

Organic Coatings: Science and Technology

Volume II: Applications,
Properties, and Performance

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CHAPTER XXXV

Architectural Coatings

In 1991 the U. S. shipments of architectural coatings were about 2×10^9 L with a value of \$4.65 billion [1]. This was about 50% of the volume and about 41% of the value of all U. S. coatings shipments. Commonly, architectural coatings are called trade sales paints. There are two overlapping markets for these paints: contractors and *do-it-yourselfers*, consumers who paint their own homes and furniture. The contractor is generally particularly concerned with cost of application, which is greater than the cost of the paint. For example, contractors want, if at all possible, paints that cover in one coat. On the other hand, the do-it-yourselfer is more likely to be concerned about cost of the paint and about things like ease of cleanup, odor, and the range of colors available. In the United States, paint is sold through several distribution systems: large merchandisers, hardware stores and lumber stores, and paint stores owned or franchised by paint manufacturing companies. Some paint is sold directly to large contractors by paint manufacturers.

There are three, sometimes overlapping, classes of paint manufacturing companies: (1) large companies that carry out extensive national advertising campaigns to promote their trade name paints; (2) small companies which sell only locally, primarily to local contractors but commonly with one or more factory stores for sales to individuals; and (3) companies which sell private label paints to large merchandisers or hardware chains. The large national companies usually make the same lines of paint for sale all over the country. Local and regional paint companies frequently design their paints to be most suitable for the climate and style trends in their market area; this can sometimes be a significant advantage.

While some paints are manufactured as colored paints, the majority are manufactured and distributed as white paints. The manufacturing company supplies an extensive line of color chips with the tinting colors and the formulations necessary to tint white paints to match the color chips. This makes it possible for the paint store to have thousands of colors of paints available for customers with only a limited inventory requirement. However, it places significant limitations on changes in paint formulations. Only in unusual cases can a paint company afford to make a change in formulation that would make the color chips, tinting pastes, and/or formulations that are out in the paint stores obsolete. In most cases, new formulations must permit continuing use of the same color matching tools.

Large companies usually make three lines of products of at least the major items: good, better, and best. The good grade is usually designed for the individual whose principal criterion for selecting paint is price per unit volume. Such paint is usually adequate for the application with fair coverage. The best paint is usually designed to give the greatest life and to have as good coverage as can be designed into that class of paint. The better is, obviously, a compromise between the two.

There is a great multitude of products manufactured and sold in the architectural coatings market. We restrict our discussion to the three largest classes of paints sold in this market: exterior house paint, interior flat wall paint, and gloss enamels. Space limitations do not allow inclusion of other smaller but still significant product lines such as stains, varnishes (see Section 9.3.2 and 12.4.1), floor paints, and many specialty products.

35.1. EXTERIOR HOUSE PAINT

Exterior house paint is defined as paint applied to exterior wall surfaces. Paint for trim such as around windows, doors, and on shutters is generally gloss enamel, as discussed in Section 35.3. The majority of exterior house paint sold in the United States is latex paint. The exterior durability of latex paint is superior to that of any air dry, solvent-borne paint for field application to the exterior of houses. Latexes are made by emulsion polymerization (see Chapter 5) and undergo film formation by coalescence (see Section 3.3).

There are two situations where solvent-borne house paint should be used: if outside painting must be done when the temperature is less than 4–5°C, since latex paints do not coalesce properly at such low temperatures; or if paint must be applied over a chalky surface, that is, a surface with a layer of poorly adherent pigment and eroded old paint, since most latex paints do not adhere adequately to such surfaces. Generally a solvent-borne primer is recommended for application over chalky surfaces.

Latex paints perform better than oil or alkyd paints on wood siding. When oil and alkyd paints were widely used on wood house siding, paint failures by blistering were common. Water can get into the siding from the back side. Since the films from oil and alkyd paints have fairly low water vapor permeability, when water reaches the back side of the paint film and starts volatilizing in the heat of the sun, blisters are blown. Latex paints are not cross-linked and have T_g values below summer temperatures and, therefore, have relatively high moisture vapor permeabilities. When water gets to the back of the latex paint film, the water vapor can pass through the film; blistering is unusual.

Further, latex paints are much more resistant to grain cracking than oil or alkyd base paints. Wood expands and contracts as the moisture content increases and decreases. A coating applied with an acrylic latex binder maintains its extensibility after many years of exterior exposure and can expand and contract with the wood. Highly unsaturated oil and alkyd coating films continue to cross-link with exterior aging, thereby becoming less and less extensible and, hence, likely to crack as the wood expands and contracts. Oil and alkyd paints also commonly fail by chalking after exposure. High-quality latex paints are less likely to fail by chalking or, at least, have much longer lifetimes before chalking occurs to a serious extent.

Leveling of latex paints is generally not as good as that of solvent-borne paints. This is not viewed as too serious a problem in exterior house paints, but it is with gloss paints discussed in Section 35.3. This disadvantage of latex paints is probably more than offset in exterior house paints by the accompanying characteristic of superior sag resistance of latex paints compared to solvent-borne paints.

Since they continue to be thermoplastic, latex paints are more prone to retain dirt on their surface than are oil or alkyd paints. While undesirable, this is not a major objection in the United States. However, in countries where lignite and soft coal are widely used for heating and cooking, white latex paint turns unsightly, blotchy gray after only a few months exposure; an extreme example is the city of Shenyang in North East China.

As discussed in Section 3.3, film formation during the application of latex paints occurs by coalescence of the polymer particles. Coalescence requires that the temperature during film formation be significantly above the T_g of the particles. If the paint is to be applied at low temperature, the T_g must be correspondingly lower. However, this means that when the temperature is high during the summer, the film will be soft and susceptible to dirt pickup even when the dirt content in the air is not excessive. To minimize this problem, latex paints are formulated with coalescing solvents. These solvents reduce the T_g of the polymer particles, permitting firm formation at lower temperatures, but the coalescing solvent slowly evaporates out of the film after application so that the T_g increases over time. Latex paints are generally formulated in the United States so that they can be applied at temperatures as low as 4–5°C. If it is necessary to paint when the temperature is still lower, solvent-borne paints must be used.

The condition of the surface of wood can be an important factor in the performance of paint. Contamination with dirt and oil can seriously interfere with adhesion. When wood is exposed outdoors, the surface degrades. As a result, after painting there can be failure that looks like adhesive failure, but is actually cohesive failure of the wood. It is said that even a 3-day exposure of freshly cut wood to weather can adversely affect the apparent adhesion [2]. It is recommended that all joints and cracks be caulked and that the wood be treated first with a water-repellent preservative and then be primed [2]. On woods like pine, a latex paint can be used for both the primer and top coat. However, some woods like redwood and cedar contain water-soluble materials that will extract into a latex paint leading to reddish brown stains. The extractives are apparently naturally occurring phenolic compounds. Special *stain-blocking* latex primers are available for use over redwood and cedar. In the early days of latex paints, these primers were formulated with a somewhat soluble lead pigment which formed insoluble salts with the phenolic compounds. In order to avoid lead compounds in the formulation, other approaches for insolubilizing the phenolics have been found. One such approach is to incorporate in the formulation a cationic ion-exchange latex.

Many houses are sided with preprimed hardboard siding; see Section 34.2 for a discussion of painting this siding.

As mentioned earlier, another potentially serious problem in the application of latex house paints can be poor adhesion to chalky surfaces. The surface of chalky paint is covered with a layer of loosely held pigment and paint particles. When latex paint is applied over such a surface, the continuous phase of the paint penetrates among the particles down to the substrate, but latex particles are large

compared to the interstices among the chalk particles and do not penetrate among them to any significant degree. Thus, when the water leaves the film and coalescence occurs, the paint film is resting on top of the chalk particles with nothing binding the chalk particles together or to the substrate. As a result, adhesion is poor. In the case of oil or alkyd paints, the continuous phase penetrates in between the chalk particles and as the film forms by solvent evaporation and cross-linking, the binder from the paint surrounds the chalk particles and penetrates through them down to the substrate surface, thereby minimizing the adhesion problem.

The adhesion of latex paints can be improved by careful cleaning of the surface to be painted to remove all chalk. However, it is difficult to do this over a whole house. Another approach is to replace about 15% of the latex polymer binder in a latex paint formulation with long oil alkyd resin or synthetic drying oil. The alkyd or oil is emulsified into the latex paint. After application, when the water evaporates, the emulsion breaks and some of the alkyd or oil can penetrate between the chalk particles providing improved adhesion. In order for the paint to have good storage life, the alkyd or oil should be as hydrolytically stable as possible. Of course, the presence of the drying oil or alkyd reduces the exterior durability of the paint as compared to pure latex paints. While there is no doubt that the adhesion of such paints over chalky surfaces is better than without the drying oil, many workers in the field prefer to prime a house that shows chalking with an oil-based primer and then apply a latex top coat over that primer. As the use of oil-based paints and "cement paints" has decreased, the problem of adhesion over chalky surfaces is becoming less common.

Table 35.1 gives a formulation recommended by a latex manufacturer for a "high-quality" exterior white house paint [3]. This formulation is not given to recommend this formulation over other formulations or these raw materials over other raw materials; rather it provides a framework for discussion of the rationale for the many components of a latex paint. The ingredients are listed in order of addition during making of the paint. Note that, as is generally the case, the formulation is given in both volume and weight terms. The total of the volume is approximately 100. This is done since quantities manufactured are generally multiples of 100 units of volume and also one can compare percentage volumes of ingredients. The weight figures correspond to the amounts of volume in units of pounds and gallons; thus the total weight gives an estimate of the weight per gallon.

Natrosol 250 MHR is hydroxyethylcellulose (HEC), which is in the formulation for two reasons: to increase the viscosity of the external phase of the paint during production and application, and to control the viscosity of the final paint. Viscosity of the paint as a function of shear rate particularly affects ease of brushing, film thickness applied, leveling, sagging, and settling. The viscosity of the external phase controls the rate of penetration of the external phase into a porous substrate such as wood. If penetration is rapid, the viscosity of the paint above the porous surface increases rapidly resulting in poorer leveling. The HEC is added at this stage since it must be dissolved and since the viscosity of the solution provides the viscosity necessary for pigment dispersion.

The ethylene glycol and the propylene glycol (further down the list of ingredients) are in the formulation for two reasons. First, they act as antifreeze to stabilize the paint against coagulation during freezing and thawing. The expansion of water when it freezes exerts substantial pressure on the latex particles and can push them

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increased enough so that the film is semisolid, but since only limited coalescence has occurred, the film is weak. The pressure of the brush or the roller can break up the film, resulting in irregular chunks of paint film along the lapped edge. This can be minimized by slowing down the rate of evaporation of the continuous phase by incorporation of the slow evaporating glycols.

The next ingredient is water. Hard water should be avoided since it can reduce the stability of dispersions; commonly, deionized water is used. The water provides the volume of liquid required for the pigment dispersion. Obviously, the amount of water is also a major factor affecting the solids of the final paint.

The next three materials, Tamol 960, KTPP, and Triton CF-10, are surfactants. Their function is to stabilize the pigment dispersion while not interfering with the stability of the latex particle dispersion or the stability of tinting color dispersions that may be added to the paint. Tamol 960 is an anionic dispersing agent. KTPP is potassium tripolyphosphate, which is an effective dispersion stabilizer, as is testified to by the wide use of polyphosphates in laundry detergents. KTPP is also desirable since it does not promote foaming. Note that the potassium salt is used, not the sodium salt. Sodium tripolyphosphate is likely to cause *frosting*. The salt is leached out of the paint film by water, and the solution evaporates on the surface, leaving a layer of crystals of the sodium tripolyphosphate. KTPP is less likely to cause this problem. Triton CF-10, a nonionic surfactant, helps stabilize the pigment dispersion and also is effective in reducing the surface tension of the latex paint so that it will wet out low surface tension substrates. It has been proposed that dynamic surface tension may be more important in wetting the substrate than equilibrium surface tension [4].

The combination of dispersing agents used in a formulation is generally empirically determined by trial and error. Careful records should be kept of the results of using different combinations with particular latexes, pigments, and surfactants, especially records of failures. This information serves to guide a formulator in selecting dispersion agent combinations for future formulations.

Colloid 643 is an antifoam agent (see Section 23.7). The minimum amount necessary for controlling foam should be used; excess antifoam agent can result in crawling when paint is applied. Selection of antifoams is empirical; the manufacturers of proprietary antifoams offer test kits with small samples of the various antifoams in their line to paint manufacturers. The formulator tries the samples to find which is most effective with the particular formulation.

As noted above, propylene glycol is part of the glycol mixture to improve freeze-thaw stability and control wet lapping. A mixture of the two glycols may have been used to help control the rate of drying: propylene glycol evaporates somewhat more rapidly than ethylene glycol.

Ti-Pure R-902 is a rutile TiO_2 pigment. While it was not stated in the formulation constants given with the formulation, the PVC of TiO_2 in the formulation is approximately 18%. As discussed in Section 16.3, this is about the optimum level of TiO_2 considering the relationship between cost and hiding. Calculation of the PVC of TiO_2 in addition to the total PVC in a white paint formulation is strongly recommended as a check on the level of TiO_2 in the final formulation. About 18% is usually an appropriate level, depending on the actual TiO_2 content of the pigment. In this formulation, dry powder TiO_2 is called for. In most cases, large manufacturers of latex paints no longer use dry TiO_2 . TiO_2 "slurries," that is, dispersions

of TiO_2 in water supplied by the pigment manufacturer (see Section 20.4), provide more economical material handling.

AZO-11 is zinc oxide. Zinc oxide is a white pigment and contributes somewhat to the hiding, but its scattering efficiency is poor because the refractive index difference between it and the binder is relatively small. Zinc oxide is in the formulation primarily as a reasonably effective fungicide. The level of zinc oxide used is often higher than that given in this formulation. The lower level may reflect the use of an additional fungicide, Skane M-8, in the formulation. The need for fungicides and bactericides is discussed later. Zinc oxide can cause catastrophic viscosity increases during storage of some latex paints [5]. The effect of the ZnO is very system dependent; Ref. [5] discusses the variables and possible formulation approaches to minimize the instability problems. Even though one may not be concerned with the use of zinc oxide in a paint, this paper is recommended since it discusses the dependence of latex paint properties on interactions of several variables.

Minex 4 is a sodium potassium aluminosilicate inert pigment, and Icecap K is an aluminum silicate inert pigment. These inert pigments have refractive indexes sufficiently similar to that of the binder in the paint that they contribute little directly to hiding. However, use of some fine particle size inert pigment is generally felt to increase the hiding efficiency of the TiO_2 . This controversial subject is discussed further in Section 35.2.

While in this formulation all of the inert pigments are clays, a wide variety of types of inert pigments can be used. Particle size, cost per unit volume, and color are major selection criteria. Calcium carbonates are inexpensive and are sometimes used as inert pigments in exterior latex paints, but there is a potential problem. Latex paint films have quite high water permeability; water and carbon dioxide, which are in equilibrium with carbonic acid, can permeate into the film. Calcium carbonate dissolves in carbonic acid to give a calcium bicarbonate solution that can diffuse out of the film. On the surface, the water evaporates, leaving a deposit of calcium bicarbonate which then reverts to insoluble calcium carbonate. The white deposit, called *frosting*, on the surface of the film is undesirable, especially with colored paints.

The gloss of this, and most, latex exterior house paints is quite low. Gloss is controlled by the PVC/CPVC ratio. Exterior durability as well as many other properties are also affected by PVC. Very importantly, cost is strongly affected by PVC. The least expensive components of the dry film of latex paints are the inert pigments. Therefore, it is desirable to maximize CPVC, since the PVC of the paint at the same PVC/CPVC ratio increases with CPVC. With a given latex, a major factor controlling CPVC of latex paints is the particle size distribution of the pigments. It is common to have multiple inert pigments so as to maximize breadth of particle size distribution which increases CPVC and permits higher pigment loading at the same PVC/CPVC (see Sections 21.2 and 21.4).

Attagel is attapulgite clay, which is in the formulation to increase the degree of shear thinning and thixotropy. The clay particles swell substantially in water. The swollen clay particles can be distorted by shear, leading to reduction in viscosity. The particles return to their unsheared shape when shear stops, leading to relatively rapid recovery of viscosity. This flow behavior gives a paint in which the pigment does not settle out on standing and does not sag appreciably on application. Leveling

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tends to be inhibited since recovery of viscosity after shearing takes place quite rapidly, but leveling is not a factor of major importance in exterior house paint. Note that the attapulgate is added last to the mill base. Since, as discussed in Section 20.4.1, high-speed impeller dispersers are not very effective in dispersing shear thinning systems, the other pigments should be thoroughly dispersed before incorporating the attapulgate clay.

After the pigment is dispersed, the high-speed impeller is slowed down and the latex, Rhoplex AC-64, is added. Latexes can coagulate at the shear rates involved when the impeller is running at high speed. Rhoplex AC-64 is an all-acrylic latex designed for exterior durability. Its composition is proprietary; like most commercial latexes, about the only information the manufacturer publishes on composition is the solids of the latex (60.5% in this case). Based on the relatively high solids of this latex, it is reasonable to guess that the latex has either a bimodal or perhaps a broad particle size distribution. This would be appropriate because such latexes tend to give higher CPVCs and hence permit higher pigment loading. It is reasonable to guess that the latex is a copolymer of methyl methacrylate (MMA) with ethyl or butyl acrylate and has a T_g of 10–15°C. Such copolymers have excellent exterior durability. Latexes with part of the MMA replaced by styrene have lower costs and reasonably satisfactory exterior durability. High vinyl acetate, vinyl acetate/acrylate copolymers are less expensive. While their hydrolytic stability is inadequate for exterior use in climates with high humidities and rainfall, they can be appropriate for exterior use in arid climates.

Colloid 643, the antifoam additive, is added a second time so as to minimize the amount needed. Texanol is a coalescing agent; it is a mixture containing the monoisobutyrate ester of 2,2,4-trimethylpentane-1,3-diol. Note the high degree of steric hindrance of ester groups of Texanol which provides necessary hydrolytic stability to the coalescing solvent.

Skane M-8 is a fungicide which supplements the ZnO listed earlier. Fungicides are needed to minimize mildew growth on the paint film after it is applied. Surprisingly, this formulation does not include a bactericide. Bactericides are needed to control bacterial growth in the can of paint. There are three adverse effects of bacterial growth: a putrid odor can develop; the metabolic processes release gases that can build up enough pressure to blow off the can lid; and, since the bacteria can digest cellulose derivatives like HEC, the viscosity of the paint can drop dramatically. The most widely used biocides in exterior paints have been aromatic mercury compounds like phenylmercuriacetate (PMA), which is a very broad spectrum fungicide and bactericide. Organomercury compounds react with hydrogen sulfide to give black mercuric sulfide. At least one large paint company does not use organomercury compounds in their exterior paint for this reason. Aromatic organomercury compounds are toxic, but not as toxic as aliphatic organomercury compounds. There are stringent controls on mercury levels in waste water discharge so extra care must be taken in plant cleanup procedures when they are used. While still permitted in exterior paints, the use of organomercury compounds in interior paints in the United States was prohibited in August 1990.

Many other compounds are used as fungicides and bactericides. Testing is difficult because fungal and bacterial growth are very dependent on ambient conditions and particularly because many fungicides and bactericides are effective against only a limited number of organisms. Diluted paints are more likely to support bacterial

growth than undiluted paints; a test method based on inoculating diluted latex paint with several bacteria and fungi has been reported to be more reliable [6]. Examples of biocides tested are: substituted 1-aza-3,7-dioxabicyclo(3.3.0)octanes, substituted 3,5,7-triaza-1-azonia adamantane chloride, 1,2-benzthiazolone, and methylchloro/methylisothiazolone. Reference [7] provides a brief review of other biocides for latex paints.

In the case of fungicides, there is the further problem that in order to be effective they must be somewhat soluble in water. However, if they are water-soluble they can be leached out of the film when it is exposed outdoors. An interesting approach to this problem is an investigation of the use of polymers with pendant fungicide groups that are time-released by hydrolysis [8].

A critical aspect of manufacturing latex paint is that housekeeping in the factory must be the equivalent of that in a food-processing factory. The best control of bacterial growth is to avoid as far as possible the contamination of the paint with bacteria. Furthermore, bactericides kill bacteria, but they do not deactivate enzymes that have been produced by bacteria. If the factory has places where bacteria can grow and the products can get into a paint tank, manufacturers have found to their chagrin that they have introduced enzymes into their paint. The enzymes split the HEC molecules and the viscosity drops even though there is adequate bactericide in the paint.

The ammonium hydroxide is added to adjust the pH of the paint. In this case, the pH of the final paint is said to be 9.5. The high pH assures the stability of the anionic dispersing agents. While all latex paints are packed in lined tin cans, it is possible to have breaks in the lining, and the high pH minimizes the possibility of corrosion of the cans. In many cases, the latex polymer is made with some acrylic acid as a comonomer; the viscosity of paints made with such a latex is very pH dependent (see Section 5.2).

The last two items in the formulation are water and a 2.5% solution of HEC. The amount of these two determines the solids of the final paint. There will be some variation from batch to batch of the viscosity with any paint formulation. The ratio of the water and the HEC solution can be varied so that the viscosity and the solids of the paint will both come out at the standard level.

The PVC of the paint is 43.9%; it is a relatively low gloss paint, as are most exterior latex paints. Commonly the gloss is lower with latex paints than with oil paints. The lower PVC reduces cost while still providing excellent exterior durability. The volume solids of the paint is 37%, substantially lower than exterior oil or alkyd-based paints. As a result, the coverage per unit volume of latex paints is lower than that of oil-based paints, but, on the other hand, the price per unit volume of latex paints is lower. The grams of VOC per liter of paint excluding water calculates to be 93, substantially lower than that of alkyd and oil-based house paints.

The "initial viscosity" refers to the viscosity taken with a "Stormer Viscometer" immediately after mixing the paint. Note that in spite of the widely recognized shortcomings of the Stormer Viscometer discussed in Section 19.3.7, in this case (and in virtually every paint lab in the United States), it is the viscometer that is used. The "equilibrated viscosity" signifies the viscosity after the thixotropic structure has time to build up again. Note that the unsheared equilibrated viscosity, that determined without stirring the paint before measuring the viscosity, is 5 KU

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units higher than the initial or the "sheared" viscosity. This shows that this paint is somewhat thixotropic. The "ICI" number refers to the viscosity run on an ICI Viscometer that measures viscosity at a high shear rate similar to that experienced in application by brush or roller. It is important to have the proper high shear viscosity because this is a major factor controlling the film thickness of the paint that is applied. The high shear viscosity of 0.1–0.12 Pa·s is on the low side for a latex paint.

35.2. INTERIOR FLAT WALL PAINT

The largest volume of trade sales paint is interior flat wall paint; essentially all of it is latex paint. Since exterior durability is not needed, lower-cost vinyl acetate copolymer latexes (see Section 5.3) are the principal binders. Since the T_g of vinyl acetate homopolymer is about 32°C, some comonomer must be used to reduce the T_g ; butyl acrylate is commonly used. For interior applications where there is need for greater water resistance, acrylic latexes are used.

The major advantages of latex paints as compared to the older oil-based flat wall paints are:

Fast drying. If desired, two coats can be applied to the walls of a room during a day, the furniture moved back, and the room used that night.

Low odor. The odor of mineral spirits and byproducts from oxidation of drying oils in solvent-borne paints is quite unpleasant for days after the walls are painted. The minor odor from latex paints dissipates quickly.

Ease of cleanup. Spills, dripped spots, brushes, and rollers can be easily cleaned with soapy water in the case of latex paints; solvent is required with oil paints. On the other hand, the cleaning up must be done promptly because once the latex has coalesced, cleaning is more difficult than with oil paints.

Low VOC emissions. Latex paints were widely adopted before there was concern about VOC emissions; but if a solvent-borne coating were to be developed, VOC emissions would have to be at least as low as those of latex paints to be acceptable. There is also the advantage of substantially reduced fire hazard with water-borne paints. Not only is solvent-borne paint flammable, but also rags wet with oil-based paints in a confined space can undergo *spontaneous combustion*, that is, ignite as a result of the heat generated by autoxidation.

Flat wall paint is usually stocked as white paint, and tinting colors are added to make a color picked by the customer from a large array of color cards. This means that it is critical to maintain equal white tinting strength in quality control. Furthermore, any new formulation has to have the same white tinting strength as the formulation being replaced or else the color cards and formulations in all the dealers stores will have to be replaced.

In each quality line, two, or sometimes three, white base paints are included. One is to be used alone as a white or tinted to make pastel color paints. At the other extreme, a deep tone base that contains little TiO_2 is used for tinting to deep colors that could not be made if the regular base paint were used. Frequently, a third base is in the line which is used for intermediate depths of shade. Intermediate depths of shade could be matched using the regular base white, but the cost would

be excessive because more tinting color would be needed to match the colors; hiding would be greater than needed.

Users are sometimes confused by the changes in color of latex paint as it dries. The color of the dry film of a latex paint is darker than the color of the wet paint. In the wet paint, the interfaces between the polymer particles ($n =$ approximately 1.5), water ($n = 1.33$), TiO_2 ($n = 2.76$), and inert pigments ($n =$ approximately 1.6) scatter the light to a much greater degree than when the paint is dry. The dry paint has fewer interfaces, since the latex particles coalesce, and smaller refractive index differences since the pigment particles are in a polymer matrix instead of the combination of polymer particles and water. Since the light scattering decreases as water evaporates and the latex particles coalesce, the color gets darker. It also follows that hiding of the wet paint is greater than hiding of the dry paint.

When painting ceilings, one is particularly anxious to get hiding in one coat since painting over one's head and moving the ladder is more of an effort than in painting walls. The problem is particularly challenging since ceiling paints are commonly plain white to give the greatest diffuse light reflection. Since there are no color pigments in a base white paint to absorb light, the hiding by white paints is poorer than that of any color paint made from it. The problem is compounded by the decrease in hiding when a latex paint film dries. The user thinks he or she has applied enough paint to hide the old marks on the ceiling, but comes back an hour or so later and finds that the marks show through the dry paint. Special ceiling paints are made that minimize this problem by pigmenting so that the PVC is greater than CPVC. Dry paint films with PVC above CPVC have voids of air with $n = 1$ adding to the light scattering by having new interfaces between air and polymer as well as air and pigment. Formulations can be adjusted so that wet hiding and dry hiding are approximately equal. Of course, the films do not have as high mechanical strength as films of paint with $\text{PVC} < \text{CPVC}$, and the resistance to staining is much poorer. But neither mechanical strength nor stain resistance is an important criterion for ceiling paints; hiding is what counts most.

Table 35.2 gives the formulation of an interior flat tint base wall paint [9]; the materials are listed in the order of addition. Kathon LX 1.5% is a biocide whose active ingredients are 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one. As noted earlier, since August 1990 organomercury biocides are not permitted in interior paints in the United States. Tamol 731 is an anionic surfactant and Tritons N-101 and N-57 are nonionic surfactants composed of nonylphenoethoxylates with an average of 9 and 5 ethylene oxide units per molecule, respectively. Colloid 643 is an antifoam. The propylene glycol is present for freeze-thaw stability and wet-lapping. Ti-Pure R-900 is a rutile TiO_2 ; the PVC of the TiO_2 in the formulation is approximately 18.4% as is appropriate for the most cost efficient hiding. Optiwhite is a calcined kaolin clay inert pigment; it has internal voids which can not wet out and hence may contribute somewhat to hiding. Its particle size (expressed as equivalent spherical diameter) ranges from 0.5 to 20 μm , with 80% by weight between 0.6 and 6 μm . Snowflake White is a ground natural calcium carbonate with a particle size distribution from about 0.3 μm to 30 μm , with 80% by weight between 1 and 17 μm . The broad range of particle sizes of the combination of pigments permits incorporation of a high amount of low cost inert pigment while still staying (presumably) below CPVC. The PVC of this formulation is stated to be 59.6%. In some other flat wall formulations, a small

Table 35.2

Material
Water
Kathon
Tamol
Triton
Triton
Colloids
Propylene
Ti-Pure
Optiwhite
Snowflake
Dispersant
Rovimate
Dowant
Colloid
Natrosol
Aqueous
Total

PVC
Volume
Weight
Viscosity
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Table 35.2. Interior Flat Tint Base Wall Paint

Materials	Weight Ratio	Volume Fraction
Water	119.9	14.39
Kathon LX 1.5% (Rohm & Haas)	1.8	0.22
Tamol 731 (25%) (Rohm & Haas)	6.0	0.65
Triton N-101 (Union Carbide)	2.0	0.23
Triton N-57 (Union Carbide)	2.0	0.24
Colloid 643 (Rhone-Poulenc)	2.0	0.26
Propylene glycol	45.0	5.20
Ti-Pure R-900 (DuPont)	175.0	5.25
Optiwhite (Burgess Pigment)	118.0	6.43
Snowflake White (ECC America)	118.0	5.24
Disperse using high speed impeller, then add:		
Rovace 9100 (55%) (Rohm & Haas)	230.0	25.37
Dowanol DPnB (Dow)	13.0	1.72
Colloid 643 (Rhone-Poulenc)	1.0	0.13
Natrosol 250 MR (2.5%) (Aqualon)	288.0	34.54
Aqueous Ammonia (28%)	1.0	0.13
Total	1122.7	100.00

Formulation Constants

PVC	59.6%
Volume solids	29.9%
Weight solids	47.7%
Viscosity, initial	97 KU
ICI	80 mPa·s
pH	9.5
VOC	179 (g L ⁻¹ excluding water)

fraction of relatively large particle size SiO₂ is incorporated in the formulation. This inert pigment improves burnishing resistance, that is, it reduces the tendency of the flat wall paint film to polish to a glossy area where it is frequently rubbed, such as around light switches. As discussed in Section 24.3, the large size particles make bumps in the film that reduce contact area and hence reduce burnishing.

Rovace 9100 is a 55% solids vinyl acetate/acrylic copolymer latex with a narrow particle size distribution averaging 0.3 μ m. Unless high scrub resistance is needed, vinyl acetate copolymer latexes are used in flat wall paints because of their lower cost. Dowanol DPnB is dipropylene glycol *n*-butyl ether; it is a coalescing agent and improves freeze-thaw stability. Colloid 643 is additional antifoam. Natrosol 250 MR is HEC. The 2.5% solution is made up in advance; it is good practice to include some bactericide in the solution to avoid bacterial growth, although there is no indication in this formulation that bactericide was included. The aqueous ammonia serves to adjust the pH which can affect the viscosity of the paint and minimize the chances of corrosion of steel that might get exposed in the can.

The VOC of this paint is well within regulations in effect in 1992. However, pressure for reductions can be expected. In 1992 latex paints of undisclosed composition were introduced which have no detectable VOC in tests sensitive to 12 g

L^{-1} (see Section 29.2). They are currently available only in stock colors since current tinting colors contain some solvent. Comparisons of performance properties with conventional latex paints have not yet been published.

The most expensive major component on a volume basis of any white flat paint is the TiO_2 . Several approaches are used to minimize the TiO_2 content required at a given level of hiding. Where applicable, as in the case of ceiling paints, PVCs above CPVC are used. The efficiency of hiding by TiO_2 is affected by the choice of inert pigments used with it. While there is some controversy, most workers accept that inert pigment with particle sizes less than that of the TiO_2 , called "spacer" inerts, increase the efficiency of the TiO_2 [10]. A mathematical model has been developed that can be used to improve TiO_2 pigment spacing by predicting the optimum inert pigment size distribution and concentration for a given formulation [11]. The results of application of this model also predict less TiO_2 crowding with small size inert pigments.

Another approach is to use a pigment (Spindrift, Dulux Australia Ltd.) that consists of resin particles which have within them air pockets that in turn contain TiO_2 particles [12]. The larger refractive index differences and the increased number of interfaces give substantial increases in light scattering and hence hiding efficiency.

Still another approach to greater hiding at lower cost is the use of a high T_g latex, such as polystyrene, as a pigment [13]. When the latex binder coalesces, the high T_g latex does not coalesce but the particles remain separate as with any other pigment. Including the dry volume of the high T_g latex particles as part of the pigment volume, paints can be formulated with a PVC greater than CPVC without making the surface of the film porous. These paints provide equal hiding at lower TiO_2 content while still retaining good enamel holdout and stain resistance. No convincing explanation of why an intact surface film forms in such paints has been published, but the method is said to be used on a large commercial scale.

Yet another approach to minimizing the TiO_2 requirement is the use of special high T_g latexes that contain air voids within the particles as pigments, such as Ropaque (Rohm and Haas Co.) [14,15] (see Section 18.1.1). Again in calculating PVC, one includes the volume of the high T_g particles since they do not coalesce with the latex binder particles during film formation. Even at PVCs below CPVC, the air voids in the latex pigment particles provide hiding which permits a reduction of the TiO_2 level in the formulation. Such paints can have stain and scrub resistance equal to other latex paints with PVC less than CPVC.

A large fraction of latex flat wall paints are applied by roller. During roller application, some latex paints *spatter* to a major degree (see Section 22.1.3). Paints with high extensional viscosity are likely to spatter severely during roller application [16]. Extensional viscosity increases when high molecular weight water-soluble polymers with very flexible backbones are used as thickeners in a latex paint [17]. Spattering can be minimized using low molecular weight water-soluble thickeners with rigid segments in the polymer backbone such as low molecular weight HEC. Since the selling price of HEC is the same for various molecular weights and more low molecular weight water-soluble polymer is needed to reach the same shear viscosity, paint cost increases when low molecular weight HEC is used. It is common to compromise by using an intermediate molecular weight or a mixture of high and low molecular weight grades of HEC.

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35.3. GLC

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While in many applications, the increase in external phase viscosity resulting from the use of water-soluble polymeric thickeners is desirable, there is an application where it is undesirable, namely concrete block walls. Concrete block surfaces contain both holes that are large compared to the pigment and latex particles and pores that are small compared to them. When a solvent-borne paint is applied to concrete block, the coverage is extremely low since so much paint penetrates into the holes. When regular latex paint is applied, the coverage is better. The lower viscosity of the external (continuous) phase relative to solvent-borne paint leads to more penetration of continuous phase into the small pores of the block so that the viscosity of the remaining paint increases rapidly and there is less penetration into the holes. The coverage with latex paint can be further improved by omitting water-soluble polymer from the formulation. This modification further reduces the viscosity of the external phase, which can penetrate more rapidly into the small pores and hence give even more rapid buildup of viscosity of the remaining paint. The effect is enhanced by the requirement that the volume fraction of internal phase in the modified paint must be significantly higher than when water-soluble polymer is present in order to have equal starting viscosity. With increasing volume fraction internal phase, the viscosity increases more rapidly as the continuous phase is drained off in the small pores so that penetration into the holes is substantially reduced. A further advantage of latex paints, especially acrylic, styrene/acrylic, or styrene/butadiene latexes, over oil or alkyd paints is that they are not subject to saponification by the basicity of the cement in the concrete block.

When latex paint films form, surfactants sometimes bloom out of the film collecting on the surface. Usually this is not noticeable; however, if water condenses on the paint surface, this surfactant on the surface can dissolve, then when the water evaporates, surfactant concentrates in the last remaining water droplets leaving brown spots of surfactant on the surface of the film. The problem can be minimized by avoiding dark-colored surfactants. However, surfactant can leave whitish spots on dark color paints. It has been shown that nonionic surfactants are more compatible with latex polymers and less likely to come to the paint surface than anionic surfactants [18].

35.3. GLOSS ENAMELS

In contrast to the situation with exterior house paints and, especially, with flat wall paints, a significant fraction of gloss enamels sold in the United States are alkyd paints rather than latex paints. The term enamel connotes a hard, glossy surface analogous to porcelain enamel. The terms enamel and gloss paint are commonly used interchangeably. The term enamel has frequently been applied to thermoset coatings, but in this case the term has carried over from thermoset alkyd enamels and thermoplastic latex paints are also called enamels. Gloss enamels are used both inside and outside for trim around windows and doors, for shutters, for wood furniture, and on kitchen and bathroom walls. Professional painters have particularly favored continued use of alkyd paints while do-it-yourself painters favor latex paints.

One advantage of alkyd enamels is that they can be made with higher gloss than can latex enamels. As discussed in Section 17.3, during film formation from solution vehicle paints, a layer having very low pigment content forms at the upper surface of the coating; this is not the case with latex paints. The ratio of pigment to binder at the surface of a latex paint film can be reduced somewhat by using a finer particle size latex, but there is still a significant difference from alkyd paint films. Another factor tending to reduce the gloss of latex paint films is the haze that results from incompatibility of surfactants (and perhaps other components) and the blooming that results when surfactants migrate to the surface of the film. These problems can be minimized by making latexes with as low monomeric surfactant content as possible and by selecting surfactants for pigment dispersion that are as compatible as possible.

Considerable work has been done in using blends of compatible water-soluble resins with latexes to achieve high gloss. In floor wax applications, morpholine salts of styrene/acrylic acid copolymers have been used. When the film forms, the solution resin concentrates in the surface layer. When the film dries the morpholine evaporates, leaving the free carboxylic acid groups. The film has reasonable water resistance but, as is an advantage for floor wax, can be removed by mopping with ammonia water. However, this level of resistance is not adequate for paint films. There have been some proprietary resins marketed that give gloss advantage with relatively smaller loss of resistance properties.

In exterior applications and to a lesser degree many interior applications, the advantage of high initial gloss alkyd enamels is more than offset by the better gloss retention and resistance to cracking exhibited by latex gloss paints. Depending on the location, alkyd enamels exposed outdoors lose so much gloss in a year or two that the coating looks like a flat paint instead of a gloss paint. While a latex paint starts out with a lower gloss it retains most of its initial gloss for several years. In interior applications, the superior color retention and greater resistance to cracking are important advantages for latex gloss paints.

The principal limitation of gloss latex paints is not, however, their lower gloss. Rather, the major problem is the difficulty of getting adequate hiding in one coat. Since the cost of application for painting contractors is higher than the cost of the paint, contractors particularly prefer alkyd paints that commonly hide in one coat (over a primed surface). There are several factors involved in the difference of hiding between alkyd and latex gloss paints.

The volume solids (NVV) of latex gloss paints is substantially lower than the NVV of alkyd paints. A typical NVV for a latex gloss paint is about 33%, whereas the NVV of alkyd gloss paints can be up to 66% or higher. Accordingly to obtain the same dry film thickness, one has to apply twice as thick a wet film of the latex paint as compared to the alkyd paint. Wet film thickness applied is primarily controlled by the high shear rate viscosity of the paint. Thus, a latex paint should be formulated to have a higher viscosity at high shear rate than an alkyd paint for maximum hiding. In practice, as is discussed later, the high shear viscosity of latex paints has usually been formulated to be lower than that of alkyd paints further compounding the problem.

Wet film thickness can be controlled to a degree by the extent to which the painter brushes out the paint. The painter tries to judge how much he should brush out by how well the wet paint is covering. In the case of alkyd paints, there is

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relatively little difference between the wet and dry hiding powers of the paint. However, the wet hiding power of latex paints is substantially greater than their dry hiding power. This increases the difficulty of judging how far to brush out a latex paint.

Another factor affecting hiding by gloss latex paints is their comparatively poor leveling. Assume that a uniform dry film thickness of say 50 μm of a paint provides just satisfactory hiding for some application. If the film has streaks of thinner film, say 35 μm , and thicker film, say 65 μm , the hiding of the uneven film will be poor; and it is likely to appear inferior to that of a uniform 35- μm dry film of the same paint. Since the 35- and 65- μm areas are immediately next to each other, the contrast emphasizes the poor hiding. Furthermore, not only is the hiding adversely affected, but also the contrast in colors resulting from the poor hiding in the valleys contrasted to the ridges emphasizes the poor leveling.

The poor leveling of latex paint films has several causes. In alkyd paints for brush application, the solvent is slow evaporating mineral spirits, whereas in latex paints the water evaporates more rapidly unless the relative humidity is high. As a result the viscosity of the latex paint increases more rapidly after application under most conditions. Also, the volume fraction of internal phase in latex paints is higher than in alkyd paints since both the latex particles and the pigment particles are dispersed phases. Therefore, even with the same loss of volatile material, there is a greater increase in the viscosity of the latex paint.

It has been demonstrated by Overdiep, as discussed in Section 23.1, that leveling of solvent-borne, brush-applied paints is promoted by surface tension differential driven flows in the wet paint film [19]. When solvent evaporation starts, the fraction of solvent lost from the valleys of the brushmarks is greater than from the thicker ridges. Since the surface tension of the solvent is lower than that of the alkyd, the surface tension of the more concentrated alkyd solution in the valleys becomes higher than that in the ridges. The resulting differential in surface tension causes the paint to flow from the ridges into the valleys to minimize overall surface tension, thus promoting leveling.

Unfortunately, there have been no published studies of the driving force for leveling of latex paints. In fact, except for a recent encyclopedia article by one of the authors [20], there does not seem to have been consideration given in the literature to the driving force for leveling in the case of latex paints. The surface tension of the water phase of latex paints is controlled primarily by the surfactants in the paint, which suggests that there probably is little change in surface tension as water evaporates. If this hypothesis is right, the driving force for leveling of latex paints is the relatively small force of surface tension driven leveling rather than the larger force of surface tension differential driven leveling as in the case of alkyd paints. Another factor that may be important is dynamic surface tension. It has been shown that with some surfactants, equilibrium surface tension is more rapidly reached than with others [4]. The need for research is evident.

Probably, however, the major factor affecting the leveling, and, therefore, hiding, of gloss latex paints has been their rheological properties. As they have been formulated for many years with water-soluble thickener polymers like HEC, latex paints have exhibited a much greater degree of shear thinning than alkyd paints. This led to latex paints having too low a viscosity at high shear rate, so that the applied film thickness tended to be too thin, and too high a viscosity at low shear

rate to permit adequate leveling. The problem is especially severe since the rate of recovery of viscosity after exposure to high shear rates is generally rapid with latex paints. The use of Stormer Viscometers (see Section 19.3.7) has been at least partly responsible for the prolonged time before the problem was well defined. This so-called viscometer measures something related to viscosity in a midrange of shear rates, but gives no information about viscosity in either of the most critical regions—at high and low shear rates.

The reasons for this greater dependency of viscosity on shear rate in latex coatings have not been fully elucidated; at least two factors may be involved, flocculation of latex particles (and/or) pigment particles in the presence of HEC, and possible entanglement of the swollen high molecular weight HEC polymer chains [21].

Real progress in minimizing the problem has been made in recent years by using *associative thickeners* in formulating latex paints. Many kinds of associative thickeners are available. They all are moderately low molecular weight, water-soluble polymers with two or more long chain nonpolar hydrocarbon groups spaced along the backbone. Examples are hydrophobically modified hydroxyethylcellulose, hydrophobically modified ethoxylated polyurethanes, and hydrophobically modified polyacrylic acid salts. Use of such thickeners gives latex paints that exhibit less shear thinning, thus permitting formulation of latex paints with higher viscosity at high shear rates so that thicker wet films are applied, together with somewhat lower viscosity at low shear rates, so that leveling is improved at the same time [21,22]. (The thick wet film in itself helps promote leveling too since, as discussed in Section 23.1, the rate of leveling depends strongly on wet film thickness.)

Reynolds [21] has reviewed the possible mechanisms of thickening by associative thickeners and factors involved in their use in the formulation of latex paints. He emphasizes that greater care and skill is required in formulating with associative thickeners than with conventional water-soluble thickeners. The results obtained can be very sensitive to the combination of particular latex and thickener and to the amounts and types of surfactant present in the formulation.

It has been shown that formulations with associative thickeners not only level better but also give somewhat higher gloss; however, more difficulty is experienced in controlling sagging [23]. Sag control is still better than alkyd paints, but leveling and gloss are still not equal to most alkyd paints. Higher gloss as well as better rheological properties have been reported by use of a combination of associative thickeners [24]. It is said that the combination reduces flocculation of the TiO_2 . Another factor in the improved gloss may be that associative thickeners are effective with small particle size latexes, which give the highest gloss [21]. It has also been shown that paints with associative thickeners spatter less when applied by roller than those thickened with HEC and that most associative thickeners resist viscosity loss by bacterial action [21].

Another shortcoming of latex paints that is particularly evident in gloss formulations is the time required to develop final film properties. Part of the problem is that users are, in a sense, fooled by the drying properties of latex paints. They dry to touch more rapidly than alkyd paints and can be handled sooner. However, they require a longer time to reach their ultimate properties. For example, even though latex paints dry more rapidly than alkyd paints, longer time is necessary to develop block resistance required to prevent windows and doors from sticking and to permit putting heavy objects on a newly painted shelf. The initial coalescence

of latex volume, helped by diffusion of particles relatively low temperature, has been recognized as a selected problem of consumer concern.

Another problem is paint surface water, so that a film is not adequate but the problem is off the surface preparative improve serious problem.

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of latex particles is rapid, but full coalescence is limited by the availability of free volume. Since the $(T-T_g)$ must be small, free volume is small. The situation is helped by using coalescing solvents. However, the loss of these solvents is controlled by diffusion rate, which is also limited by $(T-T_g)$. It has been reported that latex particles which have inner layers of relatively high T_g with a gradient down to a relatively low T_g on the outer shell of the particles, can provide film formation at low temperatures but yet relatively quickly achieve blocking resistance [25]. It has been recommended that high T_g latexes be used with larger amounts of carefully selected coalescing agents [26]. There is need for further progress, but as this problem is unlikely to ever be completely solved, there is need for better education of consumers so they are aware of the limitations of latex paints.

Another problem of gloss latex paints that can be critical is adhesion to old gloss paint surfaces when water is applied to the new dry paint film. After wetting with water, some latex paint films can be peeled off the old paint surface in sheets. Such a film is said to exhibit poor *wet adhesion*. There is always a problem of achieving adequate adhesion when repainting old gloss paint surfaces even with alkyd paints, but the problem with latex paints is more severe. It is essential to wash any grease off the surface and to roughen the surface by sanding; but even with such surface preparation, many latex paints do not show good wet adhesion. Wet adhesion does improve as the system ages, but for several weeks or even months there can be a serious problem.

Latexes have been developed by several manufacturers that minimize the problem of wet adhesion. The compositions are proprietary. A possible approach is to use an amine-substituted acrylic comonomer such as 2-(dimethylamino)ethyl methacrylate in making the latex. Amine-substituted polymers apparently decrease the ease with which the film is displaced from the interface by water.

Progress has been made in developing gloss latex paints with adequate hiding by one coat, but further efforts lie ahead. The whole problem is made more difficult by the lack of adequate laboratory tests to measure gloss (see Section 17.4) or absolute hiding (see Section 16.2.4). The lack of adequate test procedures is particularly troublesome because many of the companies supplying raw materials to the paint industry, many of the people establishing specifications and regulations, and sadly even some people working as paint formulators, are not aware that the laboratory tests are inadequate.

Gloss alkyd paints are widely used, but there is considerable pressure to reduce the VOC emissions. There is disagreement as to what level of VOC can be achieved with alkyd gloss paints while retaining reasonable application and film properties. Most workers seem to agree that alkyd paints with VOCs of 275 g L^{-1} or higher can have satisfactory performance, but many doubt that VOC can be reduced below 250 g L^{-1} . The problems include application characteristics, through dry, color change, and durability.

High solids alkyds are discussed in Section 10.2. Solids can be increased some by solvent selection, especially the use of hydrogen-bond acceptor solvents to reduce intermolecular hydrogen bonding. While solids can be increased by reducing molecular weight and with narrower molecular weight distributions, both of these approaches lead to poorer film properties and durability if carried very far. A key obstacle to developing good alkyd paints having a VOC of 250 g L^{-1} is the need to use low T_g resins to reduce viscosity. As discussed in Section 10.1, higher T_g

alkyds initially form dry films by lacquer dry, whereas paints based on lower T_g alkyds remain tacky after solvent has evaporated. Extra cross-linking functionality required to achieve adequate film properties can be built into an alkyd by increasing the proportion of highly unsaturated fatty acids; however, high linoleic acid containing fatty acids are not available at reasonable cost, and increasing the proportion of linolenic acid causes yellowing of films on aging. Use of high functionality polyols in making alkyds permits some increase in the number of unsaturated fatty acids per molecule without major increase in molecular weight. Drying can be accelerated by increasing the proportion of driers, but this expedient can lead to formation of a highly cross-linked surface layer that may slow diffusion of oxygen to the interior causing slow through cure. Use of driers containing a high proportion of zirconium salts is a partial solution to this problem, but they are expensive and tend to promote yellowing. Furthermore, while increasing drier concentration can accelerate cross-linking, the larger amount of drier also accelerates film degradation.

A promising approach to increasing solids is the use of reactive diluents (see Section 10.2). Such additives are low molecular weight materials designed to reduce viscosity almost as efficiently as solvent, but to coreact with the oxidizing alkyd during film formation. This permits the reduction in volatile solvent content while still maintaining film properties. An example is dicyclopentenloxyethyl methacrylate (see Section 10.2). This reactive diluent has both an acrylate double bond and an activated allylic position. In the presence of driers, it can coreact with an alkyd such as a long oil linseed alkyd. Using this reactive diluent with specially designed alkyds is reported to permit formulation of gloss alkyd paints with a VOC of 155 g L^{-1} . The properties of the films are said to approach those of an alkyd paint with a VOC of 350 g L^{-1} [27]. Condensation products of mixtures of drying oil acid amides and acrylamide with (hexaalkoxymethyl)melamine are another type of reactive diluent [28]. While the use of reactive diluents is attractive, the cost and performance characteristics still require further improvement.

Another approach to solvent-borne gloss paints is the use of nonaqueous dispersion (NAD) binders [29]. In contrast to the NAD acrylics used in automotive coatings, the T_g of NAD polymers for architectural paints can be low ($5\text{--}15^\circ\text{C}$). Vinyl-terminated, low molecular weight poly(12-hydroxystearic acid) is used as the steric stabilizer. Grafting ethyl acrylate on to the stabilizer leads to a stable NAD in aliphatic hydrocarbon solvent. A small fraction of a polyfunctional comonomer, such as diallyl phthalate, is used to give a low degree of cross-linking capacity to the particles. The cross-linking is said to improve the mechanical properties, durability, and resistance to blistering of coatings made with the NAD. The amount of cross-linking must be kept low so that coalescence of the film can be essentially complete. Flow properties of paints generally require using a blend with some alkyd. The work reported thus far has concentrated on less demanding applications such as undercoats and masonry paints but, presumably, the concept is applicable to gloss enamels. It remains to be seen how VOC levels and performance will compare with latex paints.

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