

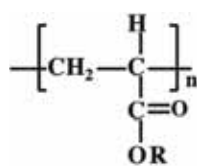
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Acrylic Polymers as Coatings Binders

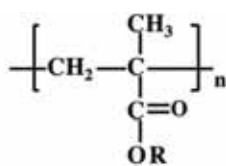
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INTRODUCTION

ACRYLIC POLYMERS, WHICH ARE USED AS COATINGS BINDERS, are comprised chiefly of esters of acrylic and methacrylic acid that are polymerized by addition polymerization, usually using a free radical mechanism:



An acrylate



A methacrylate

Interest in acrylic technology dates back to the 1920s when Dr. Otto Rohm developed a practical process for making acrylate esters from ethylene. Shortly afterwards, his associate, Otto Haas, established the first commercial production of methyl and ethyl acrylate in the United States [1]. The first commercial use of an acrylic polymer was as an adhesive-like interlayer for laminated safety glass. Probably the highest profile use of an acrylic began in 1936 with the introduction of thermoplastic, transparent methacrylate sheet. With the advent of World War II, methacrylate sheet became invaluable as a tough, weather-resistant glazing material for military aircraft. Since it could be formed easily and had excellent optical properties, the transparent plastic was used for aircraft canopies, bomber noses, and gun turrets [2].

Acrylic technology soon expanded into the coatings industry in the form of acrylic solution polymers, followed later by acrylic emulsions. The acrylics gained widespread market acceptance as coatings binders due to such outstanding properties as color stability, transparency, and resistance to weathering and aging. The good weathering resistance of acrylic polymers is primarily due to their resistance to hydrolysis and their lack of absorption of ultraviolet (UV) light, the high-energy portion of the light spectrum most responsible for degradation.

Acrylic solution polymers (often referred to as acrylic resins) are generally copolymers of acrylate and methacrylate esters prepared by direct solution polymerization in a solvent that has a solubility parameter similar to that of the polymer. Typical solvents include aromatics such as toluene and xylene, as well as ketones and esters. Acrylic resins are typically supplied at about 30 % to 50 % solids

by weight, with viscosities ranging from a few hundred to a few thousand centipoise. In later years, 100 % solid-grade versions became popular since they reduced the cost and safety concerns associated with shipping resins containing high solvent levels. The coatings manufacturer is then able to dissolve the solid-grade acrylic in a wide range of solvents, thereby having greater control over the formulation ingredients.

A wide range of properties can be built into an acrylic coatings binder by careful selection of the type and level of the acrylic monomers used. Some of the important properties (such as tensile strength and elongation of cast films) for several acrylic homopolymers can be found in Ref. [3]. Coatings for a wide range of applications can therefore be custom designed. Some of the principal applications for acrylic solution coatings include automotive finishing, factory and farm implement coatings, general-purpose pigmented coatings, aerosol lacquers, and clear coatings for a multitude of substrates. There are two types of acrylic solution polymers: (1) thermoplastic polymers, which harden simply by loss of solvent through evaporation; and (2) thermosetting polymers, which contain functional groups that react with another functional material (i.e., melamine, epoxy, isocyanate, etc.) to form a cross-linked network. The advantages and disadvantages of each are discussed in detail later in this chapter.

Acrylic emulsion polymers (often referred to as acrylic latexes) have become one of the major binder types in use in the coatings industry today. To form an emulsion polymer, the acrylic monomers are emulsified and then polymerized as small droplets in a continuous water phase. The droplets are typically stabilized by surfactants, and usually no solvent is present. While acrylic emulsions are generally associated with quality architectural coatings, they are also used to formulate industrial coatings. In fact, the use of acrylic emulsions in industrial applications is expanding at the expense of solvent-based systems because of the industry's need to control organic emissions. Over the past 20 years, acrylic emulsion manufacturers have made great strides in improving the properties of acrylic emulsions so that they now offer performance similar to the solvent-based coatings they are replacing.

When the first acrylic emulsion designed for use in house paints was introduced in 1953, it had the low-odor, quick-drying, and easy cleanup features of its water-based competitors, styrene-butadiene and poly(vinyl acetate) emulsions; but, in addition, it offered excellent exterior

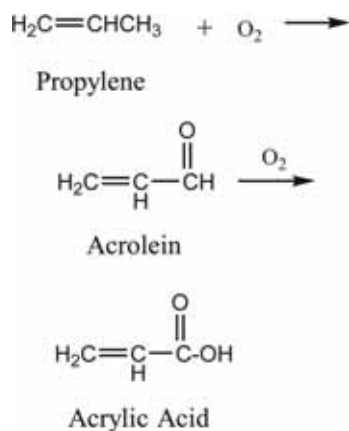
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durability that allowed use in exterior paints. During the past 40 years, it has been good exterior durability that enabled acrylic emulsions to replace solvent alkyds as the dominant binder in the exterior house paint market.

Acrylic Monomers

Virtually all of today's world-wide supply of acrylic acid is based on the two-stage vapor-phase oxidation of propylene via an acrolein intermediate:

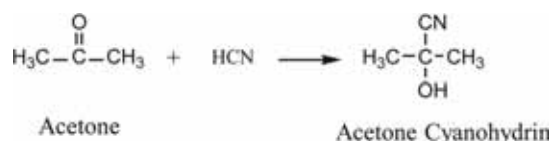


Generally in the first step, propylene is oxidized to acrolein in the presence of steam and air using a Mo-Bi-based multicomponent mixed oxide catalyst. A fixed bed tubular reactor is used to facilitate heat removal and steam generation. In a similar second reactor, containing a Mo-V mixed oxide catalyst, the acrolein is further oxidized to acrylic acid. Acetic acid is a minor byproduct. The hot reactor effluent is quenched in an absorber and the aqueous rundown is sent to a purification section where crude acrylic acid is recovered either as a distilled overhead material or as a bottoms material also containing heavies. Crude acrylic acid can either be converted to glacial acrylic acid (by removing minor levels of organic acid and aldehyde impurities) or it can be converted to acrylate esters, such as methyl, ethyl, butyl, or 2-ethylhexyl acrylate, by reacting it with the appropriate alcohol in the presence of a strong organic or mineral acid or acidic ion exchange resin.

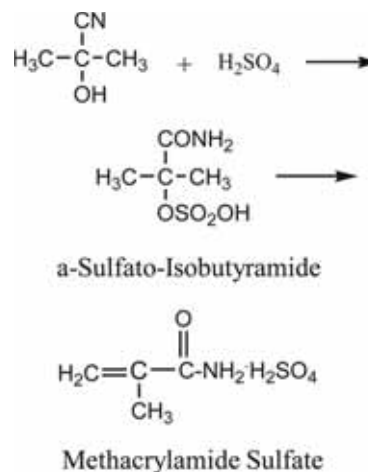
Older acrylic acid technology based on the liquid-phase carbonylation of acetylene with nickel carbonyl in the presence of water or an alcohol to yield either acrylic acid or an acrylate ester (Reppe chemistry) is no longer practiced due to cost and safety considerations. Niche chemistries, e.g., the hydrolysis of acrylonitrile, are only practiced commercially at small scale where cost is not a determining factor.

Methacrylates

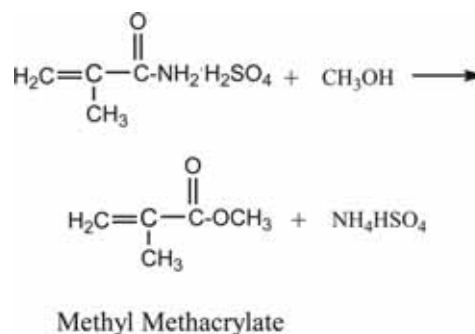
Several process technologies are currently used to produce methacrylic acid and methyl methacrylate. The conventional acetone cyanohydrin route to methyl methacrylate (MMA) has been practiced commercially since 1937 with only minor improvements to the process over the past 74 years. The basic technology remains virtually unchanged: HCN (on-purpose from natural gas and ammonia or by-product from acrylonitrile production) is reacted with acetone to form acetone cyanohydrin:



The acetone cyanohydrin is hydrolyzed with sulfuric acid to an a-sulfato-isobutyramide intermediate which rearranges to methacrylamide sulfate:



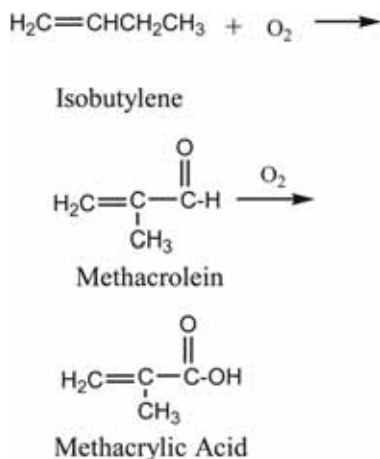
The methacrylamide sulfate is then either reacted with water to make methacrylic acid or, more commonly, it is esterified with methanol to methyl methacrylate:



Mitsubishi Gas Chemical recently developed a new route to MMA that also relies on acetone cyanohydrin as a key chemical intermediate but utilizes a different reaction pathway to methyl methacrylate: acetone cyanohydrin is reacted with water in the presence of a manganese dioxide catalyst to yield a-hydroxy isobutyramide. (The conventional technology tries to minimize the water content of the hydrolysis feed to minimize a-hydroxy isobutyramide formation.) The a-hydroxy isobutyramide is transesterified in the liquid phase with methyl formate to produce methyl-a-hydroxyisobutyrate which is, in turn, dehydrated in the vapor phase to methyl methacrylate. The transesterification step also generates formamide which is thermally decomposed to hydrogen cyanide which is recycled to the front-end of the process. This process chemistry uses no sulfuric acid and much of the HCN required to produce the acetone cyanohydrin is recycled within the process.

Today, about 80 % of the world's methyl methacrylate production capacity is based on acetone cyanohydrin chemistry.

Most of the rest of the world's supply of methyl methacrylate is produced via the conventional two-stage vapor-phase oxidation of isobutylene (or t-butanol) using process technology that is an analogue of the propylene oxidation technology described above for acrylic acid:



The methacrylic acid is subsequently esterified to methyl methacrylate.

ACRYLIC SOLUTION POLYMERS

Thermoplastic Resins

Thermoplastic acrylic resins are acrylic polymers that are polymerized directly in a suitable solvent and form a film solely by evaporation of the solvent. They do not need to be oxidized or cross-linked to form a hard, resistant finish. They are fast-drying lacquer materials, but they remain permanently soluble.

Acrylic resins are usually supplied in strong solvents such as toluene, xylene, or methyl ethyl ketone. They are clear, colorless solutions and, if left unpigmented, will also dry down to clear, colorless films. They are often used in unpigmented form as protective finishes over vacuum metalized plastics and polished metals such as brass.

Acrylic resins generally make excellent grind media for dispersing pigments. No external pigment wetting agents are required to make finely dispersed pigment grinds for high-gloss lacquers. Also, thermoplastic acrylic polymers are quite unreactive and consequently are stable when mixed with pigments, extenders, and colors. They do not discolor powdered metals, such as aluminum.

Acrylics are a uniquely versatile family of polymers since an infinite array of properties can be achieved by carefully selecting combinations of the various acrylic monomers. Each acrylic monomer brings to the polymer its own individual performance characteristics based on its molecular structure. This is particularly true for polymer hardness as determined by the glass transition temperature (T_g) of the monomers that make up the homopolymer (only one monomer) or copolymer (two or more monomers). The T_g of a polymer is a softening point: it is actually a temperature range where the polymer undergoes a second-order transition. At temperatures below the T_g , the polymer is a glass, but above the T_g the polymer is a rubbery material. To approximate the T_g for a copolymer composition, it is useful to utilize the relationship proposed by Fox [4].

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (1)$$

where

W_1 and W_2 = the weight ratios of Monomers 1 and 2, respectively,

T_{g1} and T_{g2} = the T_g 's of the homopolymers of Monomers 1 and 2 in degrees absolute.

Since thermoplastic acrylics are not cross-linked to achieve a desired level of performance, the concept of T_g and the ability to manipulate T_g as a means to control properties is crucial in designing polymers that meet the needs of the coatings market. The marked difference in T_g 's, and consequently polymer characteristics of the acrylics, can phenomenologically be explained by the free-volume theory proposed by Fox and Flory [5] and later refined by several others. The free-volume theory states that the T_g for any given polymer occurs at that temperature where the fractional free volume (i.e., unoccupied space contained within the polymer) reaches some universally constant value that remains unchanged as temperature decreases below T_g . Above this temperature, the free volume increases, permitting sufficient molecular motion so polymer flow can begin. In Fig. 1, Rogers and Mandelkern have plotted specific volume versus temperature for a series of methacrylates as a means of establishing the relationship of T_g to free volume [6]. The arrows (f) in Fig. 1 indicate the temperature at

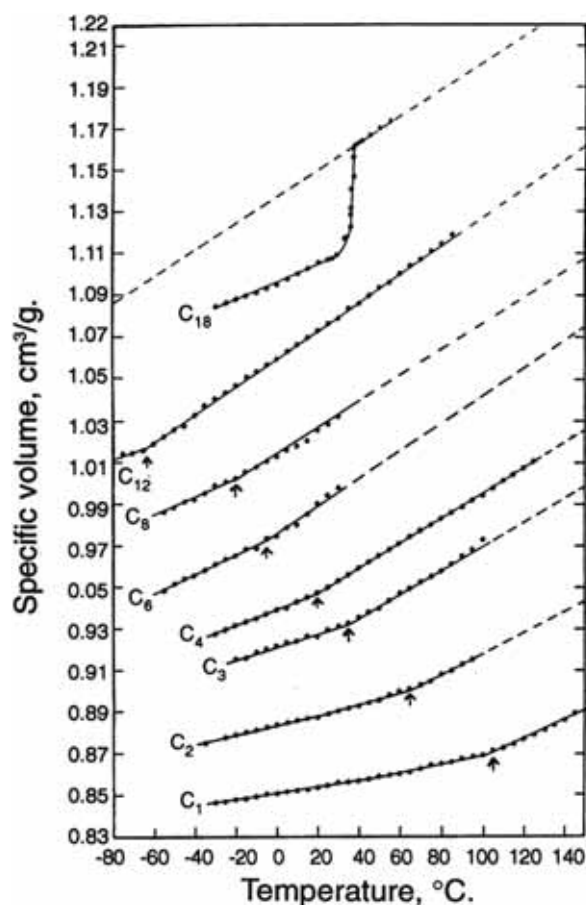


Fig. 1—Specific volume-temperature relations for the poly-(n-alkyl methacrylates). (Reprinted with permission from the American Chemical Society, Copyright 1975.)

which there is an inflection in the specific volume curve indicating a sudden increase in free volume (as temperature increases). This is the T_g . From the graph, it can be calculated that, at T_g , free volume accounts for 15 % of the total polymer volume [6]. Simha and Boyer have independently calculated that at T_g , free volume accounts for 11 % of a polymer's total volume [7].

On a molecular level, the T_g differences for the acrylic family of polymers can also be easily explained. The acrylates have an alpha-hydrogen atom next to the carbonyl group, giving them more rotational freedom and hence greater segmental chain motion than the methacrylates. The methacrylates have a bulky methyl group substituted for the alpha-hydrogen atom, which hinders molecular rotation, thereby increasing chain stiffness. The methacrylates are therefore higher in T_g , harder, higher in tensile strength, and lower in elongation than analogous acrylate polymers.

Equally important to T_g and polymer hardness is the length of the ester side chain of the monomer. As the alcohol moiety of the ester side chain becomes larger, the polymer chains are pushed further apart, creating additional free volume, thereby encouraging greater molecular rotation. Consequently, the polymers become increasingly soft (as the ester side chain becomes larger) until the effects of side-chain crystallization causes additional hardening effects. The large range of T_g 's that exist for the acrylate and methacrylate family of homopolymers can be found in Ref. [8].

The second most important parameter governing the film properties of a thermoplastic acrylic polymer is molecular weight (MW). Most dry film properties for thermoplastic acrylics improve with increasing MW up to a MW of about 100 000 and then tend to level off. Tensile strength, elongation, toughness, solvent resistance, and exterior durability are all dependent on MW. This dependence of strength, elongation, and resistance of the acrylic polymer on MW is primarily due to the greater number of chain entanglements (which act almost like cross-links), anchoring the polymer chains at higher M W (i.e., longer chain length).

However, the viscosity of a solution polymer is proportional to the MW of a polymer according to the Mark-Houwink equation [9].

$$\eta = K(MW)^a \quad (2)$$

where

η = solution viscosity

K and a = constants derived experimentally for a specific polymer/solvent combination (for polymethyl methacrylate in toluene, $K \times 10^5 = 7.1$ and $a = 0.73$). The type MW used in determining the constants should be specified.

As MW increases, the solution viscosity also increases, thereby posing handling and application problems if the MW becomes too high. For example, high spray solids are desirable for acrylic lacquers because of economy and emissions concerns. The lower the MW of the polymer, the lower the viscosity at a given solids content, or conversely, the higher the spray solids at spray viscosity. Consequently, low MW is beneficial to solids and application concerns, whereas high MW is needed for good film properties.

The obvious answer to the viscosity versus film property dilemma is to reach an optimum balance by producing an intermediate MW polymer. For this reason, most thermoplastic acrylic solution polymers have weight-average MWs in the 75 000 to 100 000 range. It is also helpful to narrow the MW distribution, reducing the amount of low-molecular-weight fractions, which have a deleterious effect on resistance and strength properties, while also minimizing high-molecular-weight portions, which increase viscosity and cause application problems such as cobwebbing of spray-applied acrylic automotive lacquers.

Since the application and drying properties of an acrylic resin are largely controlled by the physical characteristics of the solvent contained in the resin, as well as by the interaction of the polymer and solvent, it is essential to carefully select the solvent in which the acrylic is dissolved (see Chapter 18 entitled "Solvents"). To ensure good solubility of the polymer, it is important to match the solubility parameter of the solvent to that of the polymer. The solubility parameter is an estimation of the polarity of a solvent or polymer and is related to the intermolecular energy of the molecule (see Chapter 38 entitled "Solubility Parameters"). The solubility parameter concept was defined by Hildebrand [10] and applied to coatings by Burrell. Burrell has published the solubility parameters for an extensive list of solvents [11].

For polymers, the solubility parameter can be calculated by knowing the molecular structure of the repeating unit according to Small's method. Small has published a table of molar attraction constants used to calculate polymer solubility parameters [12].

Besides being helpful in estimating solubility, the solubility parameter concept is helpful in predicting the resistance of polymers to solvents or other organics. In general, the more polar acrylic polymers will have the best resistance to hydrophobic materials, such as gasoline, grease, or oil. More hydrophobic acrylics (with low δ values) will have better resistance to polar materials, such as water and alcohol.

The evaporation rate of the solvent or solvent mixture must also be carefully chosen to accommodate the expected application method and conditions. For spray application, moderately fast evaporating solvents are needed to avoid running and sagging of the low-viscosity paint. For roller coating, a much higher viscosity coating would be used; therefore, slower evaporating solvents are required to avoid skinning on the roller and to allow for flow out of roller pattern created during application of the paint. Since thermoplastic acrylics dry by evaporation of solvent alone, extremely slow-drying solvents, which retard development of properties, should be avoided.

The majority of thermoplastic acrylic solution polymers are designed for general-purpose industrial finishing (i.e., metal furniture and product finishing) and have a T_g of approximately 50°C. This T_g is generally obtained by copolymerizing combinations of methyl methacrylate (MMA), butyl methacrylate (BMA), ethyl acrylate (EA), butyl acrylate (BA), and ethylhexyl acrylate (EHA). While many other acrylate and methacrylate monomers exist, as indicated in Table 2, these few are the primary acrylic monomers that are commercially available and that are, therefore, the most economically feasible.

At a T_g of 50°C, these acrylic polymers are intermediate in hardness, having a Tukon hardness of about 11 to 12 [see ASTM Test Methods for Indentation Hardness of Organic Coatings (D1474)]. They are hard enough to dry rapidly to a tack-free state that allows early handling of the coated product and also hard enough to resist marring, print [see ASTM Test Method for Print Resistance of Lacquers (D2091)], block [see ASTM Test Method for Blocking Resistance of Architectural Paints (D4946)], and dirt pickup. Yet, they retain enough flexibility and elongation to have some impact resistance [see ASTM Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact) (D2794)], and some can even be post-fabricated, such as is done with coil coated stock to produce aluminum gutters, trim pieces, etc.

Up to the mid-1950s, nitrocellulose lacquers were the major automotive coating in use. Nitrocellulose finishes gave an excellent original appearance but had poor durability, particularly gloss retention, and required frequent polishing by the car owner for the finish to look good. This problem was eliminated in 1956 when General Motors adopted acrylic lacquers based on poly(methyl methacrylate). The acrylic lacquers gave significantly better durability and allowed for the use of the more modern eye-catching metallic pigments [13]. The acrylic lacquers generally contain external plasticizers, such as the phthalates, which contribute to improved chip resistance and cold crack resistance. No internal plasticizing monomer (i.e., acrylates) is generally contained in automotive acrylic lacquers, and consequently their T_g is approximately 105°C, with a Tukon hardness of about 22.

Since they are very hard and fairly high MW (i.e., 100 000), the thermoplastic solution polymers designed for automotive use are not capable of the excellent molecular flow that would be expected of softer/lower-molecular-weight polymers. Consequently, the acrylic lacquers require factory buffing and or baking to obtain the kind of maximum gloss required for the new-car showroom. This disadvantage was shared by the older nitrocellulose lacquers.

Also, because of hardness and high MW, the spray solids percent is low. Since these lacquers are thermoplastic, they are permanently subject to softening by strong solvents, such as toluene or acetone, if for some reason they would contact the automotive finish. Conversely, however, the thermoplastic acrylic lacquers can be easily repaired by an additional coat of paint which “melts” into the original coat, leaving no “two-coat” effects or intercoat adhesion problems.

Thermosetting Acrylic Resins

Thermosetting acrylic resins are compositionally very similar to the thermoplastic-type acrylics, with the exception that they contain functional groups, such as carboxyl or hydroxyl, that are capable of reacting with another polymeric or monomeric multifunctional material to produce a three-dimensional network structure. As has already been discussed, the mechanical properties of thermoplastic acrylic polymers for coatings are generally improved by increasing MW, but polymers with overly high MW produce solutions of unworkably high viscosity. An alternate route to improved film properties is to use a thermosetting acrylic polymer, converting linear, moderate-molecular-

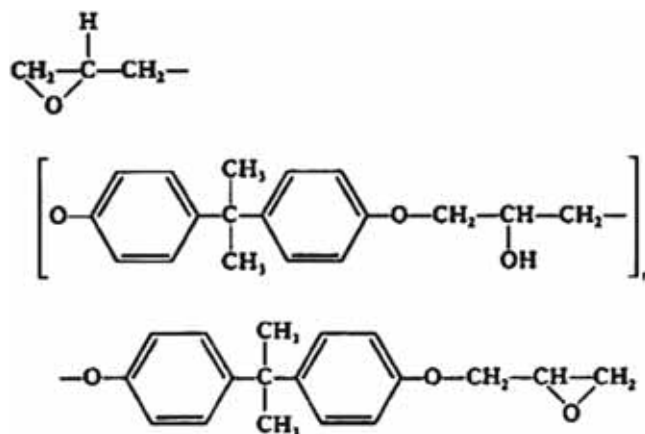
weight polymer chains to an infinite MW structure. This cross-linking reaction takes place after the coating has been applied to the substrate, often by the application of heat, hence the term “thermosetting.” To be truly cross-linked, one of the reactive species must have at least two reactive sites, while the other species has at least three reactive sites per molecule or chain.

Thermosetting acrylic polymers offer the following advantages over thermoplastic acrylics: (1) improved hardness and toughness, (2) better resistance to softening at elevated temperatures, (3) improved resistance to solvents, stains, and detergents, and (4) lower applied MW, resulting in lower solution viscosity and consequently higher application solids.

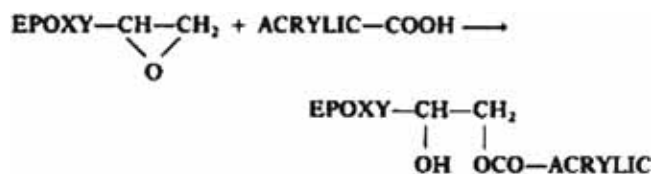
Over the years, numerous chemical reactions utilizing various functional groups have been devised as a means to cross-link acrylic polymers. However, we will elaborate on some of the more commercially significant thermosetting acrylics, namely those cross-linked with nitrogen resins, epoxies, and isocyanates.

ACID-FUNCTIONAL ACRYLICS CROSS-LINKED WITH EPOXY RESINS

Possibly the most resistant acrylic enamels are based on thermosetting acrylic solution polymers that contain acid functionality and are reacted with an epoxy resin. Typically, the epoxy resin is a condensation product of Bisphenol A and epichlorohydrin (see Chapter 10, entitled “Epoxy Resins in Coatings”).



The acrylic solution polymer is made acid functional simply by incorporating acrylic or methacrylic acid into the backbone; when cured under suitable conditions, it reacts with the epoxide to form ester linkages between the two polymers:



An alternative reactant to epoxies based on Bisphenol A/epichlorohydrin is another acrylic polymer wherein epoxide sites have been incorporated by polymerizing glycidyl acrylate, glycidyl methacrylate, or allyl glycidyl ether into the acrylic backbone. This approach is limited in use,

however, because both economics and performance favor the Bisphenol A type epoxides. Also, in recent years, epoxy manufacturers have developed many aliphatic epoxides in an attempt to mimic the benefits of the workhorse Bisphenol A based products (i.e., resistance properties) without the accompanying disadvantages (i.e., poor resistance to UV light).

The carboxyl-functional acrylic resins typically have a MW in the 10000 to 50000 range and a carboxyl content of 5 % to 20 %. Some higher solids acrylics are lower in molecular weight with higher acid content. The acid content of the acrylic polymer determines the equivalent weight of epoxy resin required to react with the acrylic to achieve a thoroughly cross-linked system.

Styrene or vinyl toluene are often incorporated into the acrylic polymer as “honorary” acrylic monomers because their reaction kinetics with acrylic monomers are fairly good and because they often improve alkali resistance and are low in cost. The cross-linking reaction between the carboxyl group on the acrylic polymer and the epoxy resin is fairly sluggish and requires a base catalyst such as dodecyl trimethyl ammonium chloride, or tri(dimethylaminomethyl) phenol. In some instances, melamine-formaldehyde resins are sufficiently basic to be used as catalyst and have the additional advantage of entering into the cross-linking reaction [13]. For improved package stability, however, it is preferable to add the base catalyst to the other components just prior to use. Even with catalyst, the baking or stoving requirements for acid/epoxide systems are fairly high, with 15 to 30 min at 150 to 190°C being typical. Of course, the higher the bake temperature, the shorter the bake time required for cure. To determine the optimum conditions for a given system, it is best to cure that system at a variety of baking conditions and then measure properties to determine the temperature and time required for maximum performance.

The primary uses for acid-functional acrylics cross-linked with epoxy resin are as appliance enamels and coatings for interior metal furniture and equipment. Acrylic/epoxy enamels fill the needs of the appliance industry primarily because of their excellent alkali/detergent resistance [see ASTM Practice for Detergent Resistance of Organic Finishes (D2248-89)], which is critical to the performance of washing machine coatings. Other properties that are important to the appliance industry include: hardness, scratch resistance, grease resistance, stain resistance, as well as flexibility, impact resistance, and adhesion to metal. Acrylic/epoxy enamels, on the whole, offer an excellent balance of these important properties. Typical properties for an enamel based on an acid-functional acrylic resin cross-linked with a Bisphenol A based epoxy are shown in Table 1.

The disadvantages associated with acrylic/epoxy coatings are usually concerns brought about by the aromatic nature of the Bisphenol A based epoxy cross-linker. Their most significant limitation is poor resistance to UV light, which restricts their use to interior applications. If used outside, the aromatic Bisphenol A portion of the epoxy would degrade rapidly, and early chalking would occur. In some of the newer high-solids acrylic/epoxies, the epoxy content is very high and can therefore cause discoloration problems even indoors due to UV light. Where this is a problem, an aliphatic epoxy can be substituted for at least

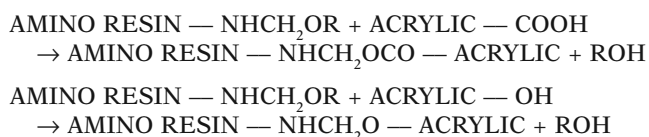
TABLE 1—Application properties for a white enamel based on an acid functional acrylic resin cross-linked with Bisphenol A based epoxy (baked 39 minutes at approximately 180°C) [14]. Reprinted with permission of The Dow Chemical Company

Tukon hardness	16.2
Pencil hardness	2H
Solvent resistance, glass	
Cellosolve acetate, 15 min	6B
Cellosolve acetate, 60 min	6B
Xylol, 15 min	5B
Stain resistance, cold-rolled steel	
Mustard, 30 min	no stain
Ink, 30 min	trace
Print resistance, cold-rolled steel	
82°C, 30 min, 2 psi	light print
Detergent resistance ^a	
1 % detergent, 74°C, 200 h	Few—6
Optical properties, CRS (two coats)	
Original 60° gloss	95.5
Gloss after 16 h at 178°C	95.4
Original color	9.2
Color after 16 hr at 178°C	13.0
Microknife adhesion, CRS “H” Value	22.8
Mandrel flexibility ^b 1/2 in., 1/4 in., 1/4 in.	
Cold-rolled steel	0-0-0
Bonderite 1000	0-0-0
Reverse impact, inch-lbs (joule)	
Cold rolled steel	22 (2.48)
Bonderite 1000	15 (1.70)
Direct impact, inch-lbs (joule)	
Cold-rolled steel	35+ (3.96+)
Bonderite 1000	50+ (5.65 +)
^a ASTM blister rating. A rating of 10 means no blistering, a rating of 0 means very large blisters, with intermediate ratings judged by ASTM photo standards.	
^b 0=no cracks; 9=delamination.	

some of the Bisphenol A based epoxy to reduce sensitivity to UV radiation (see Chapter 10 entitled “Epoxy Resins in Coatings”).

ACRYLIC POLYMERS CROSS-LINKED WITH AMINO RESINS

Acrylic polymers containing acid or hydroxyl functionality can be cross-linked with amino resins such as: urea, melamine, and benzoguanamine formaldehyde condensates (see Chapter 8 entitled “Amino Resins”) as follows:



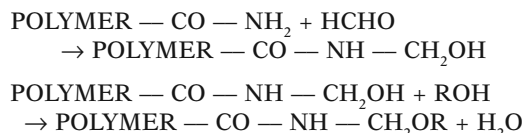
Reactions with amino resins containing an $\text{-NH-CH}_2\text{OH}$ group are possible because this group differs from a simple alcohol in that it is far more acidic and reactive. Likewise, the methylol ether (when capped with alcohol) is more reactive than a conventional dialkyl ether. The curing condition required for acid functional acrylics cross-linked with amino resins is approximately 30 min at 150°C , while for an analogous hydroxyl functional acrylic, the reaction is more facile, requiring 30 min at 125°C with an acid catalyst [15]. Since the acid-methylol reaction is relatively slow, it allows significant self-condensation of the amino resin [16]. This detracts from the overall toughness and resistance properties.

The hydroxyl-functional acrylics are, therefore, favored over acid-functional polymers and are most often used in combination with a methylolated or butylated melamine-formaldehyde or benzoguanamine-formaldehyde condensate. Urea-formaldehyde condensates are less durable and have been found to have lower gloss and poorer chemical resistance. Hydroxyl functionality is incorporated into the acrylic polymer by copolymerizing monomers such as hydroxyethyl acrylate (HEA) or hydroxyethyl methacrylate (HEMA). This type of combination produces cross-linked acrylic/amino enamels with outstanding exterior durability, good hardness, and mar resistance, as well as excellent resistance to solvent attack. Acrylic/amino thermosetting enamels were, therefore, very successful in replacing the less durable alkyd/melamine systems in automotive topcoat applications, and general industrial finishing. Over the years, the automotive industry has relied heavily on this type of thermosetting acrylic because it offers the outstanding durability of acrylic lacquers but with better resistance to solvents and elevated temperatures. It also offers significantly higher application solids. Also, it does not require factory buffing to achieve high gloss as do the acrylic lacquer coatings.

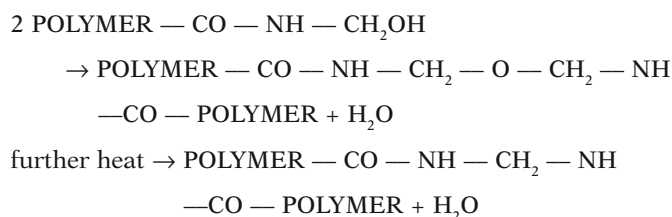
Another reason that acrylic/amino resin technology became so popular is because of the versatility of the chemistry, whereby properties can be readily altered by varying acrylic T_g , acrylic monomers, acrylic functionality level, and cross-linker type and level. This is very important in general industrial finishing, where coatings often must be custom tailored to the specific end use. Ref. [17] briefly demonstrates the kinds of variation in performance that can be obtained by a few manipulations in composition.

An alternate approach to a thermosetting acrylic polymer is to prepare an acrylic polymer that contains functionality analogous to a melamine/formaldehyde condensate. Methylol or methylol ether groups can be attached to an acrylic backbone, and the resulting polymer can self-condensate, resulting in a cross-linked structure without the need for an external cross-linking agent. Initially, an acrylic polymer is made containing acrylamide (AM). The polymerization is usually a conventional free-radical, solution polymerization carried out in alcohol or a combination of alcohol and aromatic solvent. As in most thermosetting

acrylic polymers, mercaptan is usually included to control molecular weight. After the polymerization is complete, the polymer is treated with formaldehyde to convert it to the methylol amide. An acid catalyst will bring about etherification with the alcohol present, usually butanol. The conversion proceeds as follows [18]:



As an alternative process, the AM monomer can be methylolated before being polymerized. The finalized methylolated amide acrylic polymers condense readily when acid catalyzed at bake conditions of 30 min at 150°C . The condensation process is a two-stage reaction [19]:

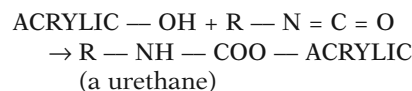


If the methylolated amide has been etherified by butanol capping, instead of water as a by-product, a mixture of butanol and dibutyl ether would be obtained. These types of self-condensing acrylic resins will also react with amino resins, but usually there is no justification for so doing (i.e., no improvements in performance). The strength of the methylol amide acrylics is that they have no glaring weaknesses and make very good general-purpose resins.

ISOCYANATE-REACTIVE ACRYLICS

Acrylic solution polymers that are cross-linked with isocyanates (often referred to as acrylic urethanes) are unique among the various cross-linking systems because they cure under ambient conditions—they don't require baking. The isocyanate group (-N=C=O) is extremely reactive and will cross-link with any type of functionality having a labile hydrogen atom. This includes amines, alcohols, ureas, urethanes, carboxylic acids, and amides. Acrylic polymers designed to be cross-linked with isocyanate resins generally contain hydroxyl functionality incorporated by polymerizing hydroxyethyl acrylate (HEA) or hydroxyethyl methacrylate (HEMA) into the acrylic backbone.

There are six basic types of curing mechanisms for urethane coatings [see ASTM Terminology for Paint, Related Coatings, Materials and Applications, Varnish, Lacquer, and Related Products (D16-75)]. The two-package polyisocyanate/polyhydroxyl coatings make up "Type V." Of this class, acrylic urethanes based on weather-resistant hydroxyl functional acrylics predominate. The hydroxyl functional acrylic reacts with isocyanate resin as follows:



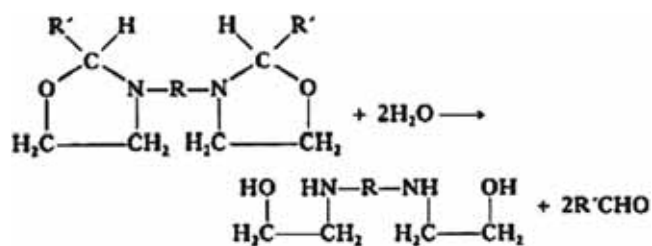
The preferred isocyanates are usually aliphatic, such as the adduct of hexamethylene diisocyanate (HMDI), because

of the poorer color and exterior durability associated with the aromatic types of isocyanates. While the aromatic varieties of isocyanate react faster than the aliphatic types, a wide range of catalysts are available, which can be used to speed up the cure of aliphatic isocyanates. A few such catalysts include triethylene diamine, zinc naphthenate, and dibutyl tin-dilaurate [20].

Acrylic solution polymers cross-linked with aliphatic isocyanates are ideal for applications where a durable, high-performance coating is required but where baking is not feasible because of the size or temperature sensitivity of the object to be coated. Acrylic urethanes are, therefore, invaluable in the transportation industry where high-quality coatings are needed for aircraft, railroad cars, trucks, buses, etc. Automobile refinishing, heavy equipment coatings, and high-performance maintenance coatings are also areas where acrylic urethanes are appropriate. The acrylic urethanes combine the inherent UV resistance and exterior durability of acrylics with the ambient cross-linking ability of aliphatic isocyanates to produce hard, tough, chemical-resistant, high-performance coatings. The major drawback of acrylic urethanes is that they are a two-package system and cannot be mixed until ready for application because they are so reactive and have a short "pot life."

Over the years, the hydroxyl-functional acrylics have been improving in performance, and now the emphasis is on higher solids content for lower VOCs. To meet more stringent VOC regulations, lower-molecular-weight, higher-solids hydroxyl functional acrylics have been developed. Increasing the solids of the acrylic reduces solvent levels in the formulated coating. To compensate for lower molecular weight, one way to improve performance is to increase hydroxyl content, which in turn requires higher levels of isocyanate.

An alternative approach to reduced solvent or higher solids is to modify the acrylic urethane with a reactive diluent which is fluid and acts like a solvent but then reacts to form part of the cross-linked network [21]. One such diluent is a low-molecular-weight, difunctional oxazolidine which is nonreactive with isocyanates until ambient moisture opens the ring, releasing both hydroxyl and amine functionality [22].



This type of functionality has the advantage that it is one package stable with isocyanates as long as moisture is excluded from the paint. Because it has four reactive sites per molecule, it increases cross-link density for maximum performance, while it decreases solvent emissions.

ACRYLIC EMULSION POLYMERS

An acrylic emulsion is a two-phase system in which acrylic polymer droplets are dispersed in an external water phase, usually with the aid of an emulsifier (i.e., surfactant). Unlike

some polymer emulsions, such as alkyds or epoxides, which are emulsified as preexisting resins, acrylic emulsions are made by an emulsion polymerization process wherein the monomer droplets are emulsified in water and then polymerized. A typical acrylic emulsion polymerization recipe is given in Table 2 [23].

The physical chemistry of acrylic emulsion polymers is much the same as for their solution polymer analogs, and the film properties of the emulsions can be controlled by manipulating polymer composition and MW just as with acrylic solution polymers. However, the viscosity of an emulsion is unaffected by polymer MW since solution principles do not pertain to emulsions (the polymer is insoluble in the continuous water phase). Therefore, for the best possible physical properties, the MW of acrylic emulsions is generally higher than that of acrylic solution polymers: 100 000 to 1 000 000 for an emulsion versus 75 000 to 100 000 for a solution polymer.

The particle size of an emulsion is also very important in determining performance and must be carefully controlled. For example, the film-forming ability of an emulsion, as well as its pigment binding capability, is dependent on particle size, with smaller particle size being better than large particle size. Particle size does affect emulsion viscosity, with large particle size generally being associated with low viscosity.

Acrylic emulsion polymers (also known as acrylic latexes) have long been a mainstay of the architectural coatings market, particularly in exterior paints where their outstanding durability is so important. However, in recent years, clean air regulations have further strengthened the position of acrylic emulsions, usually at the expense of solvent alkyds. The use of acrylic emulsions in industrial coatings applications has also grown as a result of solvent emission restrictions. At the same time, the properties of acrylic emulsion polymers in the industrial coatings market has improved so that they now offer performance similar to their solvent-borne counterparts.

Acrylic Emulsions for Architectural Coatings

Architectural coatings are generally considered to be coatings intended for on-site application to residential, commercial, or institutional buildings; they are also known as trade sales coatings. Over the last 50 years, this market has evolved from an entirely oil-based market to one dominated by emulsions. There are three underlying reasons for the takeover of the architectural coatings market by emulsion polymers. The health, safety, air quality, and odor concerns associated with the solvents in oil-based paints have moved people toward water-based latex paints whenever there is not a large penalty in performance. Also, latex paints are more tolerant of a wide variety of application conditions and can even be applied over damp substrates. Thirdly, emulsion polymers, particularly quality acrylic emulsions, have surpassed oil-based paints for long-term performance and protection in most applications.

Although acrylic emulsions generally provide a superior level of performance, their cost is somewhat higher than lower-performance emulsions such as vinyl acetates. Therefore, in segments of the architectural coatings market where performance is not critical, such as for interior flat paints, acrylic emulsions are not a dominant binder. However, in segments where performance and durability are

TABLE 2—Copolymerization of ethyl acrylate, methyl methacrylate, and methacrylic acid [23]. Reprinted with permission of The Dow Chemical Company

Materials:		
375.0 g	Deionized water	
5.1 g	Surfactant	
100.0 g	Ethyl acrylate (15 ppm MEHQ)	
100.0 g	Methyl methacrylate (25 ppm MEHQ)	
4.0 g	Glacial methacrylic acid (100 ppm MEHQ)	
4.0 mL	Ferrous sulfate solution (0.15 %)	
1.0g	Ammonium persulfate in 5 mL of water	
0.7 g	Sodium formaldehyde sulfoxylate in 5 mL of water	
5 drops	t-butyl hydroperoxide (70 %)	
Procedure:		
In a beaker, stir the surfactant with the water until dissolved and adjust the pH to 9.0 by adding 50 % sodium hydroxide solution. Transfer this solution into the reaction flask, rinse the beaker with a small amount of deionized water, and the monomers and ferrous sulfate, and stir 15 min with flow of nitrogen before adding the initiators. The maximum temperature of 77°C is attained in 12 to 15 min after adding the initiators, then cool to room temperature, adjust to pH 9.5 with 28 % aqueous ammonia, and filter: the gums amounted to 0.17 %. The free acid (unneutralized) surfactant can also be used as an emulsifier for the above copolymerization. In this case, the period of purging with nitrogen after charging the monomers should not exceed 15 min before the addition of initiators to avoid the formation of polymer emulsion product with excessive viscosity. Filtration of the finished emulsion gave only 0.05 % gums. The properties of these emulsions were:		
Surface Form	Sodium Salt	Free Acid
Solids content, %—Calculated	35.0	36.0
—Found	34.3	35.6
pH at25°C	5.6	1.8
Viscosity (Brookfield), cP	7.9 ^a	10.5 ^a
Partial size (light scattering), %	22.8 ^b	12.3 ^c
Minimum film-forming temperature, °C	22 ^a	30 ^a
^a Emulsion adjusted to pH 9.5 before measurement. ^b Measurement at 2 % solids. ^c Measurement at 0.4 % solids.		

essential, such as for exterior flat and gloss paints, acrylic emulsions control a very large portion of the market both in the United States and abroad.

INTERIOR COATINGS APPLICATIONS

The high-volume, interior-flat market is dominated by vinyl acetate copolymers plasticized with a soft acrylate monomer, usually butyl acrylate at about the 15 % weight level. Interior flat paints are aimed primarily at broad wall applications. Performance requirements for this market are fairly modest, with decorative features such as color, sheen level, and hiding being the more influential factors determining consumer preference. The one resistance property demanded in this market is scrub resistance; in this regard, vinyl/acrylics perform satisfactorily.

There is a premium segment of the interior flat market occupied by all acrylic latexes, and one of the key features which they offer is improved rheology and application characteristics resulting from the better interaction of acrylic latex particles with the new associative thickeners. Associa-

tive thickeners (also referred to as rheology modifiers) dramatically enhance flow, brushability, film build, and spatter resistance compared to conventional hydroxyethyl cellulose (HEC) thickeners.

Since interior flat paints contain a high pigment loading to increase hiding and reduce cost, the acrylic polymers used in this market tend to be fairly soft with good binding capacity. Typically, they are copolymers of a hard methacrylate monomer such as MMA with a soft, commercially available acrylate monomer such as EA, BA, or EHA. The T_g is generally around 10°C.

Interior gloss and semigloss paints have much more demanding requirements than flat paints since they are used for more diverse and challenging substrates such as windows, cabinets, and doors. Acrylic emulsions play a major role in this market, especially at the high-performance end. They are tailored to the specific needs of this market by optimizing the important variables contributing to performance: composition, hardness, MW, and particle size.

Acrylic emulsions used in gloss and semigloss paints are copolymers of acrylate and methacrylate monomers and are usually harder than emulsions used in flat paints. They generally have a T_g in the range of 20 to 50°C. The harder polymers are necessary to build in block and print resistance, which are needed to keep doors and windows from sticking and to prevent marring and film damage associated with softer polymers. Since gloss and semigloss paints are formulated at low pigment volume concentration (PVC) to obtain gloss, the pigment does not contribute significantly to film hardness; it must all come from the polymer.

Since these gloss and semigloss latexes are often used over old oil-based enamels, adhesion to aged oil-based paints is required. This may be accomplished by copolymerizing adhesion promoting functional monomers into the acrylic polymer backbone. A major breakthrough in latex adhesion technology came about with the development of ureide functional acrylic monomers [24]. The adhesion promoter particularly is needed to improve adhesion and blister resistance when the paint film becomes wet, as it might in a bathroom. Since the gloss paints are often used in wet areas such as a bathroom, the water resistance of the dry film is also an important property. To ensure good water resistance, acrylic emulsions used in this market often contain hydrophobic monomers such as styrene.

Since interior trim paints are so highly visible, overall appearance properties are critical to the success of the paint job, and features such as flow and leveling, gloss, and film build are expected to be similar to oil-based enamels. This level of outstanding appearance has been possible in recent years with the introduction of associative thickeners. The traditional thickener for latex paints has been HEC, which thickens by a flocculation mechanism and usually produces poor flow and gloss. Associative thickeners loosely bind to the surface of the latex particles through hydrophobic interactions, forming a network structure which accounts for their thickening action. The degree of interaction between the thickener and the latex particle is largely a result of the surface chemistry of the emulsion particles. Smaller particle-size emulsions have greater surface area and therefore have more interaction with associative thickeners. More hydrophobic latexes have stronger association with the new thickeners. Consequently, small-particle-size, hydrophobic acrylic emulsions have been designed specifically for use with associative thickeners. These newer acrylic emulsions optimize thickener interaction and produce exceptional flow and gloss. In fact, before these new emulsion/thickener systems, truly high-gloss latex paints were out of the question. They also improve brushability and film build, while eliminating the problem of roller spatter. Overall, the appearance properties of the newer small-particles-size hydrophobic acrylics, when used in combination with associative thickeners, rivals that of oil-based enamels.

EXTERIOR COATINGS APPLICATIONS

By far the most challenging application for any coating is as an exterior paint required to protect a multitude of substrates in diverse and extreme weather conditions. It is in this demanding role that acrylic emulsions have met virtually all requirements and impressed the industry by their outstanding durability. One primary reason for their success, as mentioned earlier for solution acrylics, is their

lack of absorption of ultraviolet light coupled with their inherent hydrolysis resistance. Over the years, acrylic emulsions have evolved from simple polymers troubled by shortcomings, such as poor adhesion or low film build, to sophisticated systems incorporating elements designed to address essentially every major challenge experienced by an exterior paint.

One of the toughest demands facing exterior flat house paints is the need to withstand the freeze-thaw type of expansion and contraction of dimensionally unstable substrates such as pine or other soft woods. To avoid the grain cracking that often occurs over this type of substrate, acrylic emulsions designed for flat house paints are fairly soft, with a T_g in the range of 10 to 15°C. A coalescing solvent is usually used in the formulation to assist film formation, particularly at lower temperatures. When the coalescent leaves, the acrylic paint film remains pliable and able to withstand substrate swelling and freezing, unlike oil-based house paints, which become harder and embrittle on exposure as they continue to cross-link. The primary concern with making the acrylic polymer too soft is that dirt pickup would worsen. Since flat house paints contain a fairly high pigment content (i.e., PVC = 40 to 60 %), dirt resistance is enhanced by the pigment loading. Experience over many years indicates that a T_g of 10 to 15°C is the optimum range to balance grain-crack resistance with dirt resistance.

For exterior flat house paints, the inclusion of an effective adhesion promoter in the acrylic backbone is crucial for good adhesion. The adhesion promoter greatly improves blister resistance. Furthermore, the improved adhesion enhances crack resistance over dimensionally unstable wood substrates. Painting over a degraded chalky surface is a common practice that can be a potential disaster if sufficient adhesion is not obtained. The chalk acts like a powdery barrier, preventing the emulsion binder from penetrating to the real substrate and establishing an adhesive bond. Studies have shown that smaller particle-size acrylic emulsions are much more effective than larger particle-size emulsions for filtering down through the chalk and obtaining adequate adhesion. For this reason, many exterior grade acrylic emulsions have been designed at a fairly small particle size of about 100 nm [25].

Small-particle-size, large-surface-area emulsions, when thickened with HEC, have poorer flow and film build than larger-particle-size emulsions, which are less aggregated by the flocculating mechanism of HEC. Therefore, 100-nm emulsions that were designed to have improved chalk adhesion sacrificed some of the flow and film build of large particle-size (500 nm) emulsions. In an attempt to combine these seemingly mutually exclusive properties, particle-size distributions have been carefully controlled to ensure a tailored mixture of small particles that give good adhesion to chalky surfaces and large particles that help to improve flow in formulations thickened with HEC. In the emulsion form, the key benefit of these bimodal polymers is their ability to be made at higher solids than unimodal latexes. Because of efficient packing of small with large particle, low emulsion viscosity can be obtained at higher emulsion solids. This packing efficiency leads to improved film properties over unimodal latexes. At the optimized particle sizes of large and small particles and optimized weight ratios, efficient packing of bimodal particles allow for longer drying times, because of less voids in the system which reduce

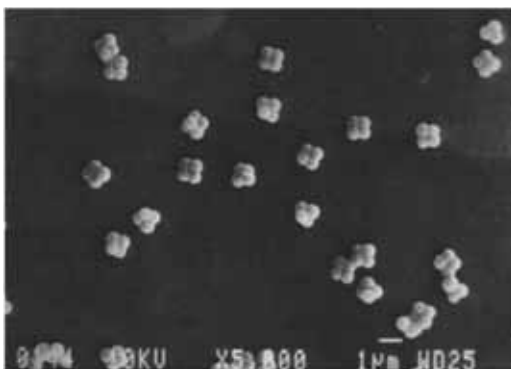


Fig. 2—Scanning Electron Micrograph of RHOPLEX™ MULTILOBE™ Acrylic Emulsion Polymer. (Reprinted with permission of The Dow Chemical Company [27].)

the surface area from which water can evaporate. Additionally, minimum film forming temperature (MFT) and water adsorption can be reduced with an optimized bimodal emulsion [26]. Compared to large-particle-size unimodal emulsions, bimodal emulsions improved adhesion properties of latex paints.

Wide particle-size distribution acrylic emulsions do not significantly address the low film build associated with smaller-particle-size emulsions when thickened with HEC. Film build is particularly important to an exterior paint because the durability of the film is usually proportional to the film thickness, i.e., how much paint is applied to the substrate. This was addressed in 1980s by the Rohm and Haas Co. with the introduction of a Multilobe® acrylic emulsion, shown in Fig. 2 [27]. This type of polymer has a lobed morphology that is grown out during the polymerization process; it does not result from particle aggregation. The lobes of this polymer are about 350 nm, but it has an effective hydrodynamic volume of about 1000 nm and is, therefore, very effective at imparting high film build in paints thickened with HEC. It also reduces the level of thickener needed to achieve a given viscosity. Since in its commercial form this technology also contains small particles, good adhesion characteristics are retained while film build is optimized.

Other important aspects of weatherability are color retention and resistance to chalking. These properties are made worse by the catalytic degradation effects of TiO_2 on the binder, so that high PVC flat paints are generally poorer than low PVC gloss paints. However, the inherent durability of the binder is still a controlling factor, and acrylic polymers have excellent resistance to sunlight and erosion, which contribute to their very good chalk resistance and color retention. Among the common acrylic copolymer compositions in use commercially, MMA/BA polymers are better than MMA/EA polymers, and higher methacrylate containing binders are better than acrylics containing higher levels of acrylate monomers. Of course, the methacrylate/acrylate levels are generally determined by the T_g required to achieve the desired balance of crack resistance and dirt pickup.

Exterior gloss and semigloss paints are required to withstand similar tortures as their flat paint counterparts and, in addition, must provide equally good dirt resistance at much lower pigment loadings. Acrylic emulsions have been designed that meet all of these challenges and perform very well in environments as diverse as the tropical regions of Asia and the Philippines to the Scandinavian regions of Europe. Since the acrylic emulsion engineered for interior gloss/semigloss paints are intended to be high-performance systems capable of good adhesion even in wet areas, they are often able to be used outside as well. Since exterior gloss paints must have good dirt resistance at low PVC, the acrylic emulsions used in these paints are harder than those used in flat paints and generally have a T_g in the area of 20 to 35°C (Fig. 3). This T_g range can provide acceptable dirt resistance while still having good grain-crack resistance. The very hardest acrylic emulsions used for interior gloss paints (i.e., above T_g 35°C) would not be appropriate outside, at least in areas subject to freezing, because they would be more prone to grain crack.

Since brush marks are much more obvious in a gloss paint than in a flat paint, good flow and leveling is much more critical for a gloss paint than for a flat paint. Consequently, older acrylic emulsions intended for semigloss paints (there were no high-gloss latex paints until about 1980) are of large particle size to have the best

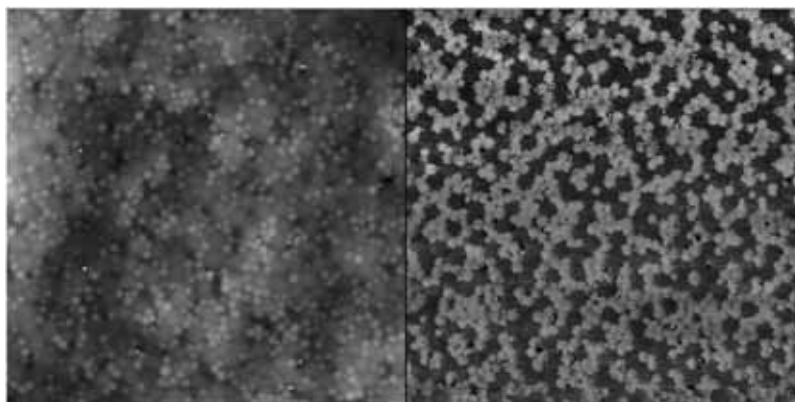


Fig. 3—Atomic force microscope (AFM) images of a bimodal blend two emulsion polymers with different T_g 's and particle size. The images on the left and right are the same images. The image on the left is a topographic image and the image on the right is a phase modulated image (allowing differentiation between soft and hard materials). Using the image on the right: The dark particles represent polymers with a particle size of 128 nm and T_g of 37°C. The light particles represent polymers with a particle size of 217 nm and T_g of 11°C. (Reprinted with permission of The Dow Chemical Company.)

possible flow with the prevailing thickener of the day, HEC. The flow of these systems could best be described as fair, but overall they have demonstrated an admirable balance of properties and are still popular today. However, newer acrylic emulsions intended for exterior gloss paint applications, particularly those generally referred to as acrylic enamel vehicles, are small in particle size (i.e., 100 nm) to take advantage of the excellent flow, gloss, and rheology available by using associative thickeners.

Over the past 20 years, the decorative as well as protective capabilities of exterior gloss paints have improved significantly to the point where acrylic emulsions are rapidly replacing alkyd enamels as the preferred coating for exterior trim.

Use of Acrylic Polymers as Property Modifier for Poly(Vinyl Acetate) Architectural Coatings

In some instances to achieve an acceptable balance between cost and film properties, blending of a low level of acrylic emulsion in a predominately poly(vinyl acetate) (PVA) paint is required. Generally, 100 % PVA binders have poor exterior paint performance properties including: adhesion, water resistance, dirt pickup resistance, efflorescence and alkali resistance. Blending of a small amount of acrylic binder will upgrade the performance of PVA paint in these properties. Also, block resistance is improved by modifying the PVA binder with a small amount of acrylic binder. Conversely, some properties such as scrub resistance may be degraded in the blended paints.

Acrylic Emulsion Maintenance Coatings

Maintenance coatings differ substantially from decorative coatings since they are used primarily for their protective features, which prevent substrate deterioration by corrosive elements. Maintenance coatings are generally used to protect metal surfaces such as bridges, storage tanks, and other industrial facilities, often in harsh chemical and corrosive environments. The first acrylic latex binders for corrosion-resistant maintenance coatings were introduced commercially in 1964. They are similar in hardness and composition to exterior flat house paint binders with the exception that they are formulated with reactive pigments and additives, which help prevent rusting. The surfactants and other "salt and pepper" ingredients used in the polymerization of maintenance acrylic emulsions are carefully selected so as to not aggravate corrosion.

These acrylic latex maintenance coatings had the usual advantages in application of water-based paints over solvent alkyd paints along with expected advantages in chalk resistance, color retention, and other decorative qualities. However, to the surprise of some segments of the maintenance industry, acrylic maintenance emulsions often outperformed solvent alkyds for corrosion resistance and overall metal protection. This is partly because the alkyds continue to harden and eventually crack, leaving the substrate exposed and subject to the elements. Acrylic emulsions do not continue to harden once the paint film is dry, and they remain sufficiently pliable to expand and contract with the substrate.

The one weakness of the acrylic latexes in the area of maintenance coatings was their low T_g , which reflected a lower hardness than the alkyd paints. This limitation was removed by the development of aqueous gloss enamel bind-

ers. These hard latex binders used in interior and exterior gloss paints were fine tuned to maximize corrosion resistance and overall protection. Commercialized in the mid-1980s, this new generation of maintenance vehicles has proved very successful in extensive field tests, particularly on bridges in the southeastern United States. The small particle size of these binders fits perfectly with associative thickener technology to give tight water-resistant films, which are an improvement over HEC-thickened paints that can have microscopic defects as a result of the flocculating mechanism of HEC [28]. In addition to use in thermoplastic maintenance coatings, acrylic latices have been developed to react with epoxy resins and iso-cyanates to allow for thermo set two component coatings with increased levels of toughness and chemical resistance.

Acrylic Emulsions for Traffic Coatings

The success or failure of a roadmarking paint will depend on its ability to: (1) dry quickly enough to prevent damage by traffic following the striping truck, (2) adhere to the road surface (concrete or asphalt) during the expected lifetime of the marking, and (3) retain a large percentage of the glass beads applied to the surface of the marking for driver visibility at night. Solvent paints based on short and medium oil alkyds with and without modification with chlorinated rubber resins have been used to meet these performance needs, but these paints do not retain glass beads for very long because the alkyd resins embrittle upon exposure to the elements. Roadmarking paints based on acrylic emulsions retain glass beads longer because they remain pliable upon exterior exposure. Before the 1990s, however, waterborne roadmarking paints based on acrylic emulsions did not dry fast enough, particularly when water evaporation is retarded by high humidity and low air flow, to viable low VOC replacement for solvent alkyd paints.

Waterborne paints based on acrylic emulsions quickly replaced solvent alkyd paints in the United States in the 1990s after the development of quick-setting acrylic emulsions. Quick-setting latex binders are stable as they are supplied and formulated at high pH (around 10). When paint films are applied, the pH drops rapidly from the evaporation of ammonia and causes the film to set. This quick-setting mechanism allows films that still retain significant water contents to resist being picked up by tires and smeared on road surfaces and being redispersed and washed away by rain. This allows waterborne paints to have sufficient dry speeds over a wide range of humidities, temperatures, and wind speeds.

Formulations for waterborne roadmarking paint differ substantially from those of typical exterior architectural paints. In order to speed the drying process, the volume solids of a waterborne traffic paint is ca. 60 %, thereby minimizing the amount of water. By way of contrast, an architectural paint would have a volume solids in the range of 35 to 40 %. Similarly, traffic paint PVCs are ca. 60 %, which is higher than their exterior architectural analogs, which have PVCs on the order of from 40 to 50 %. The acrylic emulsions used to formulate traffic paints must have good shear stability because the need for high solids necessitates dispersing the pigments in the emulsion. This allows for ca. 60 % PVC and 60 % volume solids paints with 50 % weight solids emulsions, with particle sizes ca. 200 nm.

Paints based on emulsions with significantly lower particle sizes are too viscous and those with higher particle sizes tend to cause hard sediment to form on storage.

White roadmarkings need to have some degree of dirt pickup and black tire marking resistance to maintain a visible contrast with lighter road surfaces, like concrete and some asphaltic roads. The high pigment content enhances the hardness and whiteness retention of traffic paints, but the polymer emulsions used in traffic paints are also fairly hard (T_g range from 20 to 45°C). Incorporation of styrene as the hard monomer to replace MMA in a copolymer with BA makes the composition more hydrophobic, which enhances wet adhesion to road surfaces. However, it is generally more difficult to achieve viscosity stability with styrenated compositions. Additionally, the long term retention of glass beads (in the dried coating) can be adversely affected due to the poorer UV resistance of styrene.

Acrylic Emulsions for Industrial Coatings **NONREACTIVE EMULSIONS**

Industrial coatings users, who have traditionally applied solvent-based polymers, have recently been under pressure to reduce volatile organic emissions. This is particularly true in California, which has historically been at the forefront of clean air legislation. In many instances, these coatings users have complied with the stricter environmental legislation by switching over to water-based systems. Acrylic producers have responded to the needs of these coatings users by developing more sophisticated emulsions capable of meeting the demanding performance requirements of many different end users. Early emulsions aimed at industrial coatings applications were offshoots of architectural coatings technology and were often too soft for industrial coatings uses. Also, high gloss was not possible with these older emulsions. Like the newer gloss enamel emulsions for trade sales use, however, latexes aimed at industrial coatings applications have evolved into hard, resistant binders that match the performance of their solvent-based counterparts. Without this evolution in performance, it is unlikely that industrial coatings users would switch to latex coatings even with the more severe emissions regulations.

Thermoplastic acrylic emulsions designed for industrial coatings applications generally have to be harder and faster drying than architectural emulsions and have better corrosion and chemical resistance. The typical T_g range for such acrylics is about 30 to 70°C. The film formation problems usually associated with such hard emulsions are somewhat alleviated by the controlled application conditions in the factory, so that low-temperature film formation is generally not required. For general industrial finishing over metal substrates, industrial acrylic emulsions have borrowed technology from maintenance finishes and have optimized surfactants, additives, and compositions to improve rather than detract from corrosion resistance.

Newer heterogeneous acrylic emulsions comprised of two or more phases have recently become important in the industrial coatings industry. One such type of heteropolymer, the core-shell polymer, is being used to achieve rapid hardness development with improved block and print resistance at low VOC. These properties allow the manufacturer to stack, pack, and ship coated parts more quickly [29]. Using core-shell technology, acrylic emulsions

have been able to rival the performance of traditional, high-solvent-content nitrocellulose lacquers in wood coatings and furniture finishes. The major deficiency of acrylic emulsions in these areas is the “warmth” of water-based coatings compared to solvent-based materials. “Warmth” is a quality that refers to the feel and appearance of the coated wood.

THERMOSETTING EMULSIONS

Just as is the case with solution acrylics, functional groups can be incorporated into the polymer backbone of an acrylic emulsion so that it can react with another functional material after application to the substrate, forming a cross-linked polymer. Typically hydroxyl or hydroxyl/acid functional acrylic emulsions are cross-linked with urea or melamine resins. Acid functional acrylic emulsions can be cross-linked with emulsified epoxy resins. The chemistry of these systems is identical to the cross-linking chemistry discussed earlier for solvent-based acrylic resins. After the emulsion is cross-linked, the infinite molecular weight provides for solvent and chemical resistance, along with hardness and toughness. By adjusting the level of functionality, the amount of cross-linker, and the T_g of the acrylic emulsion, a system can be custom designed for a specific application.

For many years, the construction industry has relied on hydroxyl functional acrylic emulsions reacted with urea or melamine to coat products such as hardboard, wood panels, shingles, and metal coil. In interior applications, such as over wood paneling, these emulsions offer comparable cure speed and performance to solvent-based alkyd/urea systems. In coil coating applications, the thermosetting acrylics offer high gloss, excellent durability, good corrosion protection, as well as good roll coatability. These emulsions have been applied at line speeds up to 137 m/min with good transfer, flow, and leveling. Usually these systems are catalyzed with an acid catalyst to achieve the fastest/lowest temperature cure. A very good property balance is demonstrated in Table 3 for an aqueous acrylic/melamine coil coating enamel [30]. A recent development in cross-linking acrylic emulsion technology is an epoxy cross-linking, ambient cure system, which has many applications but has been found to be particularly useful in maintenance coatings. Besides being ambient curing, an attractive feature of this system is its excellent early properties resulting from the high-molecular-weight acrylic emulsion, which provides ample resistance characteristics until the epoxy cross-linking is complete. An example of an acrylic/epoxy system compared to an epoxy/polyamide coating and an alkyd coating can be found in Ref. [31]. The strong points of the acrylic emulsion/epoxy system are its stain, solvent, and chemical resistance, along with outstanding weathering. No less a key feature is its very good corrosion performance [32].

Effect of Particle Structure and Morphology on the Properties of Latex Films

The usual method for preparing a homogeneous copolymer emulsion particle is by introducing monomers into a water/surfactant solution at a pre-assigned ratio. Once formed, the alignment of the chemical groups in the particle are not uniformly distributed throughout the particle, but rather organized to give thermodynamically stable structures. As

TABLE 3—Properties of an aqueous acrylic/melamine coil coatings enamel over aluminum and galvanized steel. Reprinted with permission of The Dow Chemical Company [30]

Substrate	Aluminum ^a	Mini-Spangle Galvanized Steel ^a
Primer thickness	0	0.2
Topcoat film thickness	0.9 to 1.0	0.8
Gloss 20°/60°65/89—/8°	65/89	—/80 ^b
Image clarity	Very good	Good
Tukon hardness (KNH)	9	9
Pencil hardness		
Initial	H	H
Wet 16 h, 38°C, H ₂ O	B	B
Flexibility—X30 microscope	2.3T	3T
Direct impact, in.-lbs	20 to 25	35
Reverse impact, in.-lbs	15	10
Metal mark resistance	Excellent	Excellent
Rheology	Excellent	Excellent
MEK rubs	200	200
Cleveland condensing cabinet 200 h at 60°C	Pass	Pass
After 1000 h salt spray exposure		
X-scribed area		
Tape adhesion, % removed	0	0
Lifting	None	None
Undercutting	1/16 in.	1/16 in.
Blistering ^c	None	Mod-Dense, No. 6, No. 8
Exposed edge		
Undercutting	...	4/16 in.
Blistering ^c	...	Mod, No. 2, No. 4
1/8-in. mandrel bend		
Blistering ^c	...	None
White rust	...	None
Flat		
Blistering ^c	None	None

^a Commercial chromate pretreatment.^b Gloss dependent on smoothness of substrate.^c 1–9: Higher number indicates smaller blisters; blister density is rated as few, moderate, or dense, 10=no blisters.

a result, when co-polymerizing hydrophilic monomers with hydrophobic monomers, the structure of the particle is not a statistical distribution of monomers throughout the particle but rather the surface of the particle is typically enriched in the hydrophilic monomers. Ultimately, the ratio of monomers used, as well as the polarity and glass transition temperature of the monomers, contribute to the morphology of the latex emulsion particle and this morphology contributes significantly to the latex film properties.

There are many instances when it is desirable to customize a particle to improve a given property of a latex film. For many cases this can be easily accomplished by adjust-

ing monomer ratios or the type of monomer in a homogeneous copolymerization. However, in some cases, adjusting the ratio or type of the monomers results in compromises in some other aspect of the polymer. One example of this is optimization of a gloss film for block resistance. Using homogeneous copolymerization to obtain a glossy film that has good block resistance calls for hardening the latex, which requires using an increased ratio of high *T_g* monomers to low *T_g* monomers. As a result, the overall *T_g* of the copolymer is increased, and a greater amount of coalescent is required to obtain good film formation. This is undesirable both from a cost and an organic emissions perspective.

Much has been written regarding conventional methods such as employing combinations of particles of high MFT with particles of low MFT [33,34]. Using this approach, emulsion particles of different monomeric composition are obtained so that the correct amount of hard particles and soft particles are present in a paint to achieve the desired film properties. If the correct polymeric compositions are used and the correct particle ratios are used it is possible to avoid phase separation and obtain films with desirable properties without the need for coalescent. Typically, in paint systems the continuous polymer phase of a film is dictated by the volume percentages of the different polymer particles present. If a soft emulsion polymer is blended with a hard emulsion polymer, the MFT of the blend will remain approximately equal to the MFT of the soft polymer until the hard polymer is about 50 % of the blend. Above 50 % hard polymer, the hard polymer becomes the continuous phase and the soft polymer becomes the dispersed phase. As a result the MFT of the blend is approximately equal to the MFT of the hard polymer. A further consideration of blending of polymers to achieve desired film properties involves the ratio of particle size of soft polymer/hard polymer. In order to achieve desired properties from blending particles, it is often desirable that a continuous network of the hard phase particles be present in a film. In order for this to occur (at volume fractions of soft particle/hard particles >50 %) the hard particles must be significantly smaller particle size than the soft particles.

In an effort to further improve the performance of acrylic emulsions, without compromises in other properties, the morphology of emulsion particles has become an additional important variable [35–37]. In the past few years, new composite acrylic emulsions have been introduced, particularly into the interior gloss area, which are made up

of two or more nonhomogeneous phases. They are prepared by a two-stage polymerization process sometimes referred to as sequential emulsion polymerization that results in various types of core-shell structures. The goal of this type of polymerization is to incorporate the best characteristics of the different phases.

In this approach, well-defined latex particles containing different phases are prepared, usually in a sequential process. To obtain these particles, the first phase of the particle is formed until a high monomer conversion is achieved (low residual monomer). Then a second phase (in the same particle) is formed as a result of a change in the monomer feed composition. The particle formed will contain discrete phases of the first and the second monomers fed into the process. Close control of the process must be achieved to avoid generation of a second particle during the second stage of the polymerization. Ultimately, the morphology of the particle is not only dependent on the materials used but also on both thermodynamic and kinetic influences. In a broad description of this technology the morphology of a multiphase particle can be described as domains of one polymer (dispersed phase) within a continuum of another polymer (continuous phase). When the dispersed phase is a single domain, the term “core-shell” morphology is used. When using polymer phases that differ in polarity, it is likely that the more hydrophilic polymer will be the continuum, and will dominate the particle surface. Nonspherical polymer morphologies containing two phases that resemble “acorns,” “mushrooms,” or “raspberries” can be made (see Figs. 4 and 5).

This tailoring of morphology can have significant effects on film properties. A study was conducted to determine the effect of changing polymer morphology on pure binder systems and gloss paints [38]. In one aspect of this

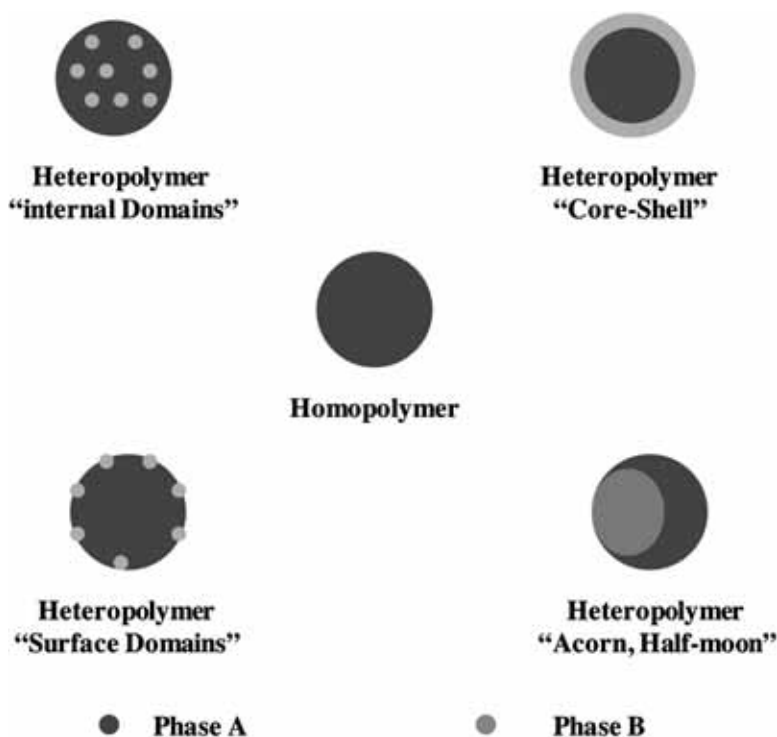


Fig. 4—Cross-sectional representations of polymer morphologies.

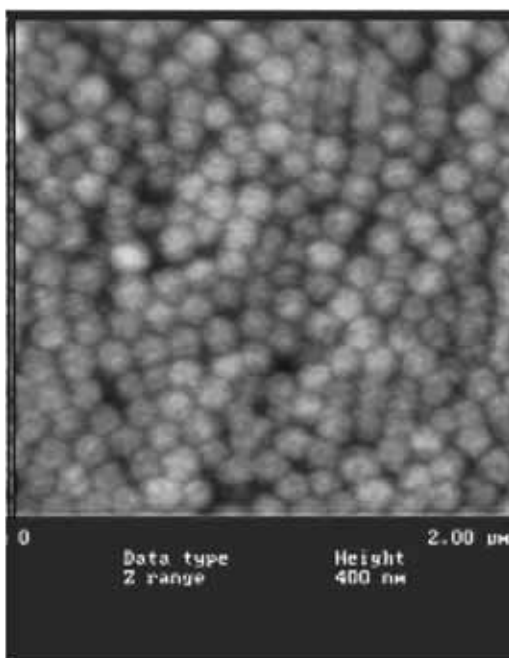


Fig. 5—AFM image of an 100 % acrylic heteropolymer. The polymer shown in this image has a “raspberry” morphology. (Reprinted with permission of The Dow Chemical Company.)

study it was found that increasing the ratio of a hard phase (98.5 % MMA and 1.5 % AA, T_g 105°C) to a soft phase (65.7 % BA, 32.8 % MMA and 1.5 % AA, T_g -4°C) led from films that had poor block resistance and poor tack, to films that had improved block resistance and tack. Additionally, it was found in a gloss paint that increasing the hard phase and improving block and tack resistance was obtained without the need for a coalescent up to ratios of 35 % hard phase. Increasing hard phase content past an optimized level requires the use of coalescent to form good films. Additionally, surface gloss is negatively affected by increased hard phase due to the hard phase of polymer sticking out of continuous soft phase polymer.

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References

- [1] *Chemicals for Industry, Rohm and Haas Company 1909–1959*, The Lakeside Press, R. R. Donnelly & Sons Co., Chicago, IL, 1959, p.20.
- [2] *Chemicals for Industry, Rohm and Haas Company 1909–1959*, The Lakeside Press, R. R. Donnelly & Sons Co., Chicago, IL, 1959, p.21.
- [3] Brendley, W. H., Jr., “Fundamentals of Acrylic Polymers,” *Paint Varnish Prod.*, Vol. 63, July 1973, pp. 19–27.
- [4] Fox, T. G., *Bull. Am. Phys. Soc.*, Vol. 1, 1956, p. 123.
- [5] Fox, T. G., Jr., and Flory, P. J., *J. Appl. Phys.*, Vol. 21, 1950, pp. 581–591.

- [6] Rogers, S., and Mandelkern, L., *J. Phys. Chem.*, Vol. 61, 1957, pp. 985–990.
- [7] Simha, R., and Boyer, R. F., *J. Chem. Phys.*, Vol. 37, No. 5, 1962, pp. 1003–1007.
- [8] Kine, B. B., and Novak, R. W., “Acrylic and Methacrylic Ester Polymers,” *Encyclopedia of Polymer Science and Engineering*, 2nd ed., H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, Eds., Vol. 1, John Wiley and Sons, New York, 1985, pp.257–258.
- [9] Rodriguez, F., *Principles of Polymer Systems*, McGraw-Hill Book Co., New York, 1970, p. 154.
- [10] Hildebrand, J. H., and Scott, R. L., *The Solubility of Non-Electrolytes*, 3rd ed., Rheinhold Publishing Corp., New York, 1949, pp. 129, 301.
- [11] Burrell, H., *Official Digest*, Vol. 27, No. 369, 1955, pp. 726–758.
- [12] Small, P. A., *J. Appl. Chem.*, Vol. 3, 1953, pp. 71–80.
- [13] Solomon, D. H., *The Chemistry of Organic Film Formers*, Robert E. Krieger Publishing Co., Huntington, NY, 1977, p. 273.
- [14] “Acryloid Thermosetting Acrylic Resins,” revised October 1966, Rohm and Haas Company promotional literature C-1 70, Spring House, PA.
- [15] Solomon, D. H., *The Chemistry of Organic Film Formers*, Robert E. Krieger Publishing Co., Huntington, NY, 1977, pp. 277–281.
- [16] Saxon, R., and Lestienne, F. C., *J. Appl. Polym. Sci.*, Vol. 8, 1964, pp. 475–488.
- [17] Petropoulos, J. C., Frazier, C., and Cadwell, L. E., “Acrylic Coatings Cross-linked with Amino Resins, Symposium on Thermosetting Acrylic Resins,” *Off. Dig.*, Vol. 33, 1961, pp. 729–736.
- [18] Solomon, D. H., *The Chemistry of Organic Film Formers*, Robert E. Krieger Publishing Co., Huntington, NY, 1977, p. 283.
- [19] Christenson, R. M., and Hart, D. P., *Off. Dig. Fed. Soc. Paint Technol.*, Vol. 33, 1961, pp. 696–698.
- [20] North, A. G., *J. Paint Technol.*, Vol. 43, No. 557, 1971, pp. 44–50.
- [21] Watson, D. M., and Schall, D. C., *Am. Paint Coatings J.*, August 19, 1991, p.58.
- [22] Schall, D. C., Rohm and Haas Co., Spring House, PA, 1991, private communication.
- [23] “Emulsion Polymerization of Acrylic Monomers,” Product Bulletin CM-104 A/cf, Rohm and Haas Co., Spring House, PA.
- [24] Hankins, E.M., U.S. Patent 2, 881, 171, 1959.
- [25] Harren, R. E., *Organic Coatings: Their Origin and Development*, R. B. Seymour and H. F. Mark, Eds., Elsevier Science Publishing Co., Inc., New York, 1990, p. 297.
- [26] Peters, A., Overbeek, G., and Annable, T., *Prog. Org. Coat.*, Vol. 29, 1996, pp. 183–194.
- [27] Rohm and Haas Company photograph.
- [28] Harren, R. E., *Organic Coatings: Their Origin and Development*, R. B. Seymour and H. F. Mark, Eds., Elsevier Science Publishing Co., Inc., New York, 1990, p. 309.
- [29] Roman, N., *Modern Paint and Coatings*, November 1991, p. 38.
- [30] Rohm and Haas Co., “82C2,” October 1980, p. 2, promotional literature.
- [31] Mercurio, A., *Am. Paint Coatings J.*, January 20, 1992, p. 43.
- [32] Klepser, R. J., *Proceedings of SSPC 91, Steel Structures Painting Council*, Pittsburgh, PA, 1991, pp. 96–97.
- [33] Friel, J., United States Patent 5, 731, 377 (1998).
- [34] Eckersley, S., and Helmer, B., *J. Coat. Technol.*, Vol. 69, No. 864, 1997, pp. 97–107.
- [35] Eliseeva, V.I., *Prog. Org. Coat.*, Vol. 13, 1985, pp. 195–221.
- [36] Waters, J. A., *Colloids Surf., A: PhysicoChem. Eng. Aspects*, Vol. 83, 1994, pp. 167–174.
- [37] Snuparek, J., *Prog. Org. Coat.*, Vol. 29, 1996, pp. 225–233.
- [38] Shuler, B., Baumstark, S., Kirsch, S., Pfau, M., Sandor, M., and Zosel, A., *Prog. Org. Coat.*, Vol. 40, 2000, pp. 139–150.