

**UNITED STATES INTERNATIONAL TRADE COMMISSION
Washington, D.C.**

Before the Honorable MaryJoan McNamara
Administrative Law Judge

In the Matter of

CERTAIN SOFT PROJECTILE LAUNCHING
DEVICES, COMPONENTS THEREOF, AMMUNITION,
AND PRODUCTS CONTAINING SAME

Inv. No. 337-TA-1325

**Commission Investigative Staff's
Markman Brief**

Respectfully submitted,

November 2, 2022

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HASBRO 2007
GEL BLASTER v. HASBRO
IPR2023-00301

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I. Introduction

In accordance with Order No. 6, Adopted Procedural Schedule (Mar. 21, 2022), the Commission Investigative Staff (“Staff”) respectfully submits this brief explaining its proposed constructions for the disputed claim terms in U.S. Patent No. 8,371,282 (“the ‘282 patent”), and U.S. Patent No. 8,640,683 (“the ‘683 patent”) (collectively, “Asserted Patents”).

The parties’ Joint Claim Construction Chart identified eight terms for construction. *See* EDIS Doc ID 782596 (Oct. 18, 2022). These eight terms remain in dispute.

Therefore, the analysis below is directed to the presently disputed claim terms. The Staff notes that insofar as fact and expert discovery has not yet been completed, it may seek to modify constructions proposed herein in light of future discovery.

II. Level of Ordinary Skill in the Art

The relevant time for assessing the level of ordinary skill in the art is the effective filing date of the patent. *Phillips v. AWH Corp.*, 415 F.3d 1303, 1313 (Fed. Cir. 2005) (en banc) (“We have made clear, moreover, that the ordinary and customary meaning of a claim term is the meaning that the term would have to a person of ordinary skill in the art in question at the time of the invention, i.e., as of the effective filing date of the patent application.”)

Factors to consider in determining the level of ordinary skill in the art include: (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. *See Env'tl. Designs, Ltd. v. Union Oil Co. of Cal.*, 713 F.2d 693, 696 (Fed. Cir. 1983). “These factors are not exhaustive but are merely a guide to determining the level of ordinary skill in the art.” *Daiichi Sankyo Co., Ltd. v. Apotex, Inc.*, 501 F.3d 1254, 1256 (Fed. Cir. 2007).

There are two Complainants: (i) Hasbro, Inc. (“Hasbro”), and (ii) Spin Master, Inc. (“Spin Master”). Spin Master adopted Hasbro’s definition of one of ordinary skill in the art. *See* Spin Master’s First Suppl. Response to Interrog. No. 33 (Oct. 25, 2022) (“Spin Master directs Respondents to Hasbro’s responses to this interrogatory, which Spin Master fully incorporates by reference.”). Hasbro put forward the following definition for the Asserted Patents:

Complainants propose that a person of ordinary skill in the art at the time of the ’282 and ’683 patents would have a bachelor’s degree in mechanical engineering, industrial design, or equivalent, with at least one year of relevant experience designing projectile launching systems but would also be a member of a team, which would include an 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. For both, equivalent work experience may substitute for educational experience, and vice versa.

Hasbro’s Suppl. Response to Interrog. No. 33 (Oct. 25, 2022).

In contrast, Respondents proposed the following definition:

The hypothetical person of ordinary skill in the art would be (i) an individual with 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 SAPs.

Respondents’ Joint Disclosure of Initial Contentions in Response to Complainants’ Common Interrog. Nos. 23 and 24 at 27 (Oct. 25, 2022).

Here, as to the educational level of the four inventors, Respondents contend that “[named inventor] Ronald Brawer has an MBA from City University of New York, and named inventor Michael Hoeting has an Industrial Design degree from the University of Cincinnati.” *Id.* The educational level of the two remaining inventors, Keith Meggs and Neil Hamilton, is currently unknown. *Id.*

As to the type of problems encountered in the art, the Asserted Patents note that:

- “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” JXM-0001 (‘282 patent) at 1:46–49.
- Paint ball guns and airsoft guns “are for adult use only due to the energy imparted to the projectile and the ability of the projectile to do serious harm.” *Id.* at 1:56–60.

Moreover, the Asserted Patents describes the patents’ purpose:

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.

Id. at 1:64–2:1. *See Best Medical Int’l, Inc. v. Elekta Inc.*, 46 F.4th 1346, 1353 (Fed. Cir. 2022)

(in discussing factors that may guide the fact finder in finding the appropriate level of skill in the art: “The patent’s purpose can also be informative.”)

The private parties’ proposed definitions are similar in that the person could have a Bachelor’s degree in Industrial Design or Mechanical Engineering. But Respondents’ definition does not require the person with such a degree to have any work experience. Moreover, without such education, Respondents’ person could be a toy designer with at least five years’ experience designing toys (including launchers). This seems reasonable in view of the evidence. Relatedly, Complainants note that “[f]or both, equivalent work experience may substitute for educational experience, and vice versa.” But it is unclear to the Staff what equivalent work experience means in this context.

Finally, Complainants’ require the person “be a member of a team, which would include an [sic] person with a bachelor’s in materials science, chemistry, or equivalent.” Similarly, Respondents’ require the person to have “access to a chemist knowledgeable regarding SAPs” *See, e.g., Indivior Inc. v. Dr. Reddy’s Lab’ys, S.A.*, 930 F.3d 1325, 1345 (Fed. Cir. 2019) (no

clear error in the court determining that a person of ordinary skill would be on a team with an engineer or scientist with certain experience). As an alternative, such concepts may be captured by indicating that such a person would have experience collaborating with others have such knowledge. Therefore, based on the current record, the Staff proposes the following definition:

A person of ordinary skill in the art would have (i) a Bachelor's degree in Mechanical Engineering, Industrial Design, or the equivalent, with at least one year of experience designing toys (including projectile launching systems), or (ii) at least five years of experience designing toys (including projectile launching systems), with both of (i) and (ii) having experience collaborating with individuals with material science or chemistry backgrounds.

Nevertheless, because the three proposed definitions are similar, the Staff does not believe that any differences will have an effect on the claim construction analysis.

III. Patents-In-Suit

A. Overview

The '282 patent, titled "Soft-Projectile Launching Device," issued on February 12, 2013, and names four inventors. JXM-0001 ('282 patent) at cover page.

The '683 patent (as depicted below) is divisional of the '282 patent and has the same title and same four named inventors as the '282 patent.¹ JXM-0003 ('683 patent) at cover page. The '683 patent issued on February 4, 2014, and is subject to a terminal disclaimer. *Id.*

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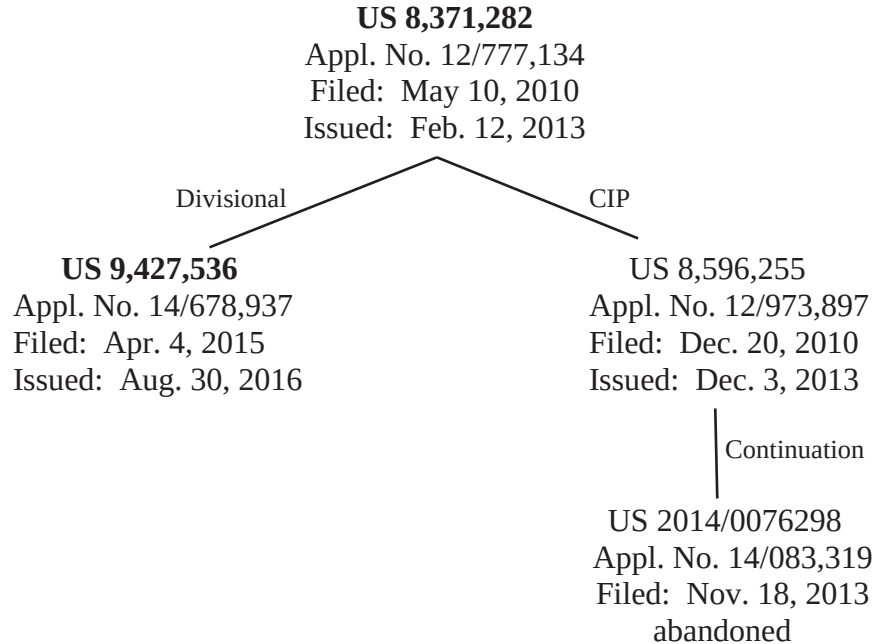
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¹ Therefore, the '282 patent and '683 patent share a common disclosure.



Interestingly, related U.S. Patent No. 8,596,255 has one named inventor, Keith Meggs, while the continuation application Appl. No. 14/083,319 (now abandoned) again identified the same four named inventors as the ‘282 and ‘683 patents.

Finally, Complainants contend that certain asserted claims were conceived as early as February 21, 2010, and reduced to practice no later than April 8, 2010. *See* Complainants’ Notice of Patent Priority Dates and Dates of Conception, EDIS Doc ID 780783 (Sept. 21, 2022). Based on the effective filing dates of the Asserted Patents, the Pre-AIA (America Invents Act) version of the statutory provisions apply.

B. Disputed Terms

1. “super absorbent polymer” (‘282 and ‘683 patents)

This term appears in claims 1, 7, 13, and 21 of the ‘282 patent; and in claims 1 and 10 of the ‘683 patent. The parties have proposed the following constructions:

Complainants	Respondents	Staff
Plain and ordinary meaning, i.e., “polymer that can absorb an extremely large amount of liquid relative to its own mass”	<u>PTT and Splat-R-Ball:</u> No construction necessary; term of art known to those skilled in the art at the time of the alleged invention <u>Gel Blaster:</u> Indefinite	No construction necessary; term of art known to those skilled in the art at the time of the alleged invention

This term—“super absorbent polymer” or SAP—in the context of the Asserted Patents has a meaning in the art as of the time of the alleged invention and is not indefinite. “The Supreme Court made clear that the factual components [of claim construction] include ‘the background science or the meaning of a term in the relevant art during the relevant time period.’” *Teva Pharms., Inc. v. Sandoz, Inc.*, 789 F.3d 1335, 1342 (Fed. Cir. 2015) (quoting *Teva Pharms. USA, Inc. v. Sandoz, Inc.*, 574 U.S. 318, 331, 135 S. Ct. 831, 841, 190 L. Ed. 2d 719 (2015)).

Beginning with the written description, the ‘282 patent indicates that “[s]uper absorbent polymers (SAPs) were first invented by the United States Department of Agriculture (USDA) in the 1960s and are commonly used in personal disposable hygiene products such as diapers, protective underwear, and sanitary napkins[.]” JXM-0001 (‘282 patent) at 3:37–41. The written description further clarifies:

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.

Id. at 3:41–42 (emphasis added). These “water absorbing polymers, classified as hydrogels, will absorb aqueous solutions through hydrogen bonding with the water molecule.” *Id.* at 4:51–53.

These water absorbing polymers or hydrogels were understood in the literature to be super absorbent polymers:

Water-absorbent polymers or hydrogels, sometimes defined as superabsorbent polymers (SAP) in the literature, are water-insoluble hydrophilic polymers, able to swell and absorb amounts of water, saline solutions, or physiological fluids as high as 10–1000 times their own weight. They consist of polyelectrolytes or other highly hydrophilic polymeric matrices, usually bearing crosslinking sites along the macromolecular chains in order to avoid

SXM-0008 (Water-Absorbent Polymers: A Patent Survey) at 607 (emphasis added). And the inventors noted that “SAP's can be constructed that would be considered ‘highly compliant’ by industry standards.” JXM-0001 (‘282 patent) at 4:16–17.

Therefore, “super absorbent polymer” is a term of art that was used by persons of skill in the relevant art at the time of the alleged invention. It follows, based on this evidence, that because “the scope of a claim would be reasonably ascertainable by those skilled in the art, then the claim is not indefinite.” *Bose Corp. v. JBL, Inc.*, 274 F.3d 1354, 1359 (Fed. Cir. 2001). Therefore, the Gel Blaster respondents’ argument that the term is indefinite fails.

2. Preamble: “Ammunition configured for use with a projectile launcher comprising” (‘282 patent)

The preamble of claim 1 of the ‘282 patent is at issue. Claims 2–21 depend from independent claim 1. Complainants are asserting claims 3, 6, 8, 13–15, 17, 19–21. The parties have proposed the following constructions:

Complainants	Respondents	Staff
Limiting	Preamble of claim 1 is not limiting as to claims 6, 8, 13, 14, 15, 17, 19, 20, and 21 Preamble of claim 1 is limiting for dependent claim 3	Limiting

Respondents agree that the preamble of claim 1 is limiting as to dependent claim 3 (and presumable unasserted, dependent claim 2). Yet Respondents maintain that the same preamble is not limiting as to asserted claims 6, 8, 13, 14, 15, 17, 19, 20, and 21 (and presumably unasserted, dependent claims 4, 5, 7, 9–12, 16, 18, 20, and 21).

However, the intrinsic evidence and Federal Circuit precedent do not support Respondents’ twisted position. The preamble discloses a fundamental characteristic of the claimed invention (i.e., the super absorbent polymer projectiles are *configured for use* with a projectile launcher), and provides antecedent basis for later claim limitations.

Whether a preamble is limiting is “determined on the facts of each case in light of the overall form of the claim, and the invention as described in the specification and illuminated in the prosecution history.” *Applied Materials, Inc. v. Advanced Semiconductor Materials Am., Inc.*, 98 F.3d 1563, 1572–73 (Fed. Cir. 1996). A preamble limits the claimed invention if it recites essential structure or steps, or if it is “necessary to give life, meaning, and vitality” to the claim. *Pitney Bowes, Inc. v. Hewlett-Packard Co.*, 182 F.3d 1298, 1305 (Fed. Cir. 1999). If the claim uses the preamble only to state a purpose or intended use for the invention, then the preamble is not limiting. *Catalina Mktg. Int’l, Inc. v. Coolsavings.com, Inc.*, 289 F.3d 801, 808 (Fed. Cir. 2002).

Here, the field of the invention, summary of the invention, detailed description, figures, and generally the title of the Asserted Patents describe the invention as a projectile launcher that launches projectiles made from super absorbent polymer. JXM-0001 ('282 patent) at 1:6–9 (“the present patent document relates to soft-projectile launching devices that launch super absorbent polymer projectiles”), 1:66–2:1 (“a projectile launching device is provided that launches projectiles made from super absorbent polymers.”), 3:45–48 (“The present patent document discloses and teaches projectile launching devices . . . that use projectiles formed from a super absorbent polymer (SAP).”).

The applicants did not invent projectile launchers. *Id.* at 1:13–14 (“Children have a variety of different types of projectile launching toys available to them.”). Nor did they invent SAPs. *Id.* at 3:37–42 (“Super absorbent polymers (SAPs) were first invented by the United States Department of Agriculture (USDA)”). Instead, based on the intrinsic evidence, the essence of the invention is this combination—a projectile launcher that launches projectiles made from super absorbent polymer.

Therefore, the preamble of claim 1 embodies the essence of the claimed invention. *See Proveris Sci. Corp. v. Innovasystems, Inc.*, 739 F.3d 1367, 1373 (Fed. Cir. 2014) (“the preamble of claim 3 is the only reference in any independent claim to the inventive concept of This fact alone is likely sufficient to support a conclusion that the preamble is limiting.”). This is highlighted by the prosecution of application claim 31 (issued claim 1).

In particular, on March 16, 2012, the applicants amended the application and added the following new application claim 31 (issued claim 1):

31. (New) Ammunition for a projectile launcher comprising:

a plurality of soft-projectiles having the same shape, each soft projectile being formed from hydrated super absorbent polymer.

JXM-0002 ('282 File History), First Preliminary Amendment at 3 (PDF p. 73) (Mar. 16, 2012).

On April 13, 2012, the Examiner issued an Office Action subjecting application claim 31 (issued claim 1), and other claims, to a restriction requirement. *Id.*, Office Action at 1–2 (PDF pp. 86–87) (Apr. 13, 2012). On October 8, 2012, the Examiner conducted a telephone interview with applicants' counsel. *Id.*, Notice of Allowability at 2 (PDF p. 173) (Oct. 11, 2012). With authorization from applicants' counsel, the Examiner then amended the preamble of application claim 31 (issued claim 1) and allowed the claim:

31. Ammunition configured for use with a projectile launcher comprising:

a plurality of soft-projectiles having the same shape, each soft projectile being formed from hydrated super absorbent polymer.

32. The ammunition of claim 31, wherein the ammunition is disposed within a feed chamber of a the projectile launcher.

Id. (emphasis added). The Examiner also amended application claim 32 (issued claim 2), thereby indicating that the preamble of claim 1 provided antecedent basis for the term “projectile launcher.”

Amending the preamble before allowing the claim is significant and captures an important aspect of the invention—a projectile launcher and SAPs configured for use with the launcher. *See Computer Docking Station Corp. v. Dell, Inc.*, 519 F.3d 1366, 1375 (Fed. Cir. 2008) (finding that terms of the preamble limited the scope of the invention because they “clearly recite a necessary and defining aspect of the invention”). The amendment was clearly made to convince the Examiner to allow the claim. *Cf. In re Cruciferous Sprout Litig.*, 301 F.3d 1343, 1347–48 (Fed. Cir. 2002) (holding that preamble was limiting in light of arguments made

during prosecution “show[ing] a clear reliance by the patentee on the preamble to persuade the Patent Office that the claimed invention is not anticipated by the prior art”).

In addition, the amended preamble no longer recites the purpose or intended use (i.e., “for . . .”), but rather describes a fundamental characteristic of the claimed invention and informs the meaning of other claim limitations. *See, e.g., Deere & Co. v. Bush Hog, LLC*, 703 F.3d 1349, 1358 (Fed. Cir. 2012) (“Unlike non-limiting preamble terms, “rotary cutter deck” does not merely state a name or a use for the claimed box section. Rather, the term describes a ‘fundamental characteristic of the claimed invention’ that informs one of skill in the art as to the structure required by the claim.”); *Poly-Am., LP v. GSE Lining Tech., Inc.*, 383 F.3d 1303, 1310 (Fed. Cir. 2004) (construing preamble as limiting where it disclosed a “fundamental characteristic of the claimed invention”).

For example, the preamble informs that the “hydrated super absorbent polymer” recited in the body of claim 1 must be configured for a projectile launcher. The written description broadly describes projectile launchers as being “a bow, crossbow, sling shot, handgun, machine gun, futuristic weapon, catapult, or shaped as any other type of weaponry.” JXM-0001 (‘282 patent) at 4:67–5:3. Moreover, as required by dependent claim 7, the SAP must be configured such that it “has a cross linking density sufficient to prevent the soft-projectiles from breaking apart when launched from the projectile launcher.” *Id.* at claim 7 (emphasis added).

The written description supports the notion that the SAPs can be configured or designed for a projectile launcher:

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

Id. at 3:62–65. In other words, the preamble defines the scope of the claims. For example, with respect to claim 1, it states that the SAP is configured for “a projectile launcher.” And with respect to claim 7, the preamble states that the SAP is configured (i.e., has a certain cross linking density) to prevent it from “breaking apart when launched from the projectile launcher.”

Finally, as already noted, the preamble provides antecedent basis for claim limitations in certain dependent claims. In particular, dependent claims 2, 3, and 7 refer to “the projectile launcher.” And dependent claims 2 and 8 refer to “the ammunition” of the preamble. Although not a model of clarity, because claim 8 refers to the “ammunition” of the preamble, the claim’s recitation of “projectile launcher” could also be referring to the “projectile launcher” of the preamble. There is thus sufficient evidence so find that the preamble is limiting not only as to claim 1 but all dependent claims. *See C.W. Zumbiel Co. v. Kappos*, 702 F.3d 1371, 1385 (Fed. Cir. 2012) (the Federal Circuit noted “that the preamble constitutes a limitation when the claim(s) depend on it for antecedent basis”).

The Staff expects the Respondents to rely on certain District Court opinions to support their position that the preamble should only be limiting as to certain limitations in the dependent claims. But Respondents did not (and presumably could not) identify any Federal Circuit precedent that supports their position. Instead, recent Federal Circuit case law appears suggest the opposite.

For example, in *Bio-Rad Labs., Inc. v. 10X Genomics Inc.*, the Federal Circuit was “disinclined to sanction finding a preamble ‘partially’ limiting by splicing it as the district court did” based on District Court’s reasoning that preamble was limiting only to the extent that it provided an antecedent basis for certain claim terms. 967 F.3d 1353, 1371 (Fed. Cir. 2020).

And in *Deere & Co. v. Bush Hog, LLC*, the Federal Circuit found a phrase in the preamble limiting as to claim 1 (and therefore all dependent claims) because of the intrinsic evidence and the fact that the phrase provided antecedent basis for the same phrase in one dependent claim. 703 F.3d 1349, 1357–58 (Fed. Cir. 2012).

Thus, reading the patent as a whole, the inventors relied on the preamble to define the scope of the invention, and relied on it to provide antecedent basis for a number of claim limitations in the dependent claims. As such, the preamble of claim 1 should be construed as limiting.

3. “the super absorbent polymer has a cross linking density sufficient to prevent the soft-projectiles from breaking apart when launched from the projectile launcher” (’282 and ’683 patents)

This term appears in claims 7 and 13 of the ’282 patent; and in claim 10 of the ’683 patent. Claim 13 of the ’282 patent and claim 10 of the ’683 patent are being asserted here. The parties have proposed the following constructions:

Complainants	Respondents	Staff
No construction needed	No construction needed	Indefinite

Section 112 requires that “[t]he specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.” 35 U.S.C. § 112, ¶ 2. “If a claim is indefinite, the claim, by definition, cannot be construed.” *Enzo Biochem, Inc. v. Applera Corp.*, 599 F.3d 1325, 1332 (Fed. Cir. 2010). A claim fails to satisfy this statutory requirement and is thus invalid for indefiniteness if its language, when read in light of the specification and the prosecution history, “fail[s] to inform, with reasonable certainty, those skilled in the art about the scope of the invention.” *Nautilus, Inc. v. Biosig Instruments, Inc.*, 572 U.S. 898, 901 (2014).

However, “the certainty which the law requires in patents is not greater than is reasonable, having regard to their subject-matter.” *Id.* at 910 (citation omitted). The definiteness standard must allow for “some modicum of uncertainty” to provide incentives for innovation but must also require “clear notice of what is claimed, thereby apprising the public of what is still open to them.” *Id.* at 909 (internal quotation marks and citations omitted).

“When a proposed construction requires that an artisan make a separate infringement determination for every set of circumstances in which the composition may be used, and when such determinations are likely to result in differing outcomes (sometimes infringing and sometimes not), that construction is likely to be indefinite.” *Halliburton Energy Servs., Inc. v. M-I LLC*, 514 F.3d 1244, 1255 (Fed. Cir. 2008) (“under Halliburton’s proposed construction in this case, an artisan would not know from one well to the next whether a certain drilling fluid was within the scope of the claims because a wide variety of factors could affect adequacy (formation geology, wellbore size, depth, angle, etc.).”).

Here, the multiple factors or variables within the relevant claims renders them indefinite. For example, dependent claim 13 recites:

1. Ammunition configured for use with a projectile launcher comprising:
a plurality of soft-projectiles having the same shape, each soft projectile being formed from **hydrated super absorbent polymer**.
8. A projectile launcher including the ammunition of claim 1 disposed within a feed chamber of the projectile launcher, and wherein the projectile launcher is adapted to load a soft-projectile from the feed chamber to a firing position.
13. The projectile launcher of claim 8, wherein the super absorbent polymer has a **cross linking density** sufficient to prevent the soft-projectiles from breaking apart when launched from the **projectile launcher**.

JXM-0001 (‘282 patent) at claim 1, 8, 13 (emphasis added).

“The written description part of the specification itself does not delimit the right to exclude. That is the function and purpose of claims.” *Markman v. Westview Instruments, Inc.*, 52 F.3d 967, 980 (Fed. Cir. 1995) (en banc). “[A] claim is indefinite if its language might mean several different things and no informed and confident choice is available among the contending definitions.” *Media Rights Techs., Inc. v. Capital One Fin. Corp.*, 800 F.3d 1366, 1371 (Fed. Cir. 2015) (internal quotations marks omitted).

Here, multiple factors affect the scope of claim 13:

- How the SAP is **hydrated**: “A SAP’s ability to absorb water is a factor of the ionic concentration of an aqueous solution.” *Id.* at 4:53–55;
- The composition of the **SAP**: “SAP projectiles can also be designed to break down at different pressures based on their composition.” *Id.* at 3:62–63; *see also* SXM-0008 (Water-Absorbent Polymers: A Patent Survey) at 608 (grouping SAPs cited in patent literature into three main classes based on their chemical structure);
- The **cross linking density** sufficient to prevent the soft-projectiles from breaking apart: “different SAP’s with different cross-link densities may be used.” *Id.* at 4:14–16; and
- The type of **projectile launcher**: The projectile launcher “can be a bow, crossbow, sling shot, handgun, machine gun, futuristic weapon, catapult, or shaped as any other type of weaponry.” *Id.* at 4:67–5:3.

Therefore, the claim fails to inform with reasonable certainty those skilled in the art about the scope of the invention. For example, one of ordinary skill in the art would not be able to design a product that falls outside the claim scope. In other words, what type of structure should the projectile launcher have; what cross linking density should the SAP have; and how long should the SAPs be hydrated and what should the PH of the water be. “Indeed, if a person of ordinary skill in the art cannot discern the scope of a claim with reasonable certainty, it may be because one or several claim terms cannot be reliably construed.” *Cox Commc’ns, Inc. v. Sprint Commc’n Co. LP*, 838 F.3d 1224, 1232 (Fed. Cir. 2016).

Finally, “examples in the specification may be used to inform those skilled in the art of the scope of the invention with reasonable certainty—thus demonstrating that the term is not indefinite—without being directly construed into the claim.” *Guangdong Alison Hi-Tech Co. v. Int’l Trade Comm’n*, 936 F.3d 1353, 1363 (Fed. Cir. 2019). But here, the written description fails to disclose any examples of a hydrated SAP having a certain cross linking density that does not break apart when launched from a certain projectile launcher.

At bottom, because the boundaries of the protected subject matter are not clearly delineated and the scope is unclear, dependent claim 13 of the ‘282 patent and dependent claim 10 of the ‘683 patent are indefinite.²

4. “a firing mechanism that directly applies a force to” a soft-projectile/the ammunition (‘282 and ‘683 patents)

This term appears in asserted dependent claim 17 of the ‘282 patent; and in asserted dependent claim 14 of the ‘683 patent. The parties have proposed the following constructions:

Complainants	Respondents	Staff
Plain and ordinary meaning, i.e. “a firing mechanism that directly applies a force to a soft-projectile”	“a firing mechanism that directly applies a force to a soft-projectile (not via an intermediary)”	Plain and ordinary meaning

The claim language here cannot be more straightforward.

Respondents, however, are seeking to inject a negative claim limitation into the analysis based on a different claim limitation: “a firing mechanism that indirectly applies a force.” JXM-0001 (‘282 patent) at claim 18 (emphasis added); JXM-0003 (‘683 patent) at claim 15 (emphasis added).

² To the extent necessary, the Staff expects forthcoming expert discovery will provide additional evidence to support the Staff’s position.

The claims containing this “indirectly” limitation are no longer asserted, but the Complainants originally proposed that the limitation be construed according to its plain and ordinary meaning to mean “a firing mechanism that applies a force to a soft-projectile via an intermediary.” As an example, the Complainants pointed to holder 14 shown in Figure 1 below.

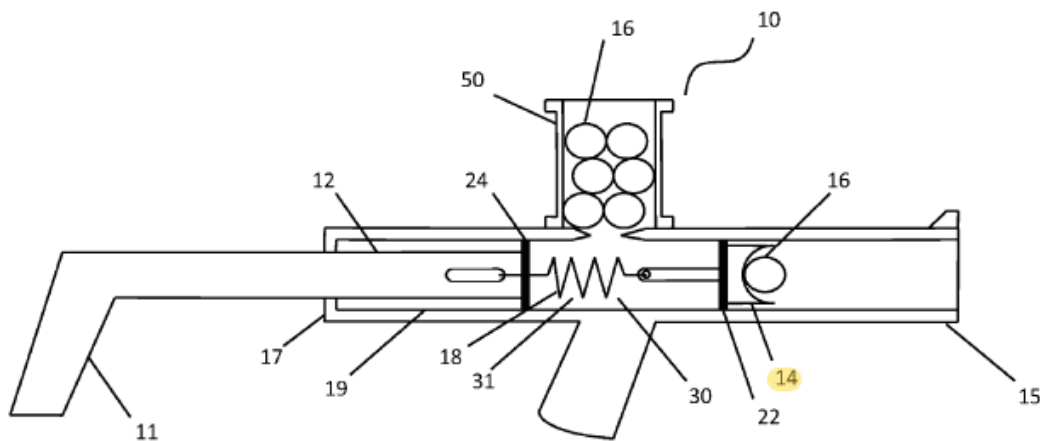


FIG. 1

JXM-0001 (‘282 patent) at Fig. 1 (emphasis added); *see also id.* at 7:25–28 (“the soft-projectile holder 14 also helps transfer the energy of the firing mechanism into the motion of the soft-projectile 16.”).

As to the “directly” limitation at issue here, Complainants have argued that the “soft-projectile holder 14 is not a requirement.” *Id.* at 7:6–8’ *see also Kaneka Corp. v. Xiamen Kingdomway Group Co.*, 790 F.3d 1298, 1305 (Fed. Cir. 2015) (“Although the specification does not specifically define the term [], the appropriate definition can be ascertained from the specification.”).

Relying on Complainants’ construction of the “indirectly” limitation (no longer at issue), Respondents are seeking to introduce a negative limitation (i.e., “not via an intermediary”) into the construction of the “directly” limitation. But rather than provide additional clarity

concerning the “directly” limitation, which is clear on its face, Respondents are attempting to define the “directly” limitation according to what it is not. *See Medicines Co. v. Mylan, Inc.*, 853 F.3d 1296, 1308 (Fed. Cir. 2017) (appellant “repeatedly criticizes the court’s negative construction as failing to define what “efficient mixing” is, as opposed to what it is not. Although there is no per se rule against negative constructions, [appellants’] argument carries some force.”).

Moreover, Respondents’ approach potentially confuses the infringement and invalidity analysis. The Staff notes that the claims at issue are open-ended (“comprising”) and the dispute appears to be more a factual dispute about what may constitute a firing mechanism that “directly applies a force to” a soft-projectile/the ammunition. Therefore, the claim limitation should be construed according to its plain and ordinary meaning.

5. “the absorbency of the super absorbent polymer is sufficiently limited to allow the soft-projectiles to be launched from the projectile launcher without breaking apart” (‘282 patent)

This term appears in asserted dependent claim 21 of the ‘282 patent. The parties have proposed the following constructions:

Complainants	Respondents	Staff
No construction needed	No construction needed	Indefinite

Claim 21 of the ‘282 patent is indefinite for the same rationale that claim 13 of the ‘282 patent and claim 10 of the ‘683 patent are indefinite. Instead of reciting “a cross linking density sufficient to prevent . . . ,” here the claim recites “the absorbency of the super absorbent polymer is sufficiently limited . . .” JXM-0001 (‘282 patent) at claim 21. The written description notes that the “total absorbency and swelling capacity of a SAP varies depending on the degree of cross-linking within the polymer.” *Id.* at 3:65–67. Thus, for the reasons discussed above in the

context of the earlier claims, a person of ordinary skill would be unable to determine the metes and bounds of claim 21 as well.

November 2, 2022

Respectfully submitted,

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CERTIFICATE OF SERVICE

The undersigned certifies that on November 2, 2022, he caused the foregoing **Commission Investigative Staff's Markman Brief** to be submitted to Judge MaryJoan McNamara (McNamara337@usitc.gov) and to be served upon the parties (one copy each) in the manner indicated below.

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Water-Absorbent Polymers: A Patent Survey

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Water-Absorbent Polymers: A Patent Survey

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1. INTRODUCTION

Water-absorbent polymers or hydrogels, sometimes defined as superabsorbent polymers (SAP) in the literature, are water-insoluble hydrophilic polymers, able to swell and absorb amounts of water, saline solutions, or physiological fluids as high as 10–1000 times their own weight. They consist of polyelectrolytes or other highly hydrophilic polymeric matrices, usually bearing crosslinking sites along the macromolecular chains in order to avoid

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dissolution. These polymers generally contain carboxylic groups that are in equilibrium with their dissociated form in the presence of water or carboxylate groups. The polymer coils extend themselves and widen in consequence of the electrostatic repulsion of negative charges. Carboxylate groups are also able to interact through hydrogen bonding with additional quantities of water. The presence of crosslinking allows swelling of the three-dimensional network and gel formation without polymer dissolution.

SAP cited in the patent literature can be grouped into three main classes based on their chemical structure:

1. Crosslinked poly(acrylate)s or poly(acrylamide)s
2. Cellulose- or starch-acrylonitrile graft copolymers
3. Crosslinked maleic anhydride copolymers

Other hydrophilic polymers, like poly(ethylene oxide), poly(vinyl alcohol), and poly(*N*-vinylpyrrolidone), have been used as SAP after treatments aimed to prevent them from dissolving, such as crosslinking or blending.

Desired features of SAP are several, depending strictly on the final use of the material. SAP should have high water absorbency and retention (they should absorb and hold high amounts of fluid) even under load or from other saturated materials ("suction power"); high water absorption rate (high amount of fluid absorbed per unit of time); good gel strength after absorption (the material should not become slimy and flow away); for some applications the fluid absorption should be reversible (the polymer should be able to absorb and release the fluid several times); further, the polymer morphology is important in many applications. Finally, they must be atoxic, they must not release traces of unreacted monomers, and monomers and production process costs should be low.

In practice, it is difficult for a polymer to meet all these requirements simultaneously. For instance, by increasing the crosslinking degree, the absorption rate and the gel strength increase as well but the absorption capacity decreases. Hence, the efforts of industrial research groups are addressed to find a better compromise among the several properties and effects.

Absorbent polymer properties performances are evaluated according to different methods, depending on the patent. Absorption capacity is measured by putting a polymer sample in water for a time sufficient to saturate it and then weighing the gel obtained. "Absorption capacity," "gel capacity," "water absorbency," "ratio of absorption," "water retention value," and "swell index," are some of the commonly used definitions. They represent either the weight ratio between swollen polymer and dry polymer or the weight ratio between the absorbed water (swollen polymer weight minus dry polymer) and dry polymer. Because the dry polymer weight is much less

than the swollen polymer weight, in practice the two figures coincide. In some cases, values are reported as percent instead of as a ratio. The same definitions are also adopted for saline or physiological solutions (synthetic urine). Saline solution is customarily 0.9–1.0% or 0.27–0.3 M aqueous NaCl. A typical synthetic urine is a water solution containing about 0.8% NaCl, 0.06% CaCl_2 , 0.1% MgSO_4 heptahydrate, and 2% urea [57]. Another reported synthetic physiological test fluid contains 0.8% sodium carboxymethylcellulose, 8% glycerin, 1% NaCl, and 0.4% NaHCO_3 [33]. In some cases, artificial blood is used for tests [124]. Water absorption capacity is usually one order of magnitude greater than saline solution absorption capacity.

Absorption rate values can be expressed in two ways: either through the amount of fluid absorbed by a weighed amount of the polymer in a fixed short time or through the time required by the polymer sample to absorb a given amount of fluid; the two parameters are in a contradictory relationship. In some cases the test is accomplished under variable applied pressure. For this reason, in the following, polymer absorption rates will be reported referred to the absorption rates of comparative polymers whose preparation is reported in the same patent. In particular, the ratio between the amount of fluid absorbed in a fixed time by the polymer of the invention and the amount absorbed by a reference polymer prepared in the same way except for the elements which represent the innovation is reported; if the patent considers the time of absorption instead of amounts, as explained above, the ratio will obviously be reversed. In this way, a value greater than 1 always means an improvement in respect to prior art materials.

Gel strength measurement methods are even more exotic; in many cases a qualitative observation is preferred to a gel strength value. Examples are the maximum diameter of a steel ball able to settle through the gel, the amount of gel free-flowing through a screen, or the pressure to be applied to the gel in order to force it to flow through a certain screen.

The most important application of SAP is for personal care and hygienic products manufacture (disposable diapers, sanitary napkins, towels, sponges, surgical pads, etc.). In this case the nontoxicity of the material is the dominant requirement; the rate of fluid absorption is also very important, particularly under pressure. SAP are also used for dehydrating oils and fuels (for this application the absorption capacity is crucial), as sludge coagulants and thickening agents, and as release control agents for pharmaceuticals or agrochemicals. Polymers having high water-absorption characteristics have been used for contact lenses and ink-receptive layers for transparent imageable materials manufacture.

The aim of this survey is to provide an up-to-date review on the state of the art concerning the industrial research activities about SAP based on

scarcely accessible patent literature. It covers all the published United States (US), European (EP), and world (WO) patents on both chemical and applicative aspects in SAP production appearing in *Chemical Abstracts* on-line data bank through Volume 119, 1993; patents cited as references in the main documents are also considered. Patents are ordered in the reference section chronologically, and they are discussed in the appropriate section.

2. SYNTHESIS AND POSTTREATMENT OF SUPERABSORBENT POLYMERS

2.1. Acrylic Superabsorbent Polymers

Superabsorbent polymers based on acrylic comonomers are generally synthesized through free-radical polymerization of acrylic or methacrylic acids, esters, amides, or salts either in water or in water/oil dispersions (less often in organic solvents). The term “(meth)acrylic” used in the following means either “acrylic” or “methacrylic.” Other unsaturated comonomers, such as maleic, fumaric, or itaconic derivatives, vinyl substituted sulfonic or ammonium salts, are occasionally used. Very often, but not always, polymer chains are crosslinked by using suitable crosslinking agents. A partial saponification stage of the polymer obtained with strong alkali is sometimes included in the process when esters or amides are the comonomers, with the aim to better refine the hydrophilic properties of the material. Absorbent properties of absorbent poly(acrylate)s are reported in Table 1. For a detailed study on SAP synthesis, see Reference 315.

Thus, type and concentration of monomers, reaction temperature, solvents, initiators, type and amount of surface-active agent, type and amount of crosslinking agent, and methods of drying are the parameters that can be changed in order to improve polymer properties.

2.1.1. Synthetic Procedures

In the oldest patents, polymerization of acrylic monomers was customarily carried out in water. Redox systems (e.g., persulfate/sulfite), azo compounds, or peroxides were the commonly used free-radical initiators.

A patent reports a method to polymerize an acrylamide/partially neutralized acrylic acid solution using high-energy ionizing radiation [91]. Crosslinking takes place simultaneously with polymerization.

Employing a thiosulfate instead of a sulfite in initiator systems is useful to moderate initial polymerization rates without adversely affecting polymer properties [242].

TABLE 1

Absorption Properties of Absorbent Poly(Acrylate)s [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
91			83.2		
242			40		
279			45.6	(48.7)	
265	835	(645)	51.3	(39.7)	
102			60		
137, 156, 158	1360		102		
166	610		65		
183	450		60		
143, 174, 180	980		96		
177, 201, 207, 230					1.58
247, 254			69.5	(48)	
297			67	(51)	4.25
305	470	(260)	55	(44)	
238			44.4		
139			70		
259			45		
248	860				
292			47		
59			75		
74	500	(250)			
107	1250	(520)	120	(50)	
179			90	(47)	3.21
160			85		
178			85	(90)	6.06
195			82	(85)	6.83
124			68	(60)	1.31
238			44.4		
212			52		
182			90		
277	> 300				
300			93	(92)	
312			42.5	(42.5)	
193			60.3		
162	180		22		

(continued)

TABLE 1. Continued

References	Water absorption capacity (g/g polymer)		Saline or physiological solution absorption capacity (g/g polymer)		Absorption rate ratio
225			80.5	(48.5)	
239	41.5	(15.6)	47.9	(48.5)	
188			55		
187	3403		147		
53			60		
47			95		
67, 70			60		
278	1900	(1024)	118	(25)	
135	98.8	(22.4) ^a			
305	470	(260)	55	(44)	
71			29.4		
294	120	(solub.)			
96	163				1.57
223	750				
55			70		
139			70		
218	300				
136	750	(680)	104	(110)	
144	598	(540)	108	(89)	2.32
198			42		
244	100				
241			17		
264			50		
43, 49, 50, 51, 54			98		
120	1250				
130	750	(550)	85	(60)	2.70
133	1300	(520)	116	(11)	4.26
69, 81, 85			34	(11.2)	
164	389	(450)	60.5	(62)	5.24
311	1282	(581)	89.9	(42.1)	0.49
194, 210			66	(60)	1.63
262			47	(39)	
148	158		31		
149	44		31		
240			57	(12.5)	2.12
184	490		45		
199	590	(610)	59	(59)	3.70
58			11.4	(2.4)	5.00
255			65		

TABLE 1. Continued

References	Water absorption capacity (g/g polymer)		Saline or physiological solution absorption capacity (g/g polymer)		Absorption rate ratio
271	1124	(512)	98	(47)	3.28
314			60	(35)	
297			67	(51)	4.25
203			55	(39)	1.70
204					1.29
263			67	(65)	1.00
215			67	(61)	0.96
138			31		
227			45		
216			62	(53)	
202			68		
161	8.3	(3.2)			2.22
41	794				
303			44		
122			25	(16)	

^apH 3 solution.

An initiator redox system, organic peroxide/erythorbic acid, is described that allows initiation of polymerization at lower temperatures as compared with more traditional systems [279], thereby decreasing the amount of heat that must be removed at high temperatures. The initial reaction temperature lies in the 20 to 30°C range, values unsuitable for persulfate/thiosulfate and similar systems. Hypophosphite salts added to the polymerization mixture give poly(acrylate) with improved gel strength and absorbent properties [265].

Storage-stable poly(acrylate)s have been obtained by employing an initiator system not based on peroxides [26]. It consists of sodium bisulfite and sorbitol or sorbitol monostearate. In the second case, the organic derivative also acts as an emulsifier.

Three patents [87, 127, 102] describe a polymerization process consisting in mixing water with neutralized acrylic acid, other (meth)acrylic comonomer(s), a crosslinking agent, a dispersant, and a photoinitiator [2,2-dimethoxy-2-phenylacetophenone, 4,4'-bis(diethylamino)benzophenone, 2-hydroxyethylacetophenone]. The mixture is spread to a desired thickness on a substrate (polyethylene, Mylar), and the liquid film is exposed to UV irradi-

ation until polymerization takes place. The method is advantageous because SAP are usually difficult to extrude or press from the powder into homogeneous films. Olefinic and styrenic comonomers can also be used [110]. UV initiation is also used for thin-layer polymerization of acrylamide and (methacryloyloxyethyl)trimethylammonium chloride, cooling the upper portion of the layer with a stream of air [185].

In typical processes the reaction mixture is charged into a stirred reactor or spread over a traveling endless conveyor belt [191, 220]; in some cases, heating is not necessary. The reaction, highly exothermic, starts spontaneously and proceeds quite fast, being completed within a short period of time, ranging from some minutes to 1–2 hours. A highly viscous aqueous gel is produced that must be dehydrated to obtain the resin in solid form. Dehydration through spray drying or the rotary drum roller method is common, but not always entirely satisfactory, because the overheating which occurs during drying may cause additional crosslinking. For these reasons, methods have been developed in order to facilitate, or eliminate, this step.

It is possible [137, 156, 158, 166, 183] to reach an acrylic monomer concentration in water as high as 70–80% (by weight of reaction mixture) when acrylic acid is partially (at least 70%) neutralized with KOH or ammonia, and acrylamide is used as comonomer; a crosslinking agent is added. In this way the reaction heat is sufficient to drive off most of the water from the polymerization mixture without the need for an additional drying step. The resulting resins have a water content lower than 15%, and they can be directly ground into the desired size. According to patents, the use of potassium hydroxide or ammonia instead of sodium hydroxide is critical because it is a unique way to prepare solutions having sufficient monomer concentrations. It was also found that addition of methylcellulose or poly(styrene) emulsion (about 2%) significantly improves the absorption characteristics.

Mixtures composed of 70% acrylic acid/potassium acrylate (1:3) and 0.01–0.1% of *N,N'*-methylenebisacrylamide or other polyvinyl crosslinking agent and initiator were polymerized in water or water/methanol (5–10%) [143, 174, 180]. Cosolvents like acetone, ethanol, and tetrahydrofuran are reported in the examples. The reaction is performed on a traveling endless belt. Also in this case the solvents are evaporated from the reaction system by the polymerization heat, giving dry solids with a low water content. Since the latent heat of evaporation of an organic solvent is smaller than that of water, the cosolvent acts as a blowing agent, making the resulting resin porous, and thus improving its absorption capacity. Remarkably, in this case only potassium hydroxide as a neutralizing base is suitable. Acrylic acid (50–60%) neutralized at least to 70% with KOH/(NH₄)₂CO₃/NH₄OH,

styrene or methyl methacrylate (<2%), a crosslinking agent, and acrylamide (optionally) were copolymerized by applying the same method [177, 253]. In another patent involving analogous polymers with a higher styrene content (about 12%), the organic cosolvent is omitted [235].

Polymers with compositions similar to those described previously [143, 174, 180] are synthesized in water solution and in the presence of styrene/maleic anhydride copolymers in a 1–3% amount [230]; the polymers are then subjected to surface crosslinking.

Itoh et al. [247, 254] disclose absorbent copolymers in which the degree of neutralization of acrylic acid with sodium hydroxide is between 35 and 45%, much lower than in other patents. Basic comonomers, such as acrylamide or 2-vinylpyridine, can be used optionally in an amount not exceeding 20%.

A process is described in three steps [196] in which water partially evaporates in the first stage of polymerization at about 70°C and 0.1–0.8 bar. In the second stage the reaction is carried out at 135°C and 4 bar, and finally the pressure is released, causing the reduction of water in the polymer to about 3%.

According to Sumiya et al. [297, 305] the sudden temperature rise caused by heat generated during polymerization increases the rate of decomposition of initiator, thereby reducing the weight-average molecular weight of the resin and broadening its molecular weight distribution. As a consequence, the resin contains a significant amount of water-soluble fraction, leading to surface stickiness of diapers made from these products. Unreacted monomer is also present in the resin, with obvious disadvantages. Moreover, absorption capacity is said to be significantly affected. Thus, a process for the synthesis of conventional acrylic absorbent resin is described where the temperature of the reaction medium is held below 70°C. Strips of hydrogels containing about 50% water are produced; they can be used as obtained or further dried with hot air and pulverized. The polymer can be further crosslinked at the surface in order to increase under-pressure absorption properties [297].

In some syntheses in aqueous solution, surface-active (or dispersing) agents are employed [220, 238]. Depending on their hydrophilic to lyophilic balance (HLB), a wide range of this kind of substance is available. Low HLB values correspond to surfactants with lyophilic characteristics, while high HLB surfactants have a prevailing hydrophilic character. In Table 1 some common surfactants are reported. According to one patent, the surfactant gives a copolymer with uniformly dispersed crosslinking monomer (trimethylolpropane triacrylate) [238].

Copolymers of long-chain, hydrophobic, alkyl acrylates are prepared in the presence of anionic surfactants (alkyl metal sulfates or sulfonates)

[139]. Addition of another, nonionic, surfactant (ethoxylated alkyl phenol or ethoxylated fatty alcohols) is reported in some examples. The surfactant makes the emulsification of hydrophobic acrylate in water easy.

Acrylic acid, sodium acrylate, and di- or triacrylates are polymerized in the presence of surfactants having HLB values between 7 and 18 [95]; in this case the surfactant renders the crosslinking agent water-compatible. Claimed surfactants are reported in Table 2. Their amounts range between 0.1 and 2% by weight of acrylate monomers. When the amount is lower than 0.1%, the resulting polymer is not uniformly crosslinked (because the crosslinking agent is poorly dissolved in water) and sticky, exhibiting a low initial absorption rate. Stickiness, causing adhesion of polymer to the reaction vessel and other metallic parts, is greatly prevented by the presence of residual surface-active agents on the polymer surface. When the amount

TABLE 2
Surface-Active Agents Used in SAP Synthesis (from Ref. 95)

Chemical class	Type	HLB range	Trade name
Polyoxyethylene alkyl ethers (alkyl = lauryl, cetyl, stearyl, oleyl)	Nonionic	9.4–17.1	
Polyoxyethylene secondary alkyl ethers (alkyl = C _{12–14} hydrocarbon radical)	Nonionic	7.9–14.5	Softanol
Polyoxyethylene alkyl phenol ethers (alkyl = octyl, nonyl)	Nonionic	7.8–18.9	Nonypol
Sorbitan monolaurate	Nonionic	8.0	Span
Polyoxyethylene sorbitan fatty acid esters (fatty acid esters = monolaurate, monostearate, monooleate, monopalmitate)	Nonionic	9.6–16.7	Tween
Polyoxyethylene fatty acid esters (fatty acid ester = monolaurate, monostearate, monooleate, monopalmitate)	Nonionic	13.4–19.1	
Sugar fatty acid esters	Nonionic	8.0–15.0	
Polyoxyethylene–polyoxypropylene glycol block copolymers	Nonionic		
Sodium alkyl sulfates and alkylbenzene sulfonates (alkyl = C _{12–14} hydrocarbon radical)	Anionic		Neoplex

of surfactant is greater than 2%, the hydrogel has low absorption capacity and low gel strength because a chain transfer reaction involving surfactant leads to low molecular weights.

A procedure aimed at reducing residual acrylic monomer content in SAP below 400 ppm is based on aging a solution containing acrylic acid with a 0.1–10% excess of alkaline base and adding additional acrylic acid (final neutralization degree 20–100%) and a triacrylic crosslinking agent before polymerization [259]. Other patents concerned with procedures for preparing low free-monomer content polymers have been filed [191,192]. SAP (360 ppm of free acrylic acid) are treated with a hydroalcoholic solution of sodium bisulfite and a water-insoluble surfactant [288]. After heating at 70°C, the monomer content is reduced to about 50 ppm. The problem of residual monomer and polymer degradation to monomer is particularly critical for methacrylamide or acrylamide ($LD_{50} = 124$) polymers because of their toxicity. Degradation is primarily due to breakage of polymer backbone by unreacted initiators and their degradation products. It is found that addition of about 1000 ppm of allylic compounds (diallyldimethylammonium chloride) prevents such degradation [269].

A method is reported by Yada et al. based on polymerization of sodium acrylate and acrylic acid in a reactor containing steam in the vapor phase [248].

A method for the continuous production of a crosslinked acrylic copolymer is described by Tsubakimoto et al. [159]. The monomers and initiator solutions are fed to a vessel provided with parallel rotary shafts equipped with stirring blades and held at constant temperature, while the polymer gel is continuously discharged, so that a fixed level is maintained in the reaction vessel. The discharged gel is dried and pulverized.

A vessel suitable for polymerization of acrylic monomers in water is described [292]; repeated batch syntheses can be performed without adhesion of polymer particles onto the inner walls or onto the stirrer. The reactor is provided with rotary stirring blades able to impart a strong shearing force to the hydrated gel; inner walls should have a surface roughness of about 0.5 μm in order to prevent deposition, and the vessel walls should be cooled under 70°C. Vessels with inner walls coated with poly(tetrafluoroethylene) have also been used [95].

Although a sharp difference exists between suspension and emulsion polymerization processes, often the patent literature hedges on this point by vague references to “dispersion polymerization” or not clearly distinguishing among “surfactant,” “emulsifier,” “suspending agent,” “protective colloid agent,” and “dispersant.” Thus, to avoid generating misunderstandings, the terms reported in the following discussion are those used in the original documents.

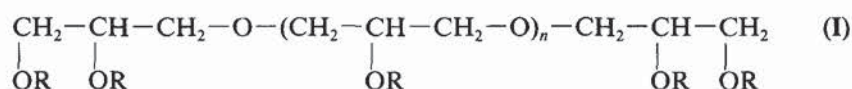
Suspension or emulsion polymerization processes allow a better control of polymer particle size, making easier the attainment of very fine powder and also simplifying water elimination: filtration and centrifugation are the customary methods. Aqueous slurries prepared from these SAP exhibit a pseudoplastic rheological behavior and do not form threads when two surfaces wetted with the medium are contacted and pulled apart. For these reasons, very small SAP particles are particularly suitable, for example, as thickening agents. Furthermore, uniformity in size of particles leads to rapid fluid absorption. As is well known, surfactant and colloid protective agents play a fundamental role in suspension and emulsion polymerizations. Many different types of such compounds have been used in SAP manufacture to obtain products with particular characteristics.

Low HLB value suspending agents are claimed [59, 88] for the persulfate-initiated polymerization of (meth)acrylic comonomers (acids, amides, 2-sulfoethylesters, 2-ammoniummethylesters), vinylbenzenesulfonate or vinylbenzylammonium salts (but specific examples cite only acrylamide and sodium acrylate), and polyvinyl monomers in water/hydrocarbons mixtures. The suspending agent employed consists of a chloromethylated poly(styrene)-dimethylamine reaction product where about 5–10% of the aromatic rings are animated. Polymer particles of less than 4 μm are obtained. By adopting emulsion polymerization, substantially similar water-absorbent microgels are obtained [88].

Acrylic acid partially neutralized with NaOH is polymerized in water/hexane or water/ligroin systems, using a surfactant with an HLB value of 3–6 and in the absence of crosslinking agents [74]. Crosslinking occurs spontaneously, activated by reaction heat (Trommsdorff effect) and controlled by the appropriate choice of solvent, surfactant, monomer concentration, and reaction temperature. In particular, the aqueous phase should be saturated with the monomer (about 45% of a 3:1 salt/acid ratio) to attain an optimum degree of crosslinking. Aromatic solvents give rise to untractable, excessively crosslinked polymers according to the author; in this case the suspension is too unstable. The same happens if the HLB of a surfactant is larger than 6; the surfactant adheres to the surface of polymer particles, rendering them sticky, if the HLB is smaller than 3. Suitable surfactants are sorbitan monostearate, sesquioleate (HLB = 3.7) or monooleate (HLB = 4.3). Because they are atoxic compounds, no safety problems arise if they contaminate SAP particles. Solid particles of 0.01–0.12 mm diameter are obtained at the end of reaction after decantation, filtration, and drying.

Improvements of the latter procedure are patented by Obayashi et al. [107] and Cramm et al. [179]; prepared poly(acrylate)s show at least a twofold increase in fluid absorption. Polymerizations are carried out in

water/cyclohexane mixtures, using a surfactant with HLB values of 8–12. Sorbitan monolaurate or monostearate are cited in examples. Such surfactants lead to the formation of monomer droplets of a diameter suitable for controlling reaction heat generation and crosslinking degree, according to the Trommsdorff effect. If a crosslinking agent is used (diglycidylethers or haloepoxides), absorption rate and gel strength stability are enhanced for a long period of time. Physiological fluids absorption is further improved by adding to the reaction mixture a chain-transfer agent such as formic acid, sodium formate, isopropyl alcohol, or 3-mercaptopropionic acid [179]. In four other patents [256, 160, 178, 195], saccharose or poly-(glycerine)-fatty acid esters (I) (HLB = 2–18) instead of sorbitan monoacyl derivatives are used.



where $n = 0-8$; $R = \text{H}$, C_{12-18} acyl group. Specific examples of compounds (I) are decaglyceryl pentastearate (HLB = 3.5), hexaglyceryl monobehenate (HLB = 13.1), diglyceryl monobehenate (HLB = 7.8), decaglyceryl heptastearate (HLB = 2.0), hexaglyceryl dipalmitate (HLB = 15.8), and hexaglyceryl monolaurate (HLB = 18.2). Polymer particle size is 100–500 μm , so no sticky or dusty material is formed and no lumps form when the SAP become hydrated.

The emulsion polymerization of partially neutralized acrylic acid or sodium 2-acrylamido-2-methylpropanesulfonate in water/hydrocarbon gives rise to SAP with a high capacity for saline and physiological fluids absorption, provided that a water-soluble surfactant with a HLB value greater than 7 is added at any stage of polymerization [124]. Better results are achieved if the addition is done after completion of the reaction. Polymerization is carried out in the presence of a crosslinking agent and an oil-soluble cellulose ester or ether that acts as a protective colloid. The water-soluble surfactant probably breaks the protective colloid film covering the SAP particles, allowing prompt wettability of SAP particles and easy hydrogel penetration by water. Nonionic and anionic surfactants are preferred: poly(oxyethylene) lauryl, nonylphenyl or stearyl ethers, sodium dialkyl sulfosuccinate, sodium oleate, or sodium sorbitan monopalmitate. The method described by Nakamura et al. [238] overrides the problem of low initial wettability of SAP prepared through reversed phase suspension processes by carrying out the polymerization in two stages. The first stage is conventional; the reaction mixture is then cooled to remove the surfactant and/or protective colloid by precipitation. After that, more monomer and

more initiator (and, eventually, more crosslinking agent) are added. They are absorbed by the polymer formed in the first stage and polymerization goes on further. In this way, particles with a large diameter and a sharp size distribution are also obtained.

A polymeric surfactant consisting of tetra- or octadecene/maleic anhydride copolymer is described [212] as a water-insoluble protective colloid in suspension polymerization of acrylic acid in water/heptane.

Acrylic acid/acrylamide copolymers are prepared using a surfactant system composed of hydrophobic clays or silicon dioxide [obtained through reaction of silica with poly(dimethyldichlorosiloxane)] and a hydrophobic poly(lauryl acrylate-co-acrylic acid) (acrylic acid molar fraction < 0.025) [182]. The amount of the two hydrophobic components depends upon desired SAP particle size distribution; their weight ratio may vary in the range 0.05–20. The procedure proceeds with monomer amounts in the aqueous phase as high as 30–40% without substantial agglomeration of the resulting polymer.

Surfactants having HLB values between 4 and 11 (for example, polyethoxylated sorbitan fatty acid esters) are used for the emulsion polymerization of ionic acrylic monomers [277]. Water/hydrocarbon or water/olive oil systems, an oil-soluble initiator, and an oil-soluble crosslinking agent are employed. The final product is an absorbent emulsion made up of fine particles (3 μm or less) dispersed in oil, useful as a spreading agent for agricultural chemicals, a dew condensation inhibitor, or a cosmetic material.

Incorporation of glycerol of about 10–25% in a polymerization mixture for the preparation of crosslinked poly(acrylate)s gives soft polymers with glass transition temperatures 50–100°C lower than those obtained without glycerin [270].

The method described by Itoh et al. [300] is characterized by the fact that the synthesis of partially salified crosslinked poly(acrylic acid) is carried out in such a way that the aqueous monomer solution is fed to the organic solvent at low temperature, so that an oil-in-water dispersion is formed. The mixture is then heated above the temperature at which the oil-in-water dispersion is transformed into a water-in-oil dispersion, then polymerization is done. The final polymer particles have a large size, a narrow size distribution, and are free-flowing due to their small content of residual organic solvent.

Agglomerated polymer particles having a large size (200–5000 μm) and excellent cohesion with unaffected absorbent properties are obtained through a two-step reversed-phase suspension polymerization [312]. In the first step the partially neutralized acrylic acid is polymerized in a water/cyclohexane suspension in the presence of sorbitan monostearate and

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



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-

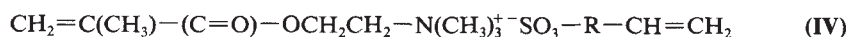
bisacrylamide). Use of (II) comonomers is also reported in other patents [124, 135, 305]. Acrylamide/sodium 2-acrylamido-2-methylpropanesulfonate copolymers are useful for removing acidic water from fuels, battery casings, etc., maintaining their absorbent properties at low pH values [135].

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 vinyl-sulfonate, a styrenesulfonate, or a vinylbenzylsulfonate (>25% by weight).



where R = alkyl; R¹ = 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].



where R = alkylene, arylene.

Dialkylaminoalkyl (meth)acrylates or (meth)acrylamides (V) are emulsion polymerized in the presence of *N,N'*-methylenebisacrylamide [294].



where R¹ = H, methyl; R², R³ = alkyl; A = OCH₂, NCH₂CH₂. 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-

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(etherdiols) [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-

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.

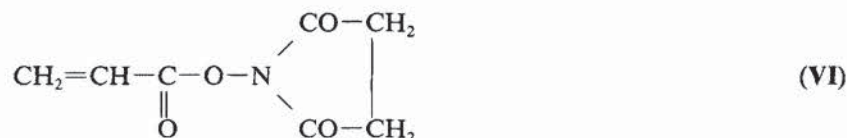
Water swellable polymers with a relatively high hydrophobic character may be used as viscosifiers for hydrocarbons instead of traditional hydrocarburic polymers [211]. They are obtained by copolymerizing about 1% of a hydrophilic monomer (acrylic acid) and a hydrophobic polar monomer (C_{6-10} alkyl 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-

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).



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 polyvinyllic 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. Alkoxyethylamido groups of *N*-alkoxyethyl (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

[53, 67, 70] or lattices [71] containing sites crosslinkable at the moment of utilization are prepared. The advantage of the invention is that only a single material or solution has to be sent to users, which eliminates any chance of operator error in the mixing of the crosslinking agent.

Nontoxic, biocompatible, swellable gels useful as prosthesis fillers are prepared by polymerization of *N*-vinylpyrrolidone with vinyltrimethoxysilane (400–50:1 weight ratio) [83]. 2-Hydroxyethyl methacrylate can be used as comonomer. Crosslinking takes place through hydrolysis and coupling of alkoxy silane groups.

The use of polyunsaturated comonomers is by far the most common method for obtaining crosslinking poly(acrylate)s. In this case, crosslinking takes place simultaneously with chain growing. Diacrylates or bisacrylamides are the more frequently used polyunsaturated crosslinkants, although trifunctional acrylates and di- or triallyl compounds are sometimes employed.

A patent reports that poly(acrylate)s with uniform crosslinking density and a low percentage of extractable materials are attainable by using a mixture of di- or triacryloyl crosslinking agent and a diallyl compound or triallylamine [272]. The two crosslinkers are preferably present in the molar ratio 1:5–7. Acrylic crosslinkers polymerize randomly and quickly with the other monomers, while the allylic one reacts slower and never with itself; so, a gel core of relatively closely spaced crosslinks is formed, with an external shell of chains with relatively farther-spaced crosslinks.

Copolymers of acrylamide, *N*-vinylpyrrolidone, sodium 2-acrylamido-2-methylpropanesulfonate, and a crosslinking agent represented by ethylene-(sodium vinylphosphonate) are described by Engelhardt et al. [116]. The phosphonate is synthesized by alkaline treatment of trichloroethyl phosphate at reflux temperature.

Crosslinking through nucleophilic attack of the carboxylate poly(acrylate) pendant group on electrophilic groups of polyfunctional compounds with a low molecular weight is described in several patents. Typical leaving groups and their corresponding substrates are listed in Table 3. The reaction usually takes place at high temperatures (80–150°C).

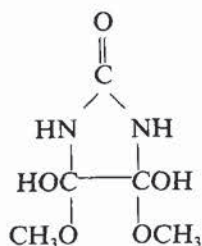
Diglycidyl ethers of glycerine, neopentylglycol or butanediol, 1,3-dichloroisopropanol, epibromohydrin, and epichlorohydrin or bisphenol-A epoxy resins are the crosslinking agents cited by Gross [32, 42, 43, 49–51, 54, 55]. Water-soluble carboxylic polymers are mixed with one of these compounds in water, then the solution is evaporated and dried at 70–80°C to obtain absorbent films. Diglycidyl ethers are used in other patents [120, 130, 153, 141, 133], even for poly(acrylate)s already crosslinked with divinyl monomers. Crosslinking may be effected by spraying an aqueous solution of diglycidyl ether over the polymer [130], treating the polymer in the

TABLE 3
Leaving Groups Suitable for Nucleophilic Substitution
Reactions in Crosslinking of Polycarboxylic Polymers
(from Reference 55)

Compound	Leaving group
Alkyl chlorides	Cl—
Alkyl bromides	Br—
Alkyl iodides	I—
Alcohols	—OH
Ethers (epoxides)	—OR
Esters	—O(C=O)R
Alkyl sulfonates	—OSO ₂ R
Alkyl sulfates	—OSO ₃ R
Alkyl sulfinates	—OSOR
Alkyl chlorosulfites	—OSOCI
Alkyl chlorophosphites	—OPCl ₂
Alkyl bromophosphites	—OPBr ₂
Tetraalkylammonium salts	NR ₃
Alkyl diazonium salts	N ₂
Trialkyl sulfonium salts	SR ₂

swollen state and in the presence of an inorganic powder (silica, alumina, titanium dioxide) with diglycidyl ether solutions [153], or finally treating a suspension of the polymer in hydrocarbon solvent with hydroalcoholic solutions of diglycidyl ether or epichlorohydrin [133, 141].

Poly(*N*-methylolacrylamide) and dimethoxydihydroxyethyleneurea (VII) act as crosslinking agents for poly(acrylate)s [47] according to the same reaction previously mentioned ([53, 67, 70, 71]).



(VII)

Amine-epichlorohydrin adducts are effective crosslinking agents for carboxylic copolymers [103], able to react very fast with the carboxylic group.

Fast cure rates are achieved. Burkholder [69, 81, 85] reports on the use of poly(amido)-poly(amine) epichlorohydrin adducts as crosslinking agents. Such adducts are structurally similar to those mentioned before; they are water-soluble resins bearing 3-hydroxyazetidinium, epoxypropyl, and chlorohydrin groups. Treating the polymer solution before the crosslinking reaction with the aforementioned adduct, poly(epoxide)s, or a cyclic sulfonium zwitterion of bisphenol-A, leads to an increased fluid absorption rate of the final material [79]. Treatment is done in water or water/alcohol mixtures containing more than 75% by weight of polyelectrolyte; air entrapped in the formulation should be sufficient to increase its volume by about 50%.

3-Glycidoxypolytrimethoxysilane is capable of crosslinking carboxylic copolymers [164]. The reaction is carried out at 80–110°C; dibutyltin dilaurate is used as catalyst.

A third way to produce crosslinking is by treatment of polymerization mixtures with polyvalent metallic cation solutions [98, 311]. Polyvalent cations form an ionic bond with carboxylic groups of two or more different poly(acrylate) chains. Zinc, calcium, strontium, or barium acetates have been used, added at the end of polymerization [98].

Treatment with polyvalent metal salts or electrophilic polysubstituted compounds can also be applied to induce surface crosslinking of already crosslinked SAP recovered from the reaction system. In fact, when a water-absorbent resin is contacted with water, swelling first occurs at the surface portion of the gel, so further penetration of water into the core of the particle is retarded. Moreover, the particles become sticky and form agglomerates ("lumps") which block the diffusion of water toward particles into the agglomerate. As a result, a low absorption rate is achieved. The phenomenon is sometimes referred as "fish-eyes" formation or "gel-blocking." A method of obviating these inconveniences is to render the gel surface structure more rigid; hence, the effectiveness of surface crosslinking was found valuable. Polyhydric alcohols [especially poly(ethylene glycol)] with aluminum compounds (aluminum isopropoxide, aluminum chloride hexahydrate, sodium aluminate) [210, 194] and polyvalent metal salts (especially aluminum sulfate) with alkali metal sulfite or thiosulfate [262] give good results [210]. Other efficient systems are reported in Section 2.4.

Polyquaternary amines bearing positively charged ammonium groups (molecular weight 300–4000) may be used instead of metal salts [207, 230, 253, 201]. Among various compounds, some of them available as commercial products, the patent cites the condensation products of hexamethylenediamine, dimethylamine, and epichlorohydrin; copolymers of acrylamide

and β -methacryloyloxyethyltrimethylammonium chloride; hydroxyethyl cellulose reacted with epichlorohydrin and quaternarized with trimethylamine; homo- or copolymers of diallyldimethylammonium chloride [148, 149]; reaction products of dimethyl sulfate with polyethyleneimines; and copolymers of vinylpyrrolidone and dimethylaminoethyl methacrylate.

Fe(II), Fe(III), Cu(II), Mn(II), V(II), Co(II), and Ni(II) salts (0.002–0.04% by weight of monomer) are used during polymerization along with polyunsaturated crosslinking agents, and polymer particles obtained are further surface-treated with 3-glycidoxypolytrimethoxysilane to give SAP with good gel strength without deteriorating the absorption capacity [311].

Surface crosslinking of crosslinked poly(acrylic acid–sodium acrylate) is accomplished by coating the particles with glycerin or other polyols and a surfactant having an HLB value of 3–10 (a polyethoxylated sorbitol lanolin derivative is satisfactory) that facilitate a homogeneous distribution of the polyol on the gel particles [307]. Then the particles are dried in an air stream at 200°C. The method is claimed also for hydrolyzed starch–acrylonitrile graft copolymers. Glycerol can be alternatively added at the end of polymerization as a dispersion [240]; better polymer properties than by using a glycerol solution are claimed.

Saotome describes a method to crosslink a SAP surface with peroxides [184, 199]. The method consists in adding the peroxide at the end of polymerization to the polymer slurry and heating the mixture at about 50–100°C above the decomposition temperature of the peroxide.

Glyoxal [58], glycols or glycerin [255, 286], polyfunctional epoxides [271, 276, 314] or polyfunctional isocyanates, polyfunctional amines, polyvalent metallic salts, alone or in combination [297], are also claimed. In particular, the procedure described by Choi et al. [271] comprises the inverse suspension polymerization of acrylic comonomers in the presence of surfactant having an HLB value in the 3–6 or 8–12 range, the azeotropic distillation of most of the water, surface crosslinking with diepoxides, and the final coagulation of the resin in inert solvents followed by drying. A similar procedure is described in another patent [314]. After the azeotropic distillation, the residual water is lowered to less than 25% of the gel. Crosslinking can be carried out in two steps before the final dehydration step.

Crosslinking reactions can be carried out directly on fiber webs impregnated with absorbent polymer [258]. Thus, a patent reports on cellulosic fibers impregnation with poly(acrylic acid) and zirconium ammonium carbonate solution, followed by application of softwood sulfite pulp fibers, spraying with vinyl acetate latex binder, and heating the composite to effect crosslinking and curing of the latex polymer. The product is useful for diapers manufacture.

2.1.4. Further Modification of Poly(Acrylate) Absorbents

One patent [203] discloses a method for preparing SAP having reactive groups on the surface. The claimed reactive groups are hydroxyl, amino, aldehyde, nitrile, and sulfonic, although examples are given only for the first two. Such absorbent polymers could potentially find high interest for enzyme immobilization, as macromolecular phase-transfer catalysts, in GPC mobile phases preparation, and in other applications. A poly(acrylic acid-co-sodium acrylate) is synthesized by reversed-phase suspension polymerization. After solvent elimination, a monomer having the desired functional groups and a crosslinking polyfunctional agent are added, and the polymerization is completed; examples report the use of 2-hydroxyethyl methacrylate and *N,N*-dimethylaminoethyl methacrylate. In this way the reactive functional groups of added monomer remain in high concentration on the surface of the final material. In fact, the product reacts with polyurethane prepolymers to give absorbent poly(urethane) film resin while, if the acrylic-monomer-bearing reactive functional groups is added at the beginning of polymerization, the resulting poly(acrylate) is released from the film. An alternative route to obtain the said highly reactive poly(acrylate) consists of impregnating the poly(acrylic acid-co-sodium acrylate) with a separately prepared homopoly(acrylate) having reactive functional groups in pendant substituents and crosslinking them.

The addition of inorganic powders (usually <5%) to SAP provides a method for increasing the gel strength, improving the handleability, and decreasing the tendency to adhesion during processing. In some cases, absorbent properties are also improved. It is reported that the addition of silica before stripping of water at the end of dispersion polymerization allows for control of polymer particle sizes (400–900 μm vs 150–400 μm without it) [189]. Silica or silica gel [139, 153, 189, 198, 204], “syloid” (silicon dioxide hydrates) [263, 276], alumina [153], titanium oxide [153, 253], mineral clays (kaolin, attapulgite, vermiculite) [35, 132, 168, 224], and insoluble silicates, carbonates, or sulfates [132, 168] have been used. According to Jacquement et al., clay (about 30% by weight) gives the polymer a greater resistance to photodegradation [224].

Absorbent poly(acrylate)s containing 0.1–1% of a metal chelating agent show an excellent absorption rate of urine and aging stability in the swollen state, without detriment of absorption capacity [215]. 1,10-Phenanthroline and 2,2'-bipyridine are cited in the examples. Patent authors state that the chelating agent likely catches a slight amount of transition metals derived from the resin or from the urine, avoiding resin decomposition caused by radical species generated from the metal.

Dihydrogenated tallow dimethylammonium chloride acts as a lubricant

counterion for poly(acrylate)s, facilitating the extrusion and spinning of the polymer [245, 274]. Other tetraalkylammonium salts having long-chain alkyl groups are effective.

Foamed water absorbent materials can be prepared by adding a blowing agent to a solution containing a poly(acrylic) electrolyte and an electrophilic crosslinking agent, and heating the mixture [138, 227]. Useful blowing agents include sodium bicarbonate [138], *p*-toluene sulfonylhydrazide, azodicarbonamide, and 4,4'-oxybis(benzenesulfonyl hydrazine) [227]. The resulting resin has an increased surface area and greater porosity than a comparable sample of absorbent in solid film or sheet form. The foamed structure allows greater fluid penetration with decreased gel blocking.

Incorporating a solution of praseodimium gallate as antioxidant into a crosslinked poly(acrylate) gives a material with good lightfastness and heat resistance [216]; incorporation of reducing salts (sodium sulfite) and organic antioxidants (phenothiazine) improves gel stability in the presence of absorbed body fluids or saline solutions [202].

Blends of partially neutralized poly(acrylic acid) crosslinked with trimethylolpropane and a thermoplastic hydrophilic polymer [poly(*N*-vinylpyrrolidone), poly(ethylene oxide)] show improved adhesion properties on woven and nonwoven fibers [291]. Polymer particles can be more effectively and permanently distributed within fibrous structure, minimizing the occurrence of gel-blocking.

Acrylic copolymers/rubbers blends are described in several patents [161, 233, 266]. Neoprene rubber is blended with poly(sodium acrylate), poly(ethylene glycol), and fillers and vulcanized to give a water-swelling elastomer composition [161]. Similarly, natural rubber is blended with poly(2-hydroxyethyl methacrylate) [266]. Poly(sodium acrylate), poly(ethylene-propylene) rubber, and poly(ethylene-vinyl acetate) (4:4.5:1.5) are melt kneaded to give materials useful in the packaging of food or as agricultural water retention sheets [233].

Absorbent fluff used in napkins and disposable pads manufacture is prepared by treating a fibrous material contacted with dry granular or powdered SAP (partially saponified crosslinked polyacrylamide) with steam [41]. The adherence of the gel to the fibers is enhanced by a pretreatment with polyethyleneimine (a similar technique is described by Harada et al. [303]). The method is also applicable to cotton clothes, rayon, wool, paper, and surgical gauzes. An improved procedure to make absorbent fluffs consists in coating a base fluffing material (fluff pulp board) with an acrylic polymer, a crosslinking agent, and a surfactant, drying, and then disintegrating the board [122]. Otherwise, the mechanical disintegration may be carried out [121] on laminates prepared according to patented procedures [69, 79, 97].

Hydration of poly(potassium acrylate) (2:1 parts of water) provides agglomerated particles that prevent shifting of the product contents and inhalation [237]. The hydrate form is more easily workable during subsequent product manufacture operations.

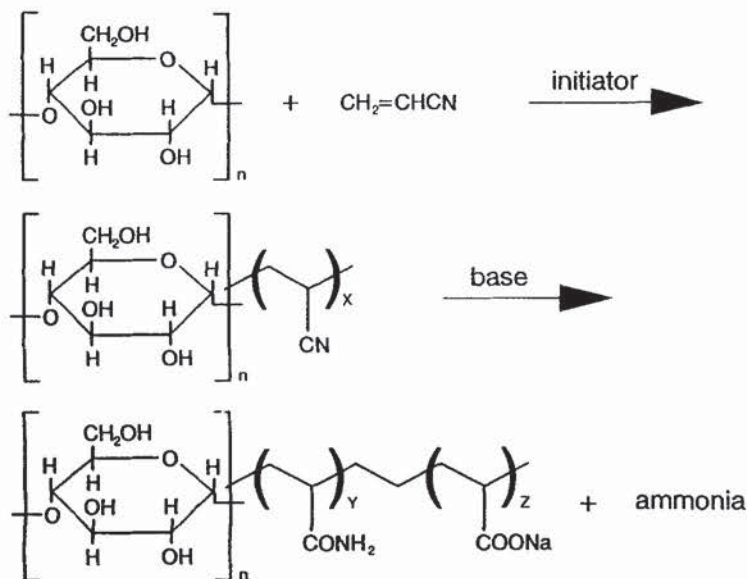
2.2. Modified Poly(Saccharide)s Absorbent Polymers

Absorbent polymers of modified poly(saccharide)s are obtained through grafting of an unsaturated monomer (acrylonitrile, acrylic acid, acrylamide) onto starch or, less frequently, cellulose.

A saponification step follows grafting when acrylonitrile or acrylamide are employed. The chemistry of the process is not completely understood, and it is not clear which is the point of attachment of the poly(acrylic) chain onto saccharidic rings; the structures in Scheme 1 are written in such a way as to evidence the uncertainty.

Polyfunctional unsaturated compounds are not commonly used to cross-link the polymer chains. The polymer insolubility arises from its saponification degree, which controls the ionic/nonionic carboxylic groups ratio.

Poly(saccharide) superabsorbents generally have better absorption capacity than poly(acrylate)s, but they are biodegradable, so their life after



SCHEME 1.

production is usually short because after a certain period they go moldy. On the other hand, their degradability by biological agents may represent an advantage for their disposability. Absorbent properties of modified poly(saccharide)s absorbent polymers are reported in Table 4.

2.2.1. Starch-Graft Copolymers

Starch-graft copolymers, as initially conceived, were prepared by radical polymerization of acrylonitrile onto starch as initiated by ceric salts [16]. Saponification with alkaline hydroalcoholic solutions is carried out either under pressure or at reflux. The product is neutralized at pH 6–8 with acetic acid, filtered, and dried. Addition of 1–2% of fumed silica improves the absorption rate of copolymers and reduces their dustiness [33]. Better performances are obtained by carrying out the grafting of acrylonitrile (9:1 mol in respect to starch) in two steps, so that the exothermicity of the reaction is controlled [65]. Moreover, extraction of starch before polymerization with alcoholic solution in order to remove fats, thinning with mineral acid to reduce the viscosity of the starch paste, and cooking the starch to paste contribute to improving the product performance. Saponification and further treatments are made as described above [16].

The method reported by Weaver et al. [34, 45, 48] leads to copolymers able to absorb an amount of water as high as 1000 times their own weight. The pretreatment of starch at 90°C in water for 30 minutes (gelatinization) before the grafting reaction is an essential stage to obtain a final product with the desired characteristics. Acrylonitrile (3–1:1 to starch) is grafted with ceric ammonium nitrate initiator; the solution is treated with KOH to hydrolyze nitrile groups by using a base:poly(acrylonitrile) molar ratio of 1.3–7:1. A viscous gel of highly swollen but insoluble microgel particles is obtained. After acidification to precipitate the product and filtration, the polymer is washed and dispersed in water, and the pH is adjusted to 6–9. Drying yields an absorbent insoluble film. Among the several reported applications, a particular relevance is given by the patents to the use of the polymers as insoluble supports for the immobilization of enzymes (amylase or glucoamylase in the examples). Higher absorption capacity (3000 times their weight of water) is reached by using flour or cereal meal as the starting material [57]. The gelatinization, grafting, saponification, and drying steps are conducted as above. A further improvement of previous procedures involves the use of a water-soluble comonomer (2–10% by moles) along with acrylonitrile during the grafting step [82]. 2-Acrylamido-2-methylpropanesulfonic acid is the preferred comonomer, but acrylic acid, vinyl sulfonic acid, and methyl methacrylate are also effective. The variation reduces the time required for saponification and allows the elimination of the

TABLE 4

Absorption Properties of Absorbent Modified Poly(Saccharide)s [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
16	84		45		
33	36.2	(28.8)	7.66	(4.87)	
65	1000		140		
34, 45, 48	1300		80		
57	2670	(820)	76	(40)	
82	5300	(820)	73	(40)	
104			11	(68)	> 30
100	369				
86	411				
68	351	(53)	82	(8)	
273, 275	65		14		
213	826	(475)			
77	152				
78	1038	(0)			
28			5.37		
75			5.6	(2.7)	
84	35		14		
63	125				
36	87				
64	183				
283	79	(33)			
92	4.5				
173			96		

gelatinization step. Nonetheless, if gelatinization is accomplished, the graft copolymers obtained are able to absorb over 5000 times their weight of water.

Starch copolymers with improved wicking properties retaining acceptable levels of absorbency are prepared by crosslinking with formaldehyde [104]. The reaction takes place preferably between dry granular hydrolyzed starch-polyacrylonitrile and paraformaldehyde. A difunctional aldehyde (glyoxal) can also be used [58].

A good balance of absorption capacity and rate is also obtained by mixing the hydrolyzed starch-poly(acrylonitrile) copolymer with basic aluminum acetate in methanol, and drying the composition [100].

Apart from acrylonitrile, other acrylic comonomers, typically acrylamide or acrylic acid, have been used in grafting reactions onto starch.

A simplification in the synthesis of starch-graft copolymers is introduced by Mooth [86]. The reaction is carried out in water at temperatures above 100°C, so that grafting and drying proceed simultaneously in the presence of persulfate initiators. The grafted monomers are acrylic acid or acrylic acid/acrylamide mixtures. In this way the steps of saponification and drying are avoided, and no heavy metal initiators are employed.

Grafting of acrylic monomers (acrylamide, acrylic acid, sodium acrylate, trimethylacryloyloxyethyl ammonium chloride) is carried out by ceric-initiated polymerization in water/methanol solvent in the presence of diacrylates (starch/acrylic monomer/diacrylate ratio 100:100–500:0.01–5) [68]. Three examples report on the use of fluff pulp instead of starch. Surgical dressing materials are obtained by spray-blending such crosslinked starch-graft poly(acrylate) with a styrene-butadiene rubber latex foam and, optionally, chitin onto a suitable web, and drying the web [273, 275].

A crosslinking agent is also used in a synthetic procedure taking place in a mixed water/toluene solvent [52]. The organic solvent confines the water phase containing the persulfate initiator and the comonomers (acrylamide, acrylic acid, or sodium acrylate) in high concentration to the water-wettable or water-soluble poly(saccharide), promoting more efficient conversion of poly(saccharide) to radicals suited for grafting, more efficient polymerization and crosslinking, and larger chain entanglements.

Heidel [213] describes grafting of partially neutralized acrylic acid onto starch in water/gasoline or water/cyclohexane, initiated by ammonium persulfate in the presence of a nonionic water-insoluble surfactant with an HLB value lower than 10 (a sorbitan fatty acid ester) and a nonionic water-soluble polyethoxylated fatty alcohol with an HLB value greater than 10. The two surfactants enable homogeneous, clump-free dispersion of starch granules in the aqueous monomer phase, and good distribution of the monomer phase as fine droplets in the organic phase, without gelation of starch.

Starch is functionalized with the acrylamidomethyl group by reaction with *N*-methylolacrylamide (**III**; R, R' = H) and then copolymerized with acrylic comonomers [77].

Blends of starch-grafted poly(acrylonitrile) or poly(acrylamide) with unmodified starch or poly(vinyl alcohol) (about 50:50 by weight) maintaining good absorption properties are described [78]. The procedure affords a simple way to produce effective thickening agents for reducing the water

content of emulsions or liquid wastes. Blends with low molecular weight unmodified starch (for example, dextrin) are also described [125].

2.2.2. *Modified Cellulose Copolymers*

Graft copolymerization similar to that performed onto starch can be accomplished onto cellulose as well [28, 75].

Grafting of acrylonitrile on cellulose pulp initiated by hydrogen peroxide and ferrous salts, followed by saponification with NaOH and acidification at pH 6–8, gives absorbent materials useful for cigarette filters and diapers manufacture [3]. Water is eliminated by freeze-drying to maintain the porous structure of the material.

Grafting of methyl methacrylate/methyl acrylate mixtures, as described by Sobolev [7], is carried out in water at room temperature using manganic pyrophosphate as initiator. The pyrophosphate stabilizes the manganic ion in its valence state by complexing it without reducing its oxidizing power. Other known complexing agents are said to lower its oxidizing power excessively.

Three types of products could be obtained from graft-cellulose poly(acrylonitrile) by varying the saponification conditions. In discrete fibers derived from paste hydrolysis, about 50% of the nitrile groups are converted to acrylamide groups. They are generally difficult to dry, and although they have high absorption capacity, about half of the material is lost during washing due to its solubility. Moreover, they show a disappointingly low gel strength. Hard gel fiber clusters derived from crumb hydrolysis are easy to dry but generally exhibit poor or fair absorbent properties. Hard fiber aggregates derived from high-pressure hydrolysis are not absorbent, and they are used as ion-exchange resins. An improvement in the absorbent properties of modified cellulose copolymers obtained by crumb hydrolysis is reported by Adams [84] by subjecting the hydrolyzed product to controlled periods of aging (about 3–6 weeks), soaking in water (10–60 minutes), and finally drying the material. It was also found that subjecting the product from cellulose–poly(acrylonitrile) crumb hydrolysis to periodic cycled storage at room temperature and then at around 70°C has beneficial consequences on polymer properties. Storage of hydrolyzed product at room temperature for 10 days, followed by four cycles of 16 hours at 68°C and 8 hours at 23°C, leads to a viscosity increase of about 160 times for a polymer–water dispersion. The dispersion is used as a thickening agent for latex paints, hand lotions, and body lotions. Similar use is reported for a water dispersion of cellulose–sodium poly(acrylate) graft copolymers with a size $< 100\ \mu\text{m}$ [17].

Water absorbent crosslinked ethers are prepared by reacting an alkaline aqueous suspension of cellulose with sodium monochloroacetate and meth-

ylene- or dimethylolbisacrylamide [63]. Cellulose can be ethoxylated prior to the grafting reaction [36], and other polyfunctional crosslinking agents are claimed, such as acrylamido methylene chloroacetamide [36], trisacryloylhexahydrotriazine, 2,4,6-trichloropyrimidine, cyanuric chloride, dichloroacetic acid, and phosphorous oxychloride. Products are partially water soluble. By using bis(acrylamido)acetic acid as a crosslinking agent in a hydroalcoholic medium, the absorption properties are enhanced and the solubility is somewhat limited [64].

Cellulose fibers are crosslinked through ester bonds with 1.5–6% by weight of a polycarboxylic acid [282, 283]. Such compounds (for example, citric acid, butanetetracarboxylic acid, or oxydisuccinic acid) are much less toxic than aldehydes. The resulting fibers have high resilience in both the wet and dry states.

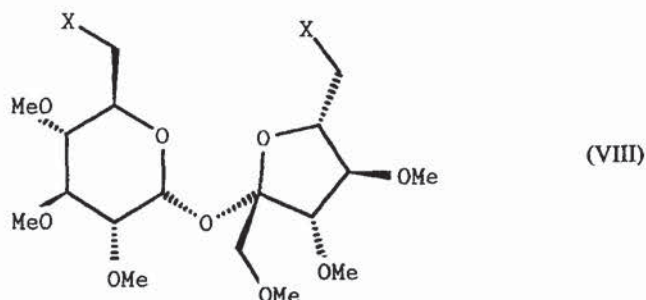
Crosslinked sodium carboxymethylcellulose may be added to cellulose before the regeneration step, processed using conventional methods, and extruded in the form of absorbent fibers or films [92]. Crosslinking of sodium carboxymethylcellulose is effected with epichlorohydrin.

Nonfibrous sodium salts of carboxymethylcellulose are prepared by reacting sodium hydroxide with carboxymethylcellulose having a molecular weight of 1300–2300 in a water/alcohol solvent [173]. The product is used in diapers.

2.2.3. Miscellaneous Poly(Saccharide) Derivatives

Poly(saccharide) absorbent fibers are obtained by treating a *N*-methylpyrrolidone dispersion of dextran with acetic anhydride and benzoyl chloride, and then spinning the solution [containing 10% modified dextran, 5% epichlorohydrin (as a crosslinking agent), and 10% cellulose acetate] into an aqueous alkaline bath [192].

6,6' - Dihalo - 6,6' - dideoxy - 1',2,3,3',4,4' - hexa - *O* - methylsucrose compounds (VIII) are claimed as intermediates for the synthesis of water-absorbent poly(ether)s through the Williamson reaction [293].



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 propoxyxylated 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, glycols, poly(etherdiols), 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

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].

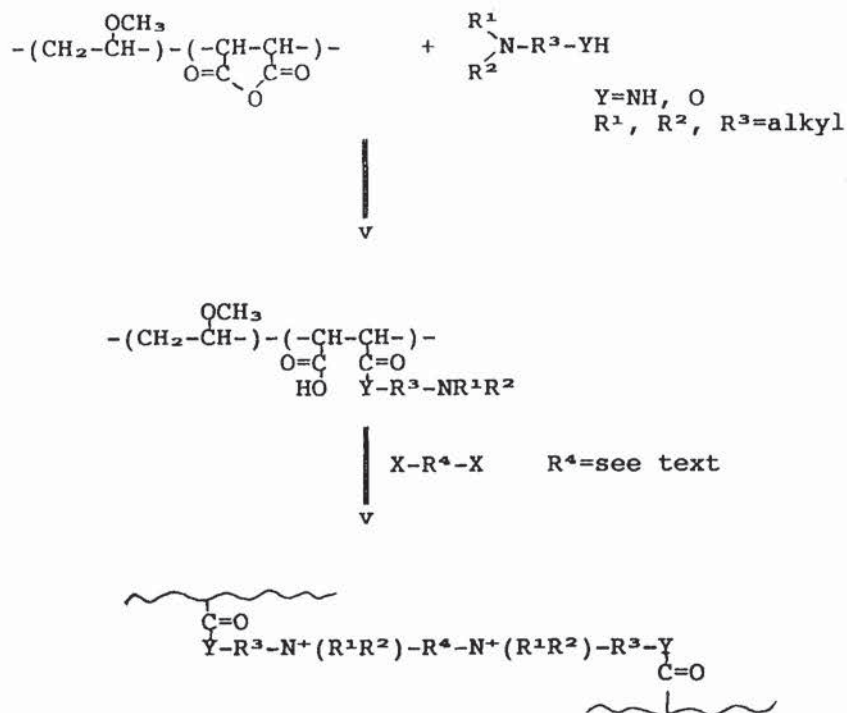
Williams et al. describe the polymerization in benzene of MA, alkyl vinyl ethers (alkyl = methyl in the examples) and divinyl ether as a crosslinking agent [109, 117]. The polymer is then reacted with ammonia or alkylamines; copolymerized anhydridic rings are opened and amide and ammonium carboxylate 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 C₂₋₄ 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-swelling 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



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



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.

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

^apH 8.5 solution.

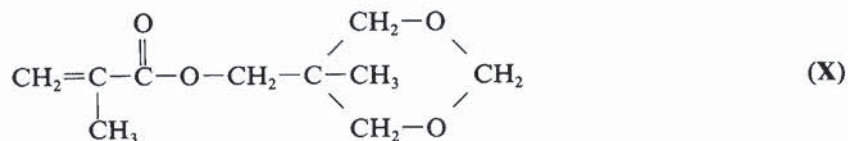
necessary, otherwise monomers (IX) give rise to linear polymers. Triallyl-methylammonium chloride is reported to be a crosslinking agent (IX: $R^1 =$ allyl; $R^2 =$ methyl; $X = Cl$).



Copolymers of monomers (IX) and acrylic acid/sodium acrylate are also described [149].

Compatible, transparent water-absorbent polymer blends formed by a hydrophilic polymer and a hydrophobic polymer (preferred weight ratio = 4–9) are useful for contact lens manufacture [209]. Examples of hydrophobic polymers are bisphenol-A/epichlorohydrin epoxy resin, poly(vinylidene fluoride), cellulose acetate, poly(carbonate), poly(phenylene ether sulfone), poly(methyl methacrylate), poly(benzyl methacrylate), poly(vinyl butyral), etc. Mentioned hydrophilic polymers are poly(*N*-vinylpyrrolidone), poly(vinyl methyl ether), poly(ethyl oxazoline), and poly(*N,N*-dimethylacrylamide). Blends are prepared either by casting a film from solution or by radical polymerization of the hydrophilic monomer containing the hydrophobic polymer dissolved (and making SIPN). The blends are able to absorb 100% or more of their own weight in water, without lack of transparency.

A transparent simultaneous interpenetrating network useful for contact lens manufacture is synthesized by simultaneous homopolymerization of a mixture of a hydrophilic monomer (*N*-vinylpyrrolidone) with a hydrophilic crosslinking agent [3,3'-ethylidenebis(*N*-vinylpyrrolidone)], and a hydrophobic monomer [(5-methyl-5-*m*-dioxanyl)methyl methacrylate] (X) with a hydrophobic crosslinking agent (neopentylglycol dimethacrylate) [140].



The material has high strength, good durability, and high oxygen permeability. Optimum formulation foresees 58–65% *N*-vinylpyrrolidone in a polymerizing mixture and about 30–33% (5-methyl-5-*m*-dioxanyl)methyl methacrylate. When 5–8% of 2-hydroxyethyl methacrylate is added, the polymer in hydrated form shows better elastic properties. Other comonomers are cited in the patent. A polymer where the hydrophobic monomer is methyl methacrylate and the crosslinking agent is absent is also reported [146].

Poly(ethylene oxide) is crosslinked with diacrylates in organic solutions in the presence of peroxide or radical azoic initiators [39, 20]. An insoluble

water-absorbent product is obtained. Crosslinking involves reaction between the double bond of the diacrylate and the carbon atom in the alpha position to the ether oxygens. The method is applicable to other poly(alkylene oxide)s. Crosslinking can also be performed via high energy irradiation, using a Van de Graaf electron accelerator (1 MeV, 0.2–1.0 Mrad) [40, 29]. In this case the reaction is carried out in bulk, with a second water-soluble polymer present [starch- or cellulose-graft copolymers, poly(acrylate)s, ethylene/maleic anhydride copolymers and the like].

Poly(acrylate)/poly(saccharide) or poly(acrylate)/poly(peptide) blends are obtained by polymerizing acrylamide in aqueous solution in the presence of *N,N'*-methylenebisacrylamide and about 30% by weight of agar-agar (or gelatin) [152]. The gel is treated with an ammonia or amine solution. By introducing physiologically active substances into the gel by permeation, the material can be used for wound dressing. Napkins, diapers, and pharmaceutical preparations are other potential uses.

Poly(amide)/poly(acrylate) blends are prepared by polymerizing 2-hydroxyethyl methacrylate and ethylene glycol dimethacrylate mixtures containing dissolved poly(caprolactam) [10]. An absorbent thermosetting film is obtained.

Poly(urethane)s containing poly(alkylene ether) soft segments show good water absorbency [21, 228, 281]. Larson describes poly(urethane)s containing sulfopolyetherester soft segments derived from the reaction product of poly(ethylene glycol) with dimethyl 5-sodiosulfoisophthalate [170, 190]. Sponges prepared from sulfonated poly(urethane)s show low shrinkage after drying.

Poly(vinyl alcohol) hydrogels are prepared by acetalizing hydroxyl groups with formaldehyde and glutaraldehyde mixtures (680:1 by mol) in the presence of sulfuric acid [15]. The crosslinked poly(vinyl alcohol) is used to concentrate water solutions of proteins.

Carboxylated aldehydes (XI) are used to transform hydroxyl groups of ethylene/vinyl alcohol copolymers into acetals with pendant carboxylic groups [313].



where R^1 , R^2 , $R^3 = H$, alkyl; $n = 0, 1$. Carboxyls are then salified through reaction with bases. At least one of the R^1 or R^2 groups should be an alkyl group. Crosslinking with dialdehydes or diisocyanates improves heat resistance of the material. Fibers with high moisture absorption can be obtained, very similar to natural fibers and useful in composite polyester of polyamide fiber preparation.

Porous beds of crosslinked poly(*N*-vinylpyrrolidone) or poly(*N*-methyl-

N-vinylacetamide) are prepared by polymerization in aqueous solution [37]. Divinylbenzene, *N,N'*-methylenebisacrylamide, and other diacrylates are used as crosslinking agents. Polymer beads are treated with phenol solutions to form complexes able to slowly release the phenolic compounds in desired circumstances. A large variety of phenolic compounds having antimicrobial (*n*-heptyl-*p*-hydroxybenzoate), slimicide (trichlorophenol), insecticide (4,6-dinitro-*o*-sec-butylphenol), algicide [2,2'-thiobis(4,6-dichlorophenol)], antioxidant (butylhydroxyanisol), or deodorant (vanillin) properties is described.

Homopolymers of *N*-vinylpyrrolidone are synthesized in water solution and crosslinked with diethylene glycol divinyl ether [23]. Homo- and copolymers of *N*-vinylpyrrolidone crosslinked through hydrolysis of trialkoxysilane pendant groups are also described [83].

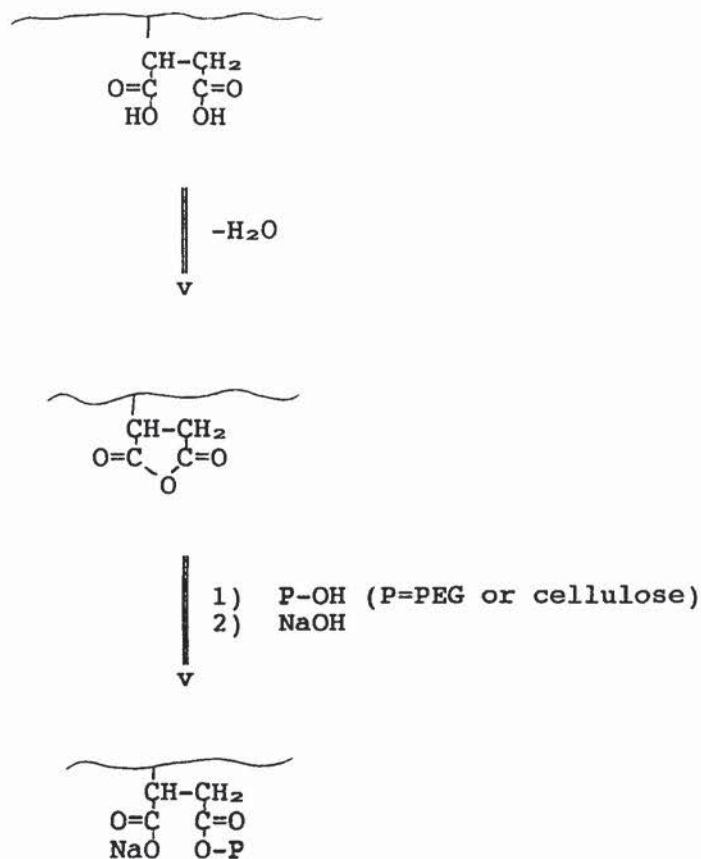
Absorbent fibers of cellulose are obtained by reaction with a polyol and an acrylic acid/itaconic acid copolymer (20–10:1 by weight) in such a way that itaconic acid units are dehydrated and transformed in the anhydridic form (Scheme 4), so that the latter reacts with the hydroxyls of polyol and cellulose, causing crosslinking and bonding to the fiber [289]. The fiber is then treated with bases to salify the carboxylic groups. The product is useful for multi-ply disposable absorbent towel manufacture.

Grafting of acrylic acid by means of gamma irradiation onto poly(ethylene) or poly(ethylene-vinyl acetate) (about 8–30% by weight of vinyl acetate units) films or tubes is described [150]. The amount of grafted acrylic acid is around 35% by weight. Grafting is followed by alkaline treatment aimed to salify the carboxylic groups. The process gives water-swellaable materials, useful for the manufacture of surgical devices.

2.4.2. Posttreatments

Absorbent polymers belonging to any of the previous classes are mixed with alcoholic or water/alcoholic solutions of a polyhydric alcohol (a glycol, glycerine, pentaerythritol, etc.) and heated at about 190°C [204]. Surface crosslinking which takes place avoids "fish-eyes" formation. Polyglycidyl ethers, polyfunctional aziridines, amines, or isocyanates may be substituted for the polyhydric alcohol [176]; the heating temperature depends in this case on the compounds used. When mixed with silica, handling of the material is greatly improved.

The properties of SAP are improved by treating them with polyvalent metal salts [72, 56]. In the first case [72], a trivalent metal salts solution is added to an uncrosslinked carboxylate copolymer solution; 0.01–1.4 meq of the following salts per gram of copolymer are found effective: aluminum acetate, chloride, or sulfate, chromium or zirconium acetate, ferric chlo-



SCHEME 4.

ride, and ferric or titanium acetylacetonate. The polymer becomes water swellable, and may uncomplex at high pH and recomplex at lower pH. In the second patent [56], a crosslinked carboxylate polymer is further surface crosslinked by dispersing its powder in an organic solvent (methanol, toluene, etc.) and adding polyvalent metal compounds (in addition to the aforementioned salts, zinc or barium acetate, aluminum or stannous octoate, and manganese, cobaltous, or aluminum acetylacetonate are cited). These polymers can be dry-blended with 40% by weight of several other organic or inorganic absorbent materials [123]. Some examples of the latter are cellulose derivatives, modified starches, clays, talc, silica, or their mixtures. The amount of absorbed fluids is greater than the weighted sum of absorbance of individual components.

A method to improve manageability of absorbent polymers, limiting "gel-blocking" phenomena and dust formation during subsequent transformation steps, is reported in several patents [295, 308]. Fine superabsorbent polymer particles (75 μm in the first case, 200 μm in the second one) are separated and backmixed with the highly viscous reaction product gel [295] or with the polymerizable monomer solution [308]. Another method comprises mixing of the particles of poly(sodium acrylate) suspended in a hydrocarbon with a polymerizable solution of acrylic acid (about 15%) and silica (0.3%), filtering, and drying [267]. The aggregates obtained are absorbent without the occurrence of gel-blocking. A last method comprises wetting of the fine particles to form a continuous amorphous gel, grinding, and drying [251].

3. APPLICATIONS OF SUPERABSORBENT POLYMERS

Artificial snow, used to produce frozen surfaces for skiing areas, is made by mixing water, natural snow, or finely ground ice with a superabsorbent acrylic polymer and freezing the mixture. The mixture can be aerated before freezing. The snow can be directly flooded on the skiing area [306, 167, 169], spread with a snow gun [284], or mechanically shattered and compacted [249]. Best results are reached when the SAP are not more than 5% by weight of the total composition. "Soft" snow is obtained with a slightly crosslinked poly(acrylate), while "hard" snow is obtained by copolymerizing acrylic acid with acrylamide and increasing the amount of the crosslinking agent [249]. Other SAP may be used instead of acrylic copolymers, and the addition of a surfactant makes it easier to drain water from the snow layer.

Water scavenger pouches may be manufactured by putting an amount of SAP into a bag made of a water-permeable hydrocarbon inert material [154]. The pouch is able to absorb settled water layers from hydrocarbon fuel and oil storage containers, and it can be reused up to 20 times.

Poly(acrylate)s are used as artificial soils for hydroponics [129]. Plant growth media are manufactured by blending a water-soluble polymer with a finely pulverized inert filler, wetting the mixture with sprayed water, and exposing the composition to ionizing radiation to crosslink the polymer [30]. The patent gives many examples of useful polymers, although poly(ethylene oxide) is the preferred one: poly(acrylate)s or poly(acrylamide)s, natural or modified starches or cellulose, poly(vinyl alcohol), poly(amine), poly(sulfonate)s, etc. As inert fillers, wood flours or pulp fluff, cotton or cellulose flocs, perlite, nylon or rayon flocs, diatomaceous earth, coal talc or dust, clay, fly ash, magnesium silicates, etc. work. The resulting free-

flowing insoluble and swellable particulate is capable of absorbing and desorbing large amounts of water, and it can be used in combination with earth or sand. Poly(acrylate)/compost mixtures are also excellent plant growth media because of the ability of the polymer to retain water [128].

A thin layer of water-swellable acrylic polymer is generated into a soil. The layer acts as a water barrier, reducing permeability in sandy soils and preventing water leakage further underground [9].

A material suited for use as a support for floral arrangements of cut flowers in containers for decorative purposes is made by mixing 1–5% of starch-poly(acrylonitrile) graft copolymers with rice hull ash, silica, or alumina [93]. After water addition, the pH should be in the 4–8.5 range, otherwise the lifetime of the flowers will be short.

Encapsulated poly(acrylamide-co-sodium acrylate)s are used as drilling fluid additives for reducing lost circulation in wellbores [175]. The casing material is a high molecular weight paraffin that dissolves or melts (for example, by raising the temperature of the mud environment in a drilling hole) at a desired time of residence in the borehole. In this way the SAP components are released. They expand by absorbing water and seal off thief zones and fissures in the wellbore, thereby lowering lost circulation.

A drilling mud with low sensitivity to high temperatures and salt impurities is prepared by mixing acrylic acid-methyl cellulose graft copolymer with clays [14].

Particles formed by a hard-core sand nucleus, a casein adhesive interlayer, and an outer coating of absorbent polymer [for example, crosslinked poly(acrylamide)] avoid water encroachment through fissures or fractures in building excavations, mines, oil and gas wells, etc. [1]. Materials for sealing underground formations, joints in water-supply pipes, building construction, and the like, based on several kinds of absorbent polymers, are described in other patents [11, 94, 112, 280]. Sealing compositions may include other ingredients, such as suitable resins [94] or rubbers [112, 280].

Polymer concrete compositions suited for use in repairing spalled or cracked concrete runways, parking structures, bridges, and the like, especially where the concrete surface is wet, comprise a thermosetting resin [unsaturated poly(ester)s or poly(esteramide)s, optionally norbornyl- or hydrocarbon-modified, vinyl ester resins], 0.1–5% of SAP, and, optionally, a mineral filler (sand, crushed stone, fly ash, and the like) [155, 200].

Water-swellable acrylic acid/vinyl alcohol or acrylonitrile/starch copolymers, added in 0.5–1.5% amounts to limestone mainly composed of calcium oxide and silicate, provide a static demolition agent used for destroying rock structures [252]. Holes are formed, for examples, in rock beds and filled with such agents. The agent changes itself to the hydrated form when it reacts with water; the large expanding force thus generated demolishes

the rigid structure. The method is an alternative to explosives, impact steel ball, oil hydraulic splitter, or pick hammer utilization.

Polymeric aggregates able to pelletize iron ores or coal fines are prepared by mixing water with poly(acrylamide-sodium acrylate) and sodium carbonate and drying the product [243]. Oil dispersion of poly(sodium acrylate), poly(acrylamide-sodium acrylate), acrylonitrile-starch graft copolymers, and a suitable oil-in-water emulsifier are used to transform a sticky mass of coal fine and water into a crumbly dry mass easy to transport [231]. Crosslinked poly(acrylamide-sodium acrylate) is also very effective in thickening sewage [165].

Absorbent copolymers [isobutylene/maleic anhydride copolymers, poly(vinyl alcohol)/maleic anhydride copolymers, starch-acrylic acid graft copolymers] incorporating magnetic materials, such as Fe_3O_4 , are used to absorb moisture from powder of coking coal. The magnetic substances allow easy separation of the polymer from the coal [296].

A resin useful as a biomass support and carrier, and also suitable for seeding, is prepared by adding Fe_3O_4 to a crosslinked methacryloyloxyethyl-dimethylbenzylammonium chloride polymer [236]. Fe_3O_4 acts as mentioned above.

A crosslinked poly(2-hydroxyethyl methacrylate) containing TiO_2 , cobalt naphthenate, and triphenyllead acetate is used as an antifouling coating for watercraft [12].

A thermal energy storage blend composed of crosslinked poly(acrylate) and decahydrate sodium sulfate is described [145]. The blend may be loaded into a heat-exchanger and heated; on cooling, latent heat of crystallization of the salt is released at room temperature.

A dew-preventing coating is described which contains a crosslinked poly(acrylate), acrylic monomers, and an inorganic filler [246].

A coating of water-swellaible polymer is applied onto an electrochemical cell electrode surface in order to prevent electrolyte leakage and electrode drowning [24, 13].

For many applications it is necessary that a poly(vinyl chloride) dispersion (either in plasticizers or organic dispersants) have thixotropic properties; that is, high viscosity at a low shear rate and low viscosity at a high shear rate. It was found that addition of 0.1% by weight of SAP to a PVC dispersion may improve its thixotropy [151].

Superabsorbent polymers dispersed in a poly(isobutylene)/poly(alkylene glycol)/silica gel matrix are used to protect wires which carry small dc currents and to heal shorts caused by moisture in such wires [226]. Alcohols, surfactants, dihydroxy-terminated oligo-olefins, or fatty acids may be substituted for the poly(alkylene glycol) component; poly(fluoroether)s may be substituted for the poly(isobutylene).

Welsh et al. describe an improved method to preserve biological specimens in HCHO [5]. To the bottle containing the specimen (a spider in the example) immersed in HCHO solution, a powder of crosslinked poly(acrylate) coated with a surfactant is added. The specimen remains suspended in the gelled solution, and no dislocation takes place when the bottle is shaken.

Poly(ethylene) or ethylene-vinyl acetate copolymer films coated with starch-poly(acrylate) SAP mixed with a urethane adhesive are useful for preserving the freshness of packed fruit and vegetables [257].

Manufacturing procedures for towels, bandages, and absorbent laminates in general, containing SAP, are described in several patents [126, 131, 172, 114, 19, 99]. A foaming agent can be incorporated into the composition before the final drying step [114]. Flexible absorbent boards are manufactured by slurrying a mixture of water, cellulosic fibers, and a modified polysaccharide SAP, pressing the product in vacuo to drive off water, and drying [108, 142].

Poly[methyl methacrylate-*N*-(1,1-dimethyl-3-oxobutyl)acrylamide-acrylic acid], treated with alkaline solution to increase water absorption, is used to prepare contact lenses [22].

Enhancement of water absorption properties of synthetic fibers like rayon or hydroxyalkylcellulose is achieved by injecting 10–20% of an acrylic SAP water slurry into a fully ripened viscose solution [62]. The viscose solution is spun or extruded in an acid bath, stretched, and finally treated with bases to transform the carboxylic groups of SAP into their salt form. The fibers show good cohesion (greater than that of prior art) and are easily cardable.

Bubble-free phantoms for NMR diagnosis are obtained by impregnating a crosslinked poly(acrylate) molding with a mixture of saline solution and gadopentetate dimeglumine [290]. Polymer synthesis is carried out by aging the polymerization mixture at -20°C , followed by UV-irradiation.

Biosensors for determination of biochemical analytes are produced by immobilizing biochemicals (antibodies, enzymes, etc.) to a biocompatible porous matrix made of a hydrogel coated on a dielectric material sensor [309].

SAP are very useful for the controlled released of drugs into the human body. The active substance is mixed with a natural or synthetic water-absorbent, water-insoluble polymer. Crosslinked sodium carboxymethylcellulose, crosslinked poly(*N*-vinylpyrrolidone), or crosslinked poly(vinyl alcohol) [299], calcium alginate [268], or sodium acrylate-starch graft copolymers [119] can be used among others. The active substance is released at a controlled rate. After the end of the dosage period, the crosslinking bonds are cleaved and the polymer dissolves.

A wound dressing gel is described which is made of gelamide, glycerin, crosslinked poly(acrylic acid), and water [222]. A wound dressing foam is prepared by impregnating a strip of poly(urethane) foam with an alcohol/ CCl_4 solution of epichlorohydrin-crosslinked dextran, poly(*N*-vinylpyrrolidone), and poly(ethylene oxide) [101].

Laminated articles which come into contact with body fluids (prosthesis implants, artificial kidneys, membranes, and tubing) are made from a blend of a water-soluble copolymer (composed of *N*-vinylpyrrolidone, vinyl acetate, and *N,N*-dimethylacrylamide) with acrylic SAP [113]. The blend is bonded by heat to a layer of water-insoluble thermoplastic polymer [PVC, cellulose acetate butyrate, poly(vinylidene fluoride), and the like].

Emulsions with moisturizing activity toward human skin [221] or having antiperspirant properties [134] are prepared by mixing grafted-starch copolymers with water, oils, surfactants, and other suitable ingredients.

Several kinds of SAP are used as gelling materials in suction equipment for absorbing medical wastes and body fluids (blood, lymph liquid, medullary fluid, amniotic fluid, urine) produced during operations in hospitals [304].

Materials capable of deodorizing air, especially from the presence of mercaptans, hydrogen sulfide, and ammonia, are obtained by dispersing an iron phthalocyanine octacarboxylic acid into SAP [261].

SAP are used as desiccant materials in refrigeration systems of buildings [250]. SAP do not lose their efficiency even if coated by oil (by Freon or lubricating oils).

An aqueous gel for use in fighting fire comprises water, a water-swellaable poly(acrylate), a nonionic water-insoluble inorganic filler (TiO_2 , alumina, kaolin, etc.), and, optionally, a water-insoluble dye [2]. An aqueous gel sprayed by automatic fire extinguishing sprinkler systems comprises silica and a water-swellaable polymeric component, coated by a poly(alkylene glycol) monoether, which delays the polymer from contacting water for the short time needed for uniform dispersion [18].

Crosslinked poly(ether)s are used as water desalination media [6]. The polymer absorbs water from saline solutions at one temperature and gives it up at another temperature.

Filtration media made of biogenetic silica (silica obtained from the combustion of plants rich in silica, like rice hulls and equisetum) and 1–2% of a starch-acrylonitrile graft copolymer show good porosity and selectivity, do not compact or become sticky, and are dimensionally stable [171].

Poly(urethane) foams, used in sponge manufacture, often have poor absorption characteristics. Incorporating SAP into a poly(urethane) may greatly enhance the capability of the sponge to retain liquids. SAP can be added (5–10%) to most conventional poly(urethane) formulations com-

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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