

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 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 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 metallized 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 ($\uparrow$) in Fig. 1 indicate the temperature at 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].

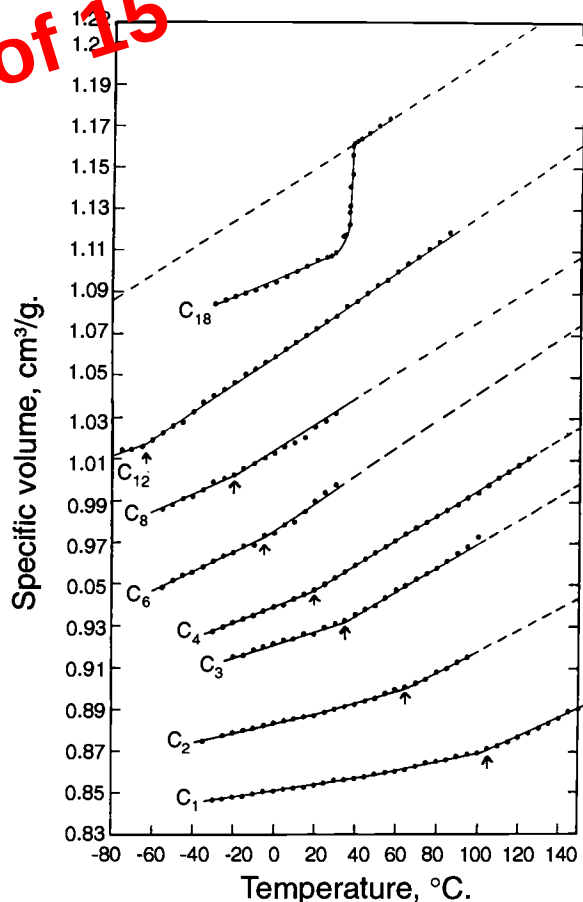


FIG. 1—Specific volume-temperature relations for the poly-(*n*-alkyl methacrylates). (Reprinted with permission from the American Chemical Society. Copyright 1957.)

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 35 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 flowout 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 (D 1474)]. 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 (D 2091)], block [see ASTM Test Method for Blocking Resistance of Architectural Paints (D 4946)], 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) (D 2794)], 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 molecular weight (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 molecular weight, 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 molecular weight, but polymers with overly high molecular weight 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 molecular weight 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 molecular weight, resulting in lower solution viscosity and consequently higher application solids.