG. **7B** illustrates a side view of the magazine of FIG. **7A**. FIG. **7C** illustrates a bottom view of the magazine of FIG. **7A**. FIG. **7D** illustrates a cross-sectional side view of the magazine of FIG. **7A**.

In order to minimize the risk that objects other than the desired ammunition, such as soft-projectiles **16** made from a SAP are used with projection device **10**, complementary locking mechanisms **60** and **70** may be used as part of both the magazine **50** and the projection device **10**, respectively. The complementary locking mechanisms **60** and **70** are designed to prevent access to the interior of the magazine **50** and projection device **10**, respectively, except when the two are mated together, or another device with a corresponding locking mechanism. The locking mechanism **60** prevents loading of foreign objects into the magazine **50** and locking mechanism **70** prevents foreign objects from being directly loaded into the firing chamber of the projection device **10**. Numerous types of locking mechanisms may be used for complementary locking mechanisms **60** and **70** without departing from the scope of the present patent document. The complementary locking mechanisms **60** and **70** of magazine **50** shown in FIGS. **7A-7D** and projection device **10** shown in FIGS. **4-6** are explained below as examples of the types of complementary locking mechanisms that may be used for magazine **50** and projection device **10**, respectively.

Before explaining the operation of the complementary locking mechanisms **60** and **70**, however, it is noted that FIG. **8** illustrates, in a perspective view, complementary locking mechanism **70** of projection device **10**, or potentially another authorized mating device, in isolation. Although FIG. **8** depicts the mating component **70** as a separate component, the features of the complementary locking mechanism **70** in isolation, complementary locking mechanism **70** may be integrated into any device to which it is desired to mate magazine **50**, including, for example, projection device **10** or a magazine refill device.

The locking mechanism **60** of magazine **50** shown in FIGS. **7A-7D** includes an opening **52**. Corresponding locking mechanism **70** includes a corresponding opening **72** meant to

mate with the opening **52** of the magazine **50** when magazine **50** is engaged with complementary locking mechanism **70**.

FIG. **9** illustrates a cross-sectional view of magazine **50** engaged with locking mechanism **70**. When the two parts are not engaged, both the opening **52** in the locking mechanism **60** of magazine **50** and the opening **72** in the locking mechanism **70** are obstructed by trap doors **69** and **79**, respectively, slideably disposed behind the corresponding openings. For example, the trap door **69** of the magazine **50** is slideably contained within slot **64** of locking mechanism **60** of magazine **50** shown in FIGS. **7**D. Likewise, trap door **79** of locking mechanism **70** is slideably disposed behind opening **72** of locking mechanism **70** of projection device **10**. Preferably the trap doors **69** and **79** are biased by springs **65** and **75** to force them over their respective openings when the magazine **50** and projection device **10** are not engaged.

When the magazine **50** is correctly mated with the corresponding locking mechanism **70** of projection device **10** or other desired device, the trap doors **69** and **79** are both retracted against the biasing force of springs **65** and **75** so that they no longer block their respective openings **52** and **72**, and soft-projectiles may thus pass between the magazine **50** and projection device **10** or other corresponding device.

In the embodiment shown in the figures, the magazine **50** is initially mated to the corresponding locking mechanism **70** forward of its final position and is then slid back into its final position where a small tongue spring **66** snaps into a groove **76** provided on the corresponding locking mechanism **70**. The tongue spring **66** prevents the magazine **50** from accidently sliding forward and becoming disengaged from the corresponding locking mechanism **70** of projection device **10** or other mating device, during use. However, when the user desires to reload the magazine with additional super absorbent polymer projectiles **16**, the user may reverse the process by sliding the magazine forward so that it may removed from corresponding locking mechanism **70** of projection device **10**.

The tabs **58** located on the bottom of the magazine **50** correspond to a set of flanges **78** provided on corresponding locking mechanism **70** such that the magazine **50** must be initially engaged forward of its final position and then slid back into place. Once the magazine **50** is slid back into place on the corresponding locking mechanism **70**, the tabs **58** are disposed under the corresponding flanges **78**. The tabs **58** and the flanges **78** thus cooperate to further secure the magazine **50** to the corresponding locking mechanism **70**.

As may be seen from FIGS. **7**A-**7**C, magazine **50** includes a key **61**. As shown in FIG. **8**, the corresponding locking mechanism **70** also includes a key **71**. Furthermore, both the locking mechanism **60** of magazine **50** and the corresponding locking mechanism **70** have a mating slot **63** and **73** for the keys **61** and **71**, respectively. When the locking mechanisms **60**, **70** are initially mated, each of the keys **61** and **71** extends through corresponding slot **63** and **73**, respectively, on the other locking mechanism. More particularly, the key **61** located on the locking mechanism **60** of magazine **50** extends through the slot **73** at one end of the slot **73**, and the key **71** located on the corresponding locking mechanism **70** extends through the slot **63** on the locking mechanism **60** of the magazine **50** at one end of the slot **63**. Each of the keys **61**, **71** extends through the corresponding slot **63**, **73** and engages a key receiver in trap doors **69**, **79**, respectively. Each of the key receivers in trap doors **69**, **79** is specifically designed to mate with the corresponding key **61**, **71**. Accordingly, when the magazine **50** is slid back into its final mating position on the corresponding locking mechanism **70**, the key **61** on the locking mechanism **60** of the magazine **50** pulls open the trap door **79** on the corresponding locking mechanism **70**. Similarly, the key **71** located on the corresponding locking mechanism **70** pulls open the trap door **69** on locking mechanism **60** of the magazine **50**. Thus once the complementary locking mechanisms **60**, **70** are mated, both trap doors **69**, **79** are pulled back against the bias of their respective springs and the openings **52** and **72** are aligned and projectiles **16** may pass between without interference by the trap doors **69**, **79**.

Although as illustrated in FIGS. **7**A-**7**D and **8** and discussed above the keys **61**, **71** are shaped as a simple post and trap doors **69**, **79** contain a key receiver in the shape of a hole, more complicated key and key receiver combinations are possible. For example, similar to the sophisticated notches on a car key or house key, keys **61** and **71** may contain a more sophisticated design to further ensure that the trap doors **69**, **79** are not opened without the parts being engaged to an authorized mating component. Similarly, the mating key receiver for keys **61** and **71** may include the required sophistication to ensure they may operatively mate with keys **61**, **71**, respectively. Furthermore, more than one key may be incorporated into each part such that a plurality of keys must mate in order to release the trap door **69** or the trap door **79**.

In general, any type of keying system may be used to ensure that the openings **52** and **72** remain blocked and are only opened when complementary locking mechanisms **60**, **70** are mated with an approved corresponding device. As just one example, additional steps may be required such as turning or sliding an additional switch after the complementary locking mechanisms **60**, **70** are engaged to open trap doors **69**, **79**. In yet another embodiment, the opening and closing of the trap doors **69**, **79** may be controlled by electronics and a digital key may be exchanged when the locking mechanisms **69**,**79** are mated to signal to one or more trap door drivers to open the trap door **69**, **79** or allow the trap doors **69**, **79** to be opened.

In addition to preventing foreign objects from being loaded into the projection device **10** via the magazine **50**, in a preferred embodiment, a safety mechanism **100** may also be provided at the end of the barrel **15** to prevent foreign objects, or at least foreign objects larger than a predetermined size, from being loaded down the barrel **15** of the projection device **10**. For projection devices formed in the shape of a gun, a safety mechanism **100** at the end of the barrel **15** will minimize the likelihood that a foreign object can be loaded musket style down the barrel **15**.

FIG. **10** illustrates one embodiment of a safety mechanism **100** to prevent foreign objects from entering the barrel **15** while still allowing soft-projectiles **16** to exit barrel **15**. However, numerous other types of safety mechanisms may be used without departing from the scope of the present patent document. The safety mechanism **100** of the embodiment of FIGS. **10** and **11** is explained below as an example of one type of safety mechanism that may be used.

Safety mechanism **100** of the illustrated embodiment includes barrel cap **90**, stop **92**, shields **94**, triggers **96**, and springs **98**.

In the embodiment shown in FIGS. **4**-**6** and **10**, the soft-projectile holder **14** is slideably contained by the barrel **15**, but is not otherwise attached to the firing mechanism. At the distal end of the barrel **15**, stop **92** retains the soft-projectile holder **14** within a desired operating region of the barrel **15**.

In the embodiment of FIG. **10**, the stop **92** is slideably contained between the distal end of the barrel **15** and an annular flange of barrel cap **90**. The stop **92** is thus allowed to slide axially within the gap **93** provided by barrel cap **90**. The stop **92** in the embodiment shown in FIG. **10** is designed as a hollow cylinder. The circumference of the stop **92** is sized to

engage with the soft-projectile holder **14** so as to retain the soft-projectile holder within the barrel **15**. The inside radius of the stop **92**, however, is designed so as to let a soft-projectile **16** pass through. As noted above, barrel cap **90** also includes an annular flange to retain stop **92** in gap **93**.

The safety mechanism **100** shown in FIG. **10** also includes shields **94**, triggers **96**, and springs **98**. FIG. **11**, illustrates an end view down the barrel **15** of the projection device **10** of FIG. **10** including a safety mechanism **100**. As may be seen from FIG. **11**, a plurality of shields **94** are designed to cover the opening in the barrel **15** and prevent foreign objects from entering. The embodiment shown in FIGS. **10** and **11**, includes 3 pie shaped shields **94** that are spaced evenly at 120 degrees, however, any number of shields **94** may be used to cover the opening in the barrel **15**. In addition, the shields **94** may have other sizes or shapes so long as they cooperatively cover the opening in the barrel **15**.

In the embodiment shown in FIGS. **10** and **11**, shields **94** are connected to triggers **96**. Each shield **94** is connected to an individual trigger **96**. However, other embodiments may use a single trigger **96** to activate multiple shields **94**. Generally, any number of triggers **96** and shields **94** may be used in combination.

Triggers **96** are pivotally connected to the barrel cap **90**. Furthermore, each trigger **96** is biased by a spring **98** to the closed position. The shields **94** and triggers **96** are arranged with the springs **98** such that the shields rotate about the outer circumference of the barrel **15** outward and away from the center axis of the barrel **15**. In addition, the shields **94** and triggers **96** are operatively arranged with springs **98** such that the shields **94** may not rotate inward back into the barrel **15**. Because the shields may not rotate inward towards the center axis of the barrel **15**, access to the interior of the barrel **15** is prevented by the shields **94**.

The operation of the safety mechanism **100** when the projection device **10** launches a soft-projectile will now be described. As the soft-projectile holder **14** nears the end of the barrel, the soft-projectile holder **14** impacts stop **92**. As a result, stop **92** is slides within gap **93** of barrel cap **90** towards the annular flange provided in barrel cap **90**. By contrast, in the steady state condition, stop **92** is urged against the end of the barrel **15** by the spring bias of triggers **96**.

When the soft-projectile holder **14** impacts the stop **92**, the momentum stored in the soft-projectile holder **14** is transferred to the stop **92** and the stop is thus caused to slide forward in gap **93**. As stop **92** slides forward in gap **93**, the stop **92** engages the triggers **96**. Triggers **96** are shaped such that when the stop **92** engages triggers **96** it causes them to rotate outward as stop **92** slides axially within the barrel cap **90**. When stop **92** has slid axially to its full extent within gap **93** of barrel cap **90**, triggers **96** are caused to rotate enough to rotate the corresponding shields **94** outwardly away from the axis of the barrel **15** and allow a sufficient opening for a soft-projectile **16** to exit unscathed.

Once all the momentum of the soft-projectile holder **14** has been transferred into the stop **92**, the biasing force provided by springs **98** forces the triggers **96** to rotate back towards the axes of the barrel and return to their steady state position with the shields **94** covering the opening in the barrel **15**. The triggers **96** in turn force the stop **92** to slide back across gap **93** toward the distal end of barrel **15**. Stop **92** is held against the distal end of the barrel **15** ready for the next soft-projectile **16** to be launched.

FIG. **12** illustrates a hand gun embodiment of a projection device **10** designed to launch a soft-projectile. Projection device **10** is a smaller hand gun version of the projection device of FIG. **4**. The projection device **10** shown in FIG. **12** includes a magazine **50** and a handle **11**. The projection device **10** operates internally in a similar manner to the embodiment of FIG. **5**.

FIG. **13** illustrates another embodiment of a projection device **10** designed to launch a soft-projectile. Projection device **10** is a medium sized gun version of the projection device of FIG. **4**. The projection device **10** shown in FIG. **13** includes a magazine **50** and a handle **11**. The projection device **10** operates internally in a similar manner to the embodiment of FIG. **5**.

Although the inventions have been described with reference to preferred embodiments and specific examples, it will readily be appreciated by those skilled in the art that many modifications and adaptations of the methods and devices described herein are possible without departure from the spirit and scope of the inventions as claimed hereinafter. Thus, it is to be clearly understood that this description is made only by way of example and not as a limitation on the scope of the inventions as claimed below.

What is claimed is:

1. A device for projecting a soft-projectile made from a super absorbent polymer, the device comprising:

a feed chamber including a plurality of soft-projectiles having the same shape, each soft-projectile being formed from a hydrated super absorbent polymer, wherein the device is adapted to load a soft-projectile from the feed chamber to a firing position;

a firing mechanism operatively arranged to accelerate the soft-projectile made from a super absorbent polymer, from the firing position, down a barrel; and

a safety mechanism obstructing an end of the barrel and designed to prevent access to the interior of the barrel but allow a soft-projectile accelerated by the firing mechanism to exit the barrel.

2. The device for projecting a soft-projectile made from a super absorbent polymer of claim **1**, wherein the feed chamber is a removable magazine.

3. The device for projecting a soft-projectile made from a super absorbent polymer of claim **2**, further comprising a magazine interface including a locking mechanism between the magazine and the projectile device.

4. The device for projecting a soft-projectile made from a super absorbent polymer of claim **3**, wherein the locking mechanism includes at least one key.

5. The device for projecting a soft-projectile made from a super absorbent polymer of claim **3**, wherein the locking mechanism includes a slideable door operatively arranged to obstruct an opening designed to receive a soft-projectile.

6. The device for projecting a soft-projectile made from a super absorbent polymer of claim **5**, wherein the locking mechanism includes a key receiver.

7. The device for projecting a soft-projectile made from a super absorbent polymer of claim **6**, wherein the key receiver is located on a slideable door operatively arranged to obstruct an opening designed to receive a soft-projectile.

8. The device for projecting a soft-projectile made from a super absorbent polymer of claim **1**, wherein the soft-projectiles have a diameter of 10 millimeters or less.

9. The device for projecting a soft-projectile made from a super absorbent polymer of claim **1**, wherein the device is designed to use air pressure to launch the soft-projectiles.

10. The device for projecting a soft-projectile made from a super absorbent polymer of claim **1**, wherein the firing mechanism applies a force directly to the soft-projectile located in the firing position to accelerate the soft-projectile, from the firing position, down the barrel.

11. The device for projecting a soft-projectile made from a super absorbent polymer of claim 1, wherein the device is a toy.

12. The device for projecting a soft-projectile made from a super absorbent polymer of claim 1, wherein the device is in the shape of a gun.

13. A device for projecting a soft-projectile made from a super absorbent polymer, the device comprising:

a feed chamber including a plurality of soft-projectiles having the same shape, each soft-projectile being formed from a hydrated super absorbent polymer, wherein the device is adapted to load a soft-projectile from the feed chamber to a firing position; and

a firing mechanism operatively arranged to accelerate the soft-projectile made from a super absorbent polymer, from the firing position, down a barrel.

14. The device of claim 13, further comprising a plurality of shields obstructing an end of the barrel and designed to prevent access to the interior of the barrel but allow a soft-projectile accelerated by the firing mechanism to exit the barrel.

15. The device of claim 13, wherein the feed chamber is a removable magazine.

16. The device of claim 13, wherein the soft-projectiles have a diameter of 10 millimeters or less.

17. The device of claim 13, wherein the device is designed to use air pressure to launch the soft-projectiles.

18. The device of claim 13, wherein the firing mechanism applies a force directly to the soft-projectile located in the firing position to accelerate the soft-projectile, from the firing position, down the barrel.

19. The device of claim 13, wherein the device is a toy.

20. The device of claim 13, wherein the device is in the shape of a gun.

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