COATINGS

1. Introduction

Coatings are ubiquitous in an industrialized society. United States shipments of coatings in 1999 were $\sim 5.3 \times 10^9$ m^3 having a value of $18 billion (1). Coatings are used for decorative, protective, and functional treatments of many kinds of surfaces. The low gloss paint on the ceiling of a room is used for decoration, but also diffuses light. Exterior automobile coatings fulfill both decorative and protective functions. Still others provide friction control on boat decks. Some coatings control the fouling of ship bottoms, others protect food and beverages in cans. Other coatings reduce growth of barnacles on ship bottoms, protect optical fibers against abrasion, etc.

Each year tens of thousands of coating types are manufactured. In general, these are composed of one or more resins, a mixture of solvents (except in powder coatings), commonly one or more pigments, and frequently one or more additives. Coatings can be classified into thermoplastic and thermosetting coatings. Thermoplastic coatings contain at least one polymer having a sufficiently high molecular weight to provide the required mechanical strength properties without further polymerization. Thermosetting coatings contain lower molecular weight polymers that are further polymerized after application in order to achieve desired properties. This article is organized to discuss succesively: Properties of coatings, components of coatings, application of coatings, end uses of coatings, and economic aspects.

2. Film Formation

Coatings are manufactured and applied as liquids and are converted to solid films after application to the substrate. In the case of powder coatings, the solid powder is converted after application to a liquid, which in turn forms a solid film. The polymer systems used in coatings are amorphous materials and therefore the term solid does not have an absolute meaning, especially in thermoplastic systems such as lacquers, most plastisols, and most latex-based coatings. A useful definition of a solid film is that it does not flow significantly under the pressures to which it is subjected during testing or use. Thus a film can be defined as a solid under a set of conditions by stating the minimum viscosity at which flow is not observable in a specified time interval. For example, it is reported that a film is dry-to-touch if the viscosity is greater than $\sim 10^6$ $mPa \cdot s(=cP)$ (2). However, if the definition of dry is that the film resists blocking, ie, sticking together, when two coated surfaces are put against each other for 2 s under a mass per unit area of 1.4 kg/cm^3 (20 psi), the viscosity of the film has to be $>10^{10}$ $mPa \cdot s(=cP)$.

The viscosity of amorphous systems is a function of free-volume availability. The free volume of a material is the summation of the spaces or holes that exist between molecules of a material resulting from the impact of one molecule or molecular segment striking another. Such holes open and close as the molecules vibrate. Above the glass-transition temperature (T_g) the holes are large enough and last long enough for molecules or molecular segments to move into them. Free volume increases as temperature increases and the rate of volume increase is higher above T_g. An important factor affecting the free volume of a system is thus the difference between the temperature, T, and the T_g. The relationship between viscosity, η, and T_g is expressed in the Williams–Landel–Ferry (WLF) equation. Using so-called universal constants and assuming that viscosity at $T_g = 10^{15}$ mPa · s(= cP) the WLF equation, when η is in units of Pa · s, becomes equation 1:

$$\ln\eta = 27.6 + \frac{40.2(T - T_g)}{51.6 + (T - T_g)} \tag{1}$$

Using this equation, the approximate $(T - T_g)$ value required for a film of a thermoplastic copolymer to be dry-to-touch, ie, to have a viscosity of 10^6 mPa · s(= cP), can be estimated (3). The calculated $(T - T_g)$ for this viscosity is 54°C, which, for a film to be dry-to-touch at 25°C, corresponds to a T_g value of −29°C. The calculated T_g necessary for block resistance at 1.4 $\mathrm{kgcm^{-3}}$ for 2 s and 25°C, ie, $\eta = 10^{10}$ mPa, is 4°C. Because the universal constants in the WLF equation are only approximations, the T_g values are estimates of the T_g required. However, if parameters such as the mass per area applied for blocking were larger, the time longer, or the test temperature higher, the T_g of the coating would also have to be higher.

For practical coatings, it is not sufficient just to form a film; the film must also have a minimum level of strength depending on product use. Film strength depends on many variables, but one critical factor is molecular weight. For example, the acrylic polymers used in lacquers for refinishing automobiles must have a weight average molecular weight (M_w) >75,000. This required molecular weight varies according to the chemical composition of the polymer and the mechanical properties required for a particular application.

2.1. Solvent Evaporation from Solutions of Thermoplastic Polymers. A solution of a copolymer of vinyl chloride (chloroethene) [75-01-4], vinyl acetate (acetic acid ethenyl ester) [108-05-4], and a hydroxy-functional vinyl monomer having a number average molecular weight (M_n) of 23,000 and a T_g of 79°C, gives coatings having good mechanical properties without cross-linking (4). A simple coating having only the resin and 2-butanone (methyl ethyl ketone, MEK) [78-93-3] as the sole solvent would give a polymer concentration of ~19 wt% solids or ~12 vol% in order to have a viscosity of ~100 mPa · s(= cP) for spray application. Because of the relatively high vapor pressure under application conditions, MEK evaporates rapidly and a substantial fraction of the solvent evaporates in the time interval between the coating leaving the orifice of the spray gun and arrival on the surface being coated. As the solvent evaporates, the viscosity increases and the coating reaches the dry-to-touch stage very rapidly after application and does not block under the conditions discussed. However, if the film is formed at 25°C, the dry film contains several percent retained solvent.

In the first stages of solvent evaporation from such a film, the rate of evaporation depends on the vapor pressure at the temperatures encountered during the evaporation, the ratio of surface area to volume of the film, and the rate of air flow over the surface. The rate of evaporation is essentially independent of the presence of polymer. However, as the solvent evaporates the T_g increases, free volume decreases, and the rate of loss of solvent from the film, at some point, becomes dependent not on how fast the solvent evaporates, but on how rapidly the solvent molecules can diffuse to the surface of the film. In this diffusion-control stage, solvent molecules must jump from free-volume hole to free-volume hole to reach the surface where evaporation can occur. As solvent loss continues, T_g increases, and free volume decreases. When the T_g of the remaining polymer solution approaches the temperature at which the film is being formed, the rate of solvent loss becomes very slow. If the film is being formed at 25°C from a solution of a resin having a higher T_g, eg, 79°C, loss of solvent becomes very slow when the T_g of the film exceeds 25°C and a significant amount of MEK remains in the hard, dry film indefinitely, acting as a plasticizer. In order to remove the last of the MEK in a short time, it is necessary to heat the film to a temperature significantly above the T_g of the solvent-free polymer.

The rate of solvent diffusion through the film depends not only on the temperature and the T_g of the film but also on the solvent structure and solvent–polymer interactions. The solvent molecules move through free-volume holes in the films and the rate of movement is more rapid for small molecules than for large ones. Additionally, linear molecules may diffuse more rapidly because their cross-sectional area is smaller than that of branched-chain isomers. For example, although isobutyl acetate (IBAc) [105-46-4] has a higher relative evaporation rate than *n*-butyl acetate (BAc) [123-86-4] IBAc diffuses more slowly out of a film of a nitrocellulose lacquer than BAc during the second stage of drying (5). Similarly, *n*-octane [111-65-9] diffuses more rapidly out of alkyd films than isooctane (2,2,4-trimethylpentane) [540-84-1] although isooctane has the higher relative evaporation rate (6).

Film thickness is a factor in solvent loss and film formation. In the first stage of solvent evaporation, the rate of solvent loss depends on the first power of film thickness. However, in the second stage when the solvent loss is diffusion rate controlled, it depends on the square of the film thickness. Although thin films lose solvent more rapidly than thick films, if the T_g of the drying film increases to ambient temperature during the evaporation of the solvent, then, even in thin films, solvent loss is extremely slow. Models have been developed to predict the rate of solvent loss from films as functions of the evaporation rate, thickness, temperature, and concentration of solvent in the film (7).

Thermoplastic polymer-based coatings have low solids contents because the relatively high molecular weight requires large amounts of solvent to reduce the viscosity to that required for application. Air pollution regulations limiting the emission of volatile organic compounds (VOC) and the increasing cost of solvents has led increasingly to replacement of such coatings with types that require less solvent for application.

2.2. Film Formation from Solutions of Thermosetting Resins.

Substantially less solvent is required in formulating a coating from a low molecular weight resin that can be further polymerized to a higher molecular weight after application to the substrate and evaporation of the solvent. Theoretically, difunctional reactants could be used. However, this is not feasible for coatings where the close control of stoichiometric ratio and purity required to achieve a desired molecular weight reproducibly with difunctional reactants is impractical. Therefore, the average functionality must be >2 in order to ensure that the molecular weight of the final cured film is high enough for good properties. Not only should the average functionality be >2, it is usually preferable for the number of monofunctional molecules to be at a minimum because these terminate polymerization. If any of the resin molecules have no functional groups, they cannot react and remain in the film as a plasticizer. The reactions are commonly called cross-linking reactions. A cross-linked film not only has very high molecular weight it is also insoluble in solvents. For many applications, this solvent resistance is an advantage of thermosetting coatings over thermoplastic coatings.

The mechanical properties of the cross-linked film depend on many factors; two of the most important are the lengths of the segments between cross-links and the T_g of the cross-linked resin. Segment length depends on the average equivalent weight and the average functionality of the components and the fraction of cross-linking sites actually reacted. The size of the segments between cross-links is often expressed as cross-link density (XLD); the closer the cross-links, the higher the XLD. Everything else being equal, the higher the XLD, the higher the modulus, ie, the harder the film. The T_g of cross-linked polymers is controlled by four factors and corresponding interactions: T_g of the segments of polymer between cross-links, the cross-link density, the presence of dangling ends, and the possible presence of cyclic segments (8). The T_g of the polymer segments between cross-links is governed by the structure of the resin and cross-linking agent and by the ratio of these components. Because cross-links restrict segmental mobility, T_g increases as XLD increases. The parameter T_g also increases as the fraction of dangling ends decreases, ie, as cross-linking reactions proceed. Cyclization would be expected to restrict chain mobility, and hence to increase T_g.

In the initial steps of cross-linking low molecular weight resins, the molecular weight and XLD increase whereas the fraction of dangling ends decreases resulting in an increase in T_g. As the cross-linking reaction continues, a gel forms. Reaction does not stop at gelation but continues as long as there are functional groups to react and there is sufficient mobility in the matrix to permit the reactive groups to move into position for reaction. As the reaction continues, modulus above T_g increases and the film becomes insoluble in solvent. Solvent can still dissolve in a cross-linked film leading to swelling; the extent of swelling decreases as XLD increases.

A problem in thermosetting systems is the relationship between stability of the coating before application and the time and temperature required to cure the film after application. It is generally desirable to be able to store a coating for many months or even years without significant increase in viscosity that would result from cross-linking during storage. On the other hand, after application, the cross-linking reaction should proceed in a short time at as low a temperature as possible. Because reaction rates depend on the concentration of functional groups, storage life can be increased by using more dilute coatings, ie, adding more solvent increases storage life. When the solvent evaporates after application, the reaction rate increases initially. However, VOC regulations are forcing the use of less and less solvent, increasing the problem of storage stability.

The reaction rates are also dependent on the rate constants for the reactions at the temperatures of storage and curing, equation 2. The rate constant k changes most rapidly with temperature if the activation energy, E_a, of the reaction is high. However, the reaction rate is slow unless the preexponential term A is also large. Under the assumptions of required ratios of rate constants, rate equations and Arrhenius equations have been used to calculate what orders of magnitude of E_a and A are required to permit various combinations of storage times and curing temperatures (9). Such calculations show that to formulate a coating stable for 6 months at 30°C, the calculated kinetic parameters become unreasonable if cure is desired in 30 min below ~120°C. No known chemical reactions have a combination of E_a and A that would permit design of such a system.

$$\ln k = \ln \mathrm{A} - E_a/RT \tag{2}$$

More reactive combinations can be used in two-package coatings where one package contains a resin with one of the reactive groups and the second package contains the component with the other reactive group. The packages are mixed shortly before use. Two-package coatings are used on a large scale commercially but are not generally desirable. They take extra time and are generally more expensive. Material is usually wasted and there is a chance of error in mixing. Two-package coatings are referred to as “2K coatings” and single-package coatings as “1K coatings”.

Design of stable coatings that cure at lower temperatures or shorter times must be based on factors other than the kinetics of the cross-linking reaction. Several techniques are used: ultraviolet-curing systems; systems requiring an atmospheric component as a catalyst or reactant, eg, oxygen or moisture; use of a volatile inhibitor; use of a cross-linking reaction that is a reversible condensation reaction involving the loss of a volatile reaction product that includes some of this monofunctional volatile by-product as solvent in the coating; and use of catalysts or reactants that change phase over a narrow temperature range.

Before two functional groups can react, they must be in close proximity. As low molecular weight resins and cross-linking agents react, T_g increases and free volume decreases. If the cure temperature is at least somewhat higher than the T_g of the fully reacted system, the reaction can go to completion at rates governed by kinetic parameters. If the cure temperature is below the T_g of the fully reacted system, the reaction slows to a rate controlled by diffusion. If the cure temperature is >50°C below the T_g of the fully reacted system, the reaction will stop before completion. A general review of the effect of variables on mobility control on reaction rates is available (10).

An example of the importance of free-volume availability on cross-linking has been reported in the evaluation of a trifunctional derivative of an aliphatic isocyanate that contains an aromatic ring, *m*-tetramethylxylidene diisocyanate (TMXDI) (1,3-bis(1-isocyanato-1-methylethyl)-benzene) [2778-42-9], as a cross-linking agent for hydroxy-functional resins (11). Because of steric effects, TMXDI is less reactive than the trifunctional derivatives of hexamethylene diisocyanate (HDI) (1,6-diisocyanatohexane) [822-06-0] but this can be overcome by catalyst composition and concentration. Although essentially complete reactions were obtained for films cured at elevated temperatures using a TMXDI/TMP (trimethylolpropane) (2-ethyl-2-(hydroxymethyl)-1,3-propanediol) [77-99-6] prepolymer, when cured at 21°C the reaction was slow and essentially stopped at ~50% completion. The acrylic resin being cross-linked had been designed for use with a more flexible triisocyanate cross-linking agent derived from hexamethylene diisocyanate. In a series of acrylic resins having lower T_g, as the T_g decreased, the cross-linking reaction with TMXDI at 21°C was faster and went more nearly to completion. Using an appropriately designed acrylic resin and catalyst, TMXDI gave films that cured fully at room temperature. Resins and cross-linking agents must be selected or designed for use with each other, especially for curing systems used at ambient temperature.

2.3. Film Formation by Coalescence of Polymer Particles.

Latex paints have low solvent emissions as well as many other advantages. A latex is a stabilized dispersion of high molecular weight polymer particles in water. Because the latex polymer is not in solution, the rate of water loss by evaporation is almost independent of concentration until near the end of the evaporation process. When a dry film is prepared from a latex, the forces that stabilize the dispersion of latex particles must be overcome and the particles must coalesce into a continuous film. As the water evaporates, the particles come closer and closer together. As they approach each other, they can be thought of as forming the walls of capillary tubes in which surface tension leads to a force striving to collapse the tube. The smaller the diameter of the tube, the greater the force. When the particles get close enough together so that that force pushing them together exceeds the repulsive forces holding them apart, coalescence is possible. A surface tension driving force also promotes coalescence because of the decrease in surface area when the particles coalesce to form a film. Both factors have been shown to be important in film formation from latexes. Reference (12) gives a discussion of the various theories of the factors affecting film formation. Coalescence, however, also requires that the polymer molecules in the particles be free to intermingle with those from adjoining particles. This movement can occur only if there are a sufficient number and size of free-volume holes in the polymer particles into which the polymer molecules from other particles can move. In other words, the T_g of the latex particles must be lower than the temperature at which film formation is being attempted.

The rate of coalescence is controlled by the free-volume availability, which in turn depends mainly on $(T - T_g)$. The viscosity of the coalesced film is also dependent on free volume. If a film is to resist the mild blocking test described earlier, $(T - T_g)$ would have to be on the order of 21°C. If the film is to resist blocking at 40°C, the T_g would have to be >19°C. However, in many cases the paint must be formulated in such a way that it can be applied at a temperature as low as 5°C, and therefore, the T_g of the latex particles would have to be <5°C. This problem can be solved by adding a coalescing agent, such as 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (2-methylpropanoic acid 2,2,4-trimethyl-1,3-pentanediyl ester) [132503-14-1], tributyl phosphate [126-73-8], and 2-butoxyethanol [111-76-2], among others. The coalescing agent dissolves in the latex particles, acts as a plasticizer, increases free-volume availability, and hence permits film formation at a lower temperature. After the film has formed, the coalescing agent diffuses slowly to the surface and evaporates. Because the free volume in the film is relatively low, the last traces of coalescing solvent evaporate slowly.

Even though the films feel dry, they block and pick up dirt for a long time after application.

Coalescing solvents contribute to VOC emissions, there has been increasing emphasis on reducing or eliminating use of coalescing solvents. References (13) and (14) discuss some of the approaches. An approach is to use latexes in which the particles have outer shells of low T_g and interiors of higher T_g. The T_g of the outer shell is low, permitting coalescence at low temperatures, but in time, after application, intermixing occurs, leading to a higher average T_g and permitting block resistance at higher temperatures. Another approach is to use thermosetting latexes that have a low T_g but attain adequate film properties by cross-linking. Hydroxy-functional latexes can be formulated with MF resins or a water-dispersible polyisocyanate for wood and maintenance coatings (15). Carboxylic acid functional latexes can be cross-linked with carbodiimides (16), or polyfunctional aziridines (17). *m*-Isopropenyl-α,α-dimethylbenzyl isocyanate (TMI) [1-(1-isocyanato-1-methylethyl)-3-(1-methylethenyl)benzene] [2094-99-7] reacts slowly with water and can be used to make thermosetting latexes (18).

Other thermosetting latexes cross-link at room temperature and are storage stable. Carboxylic acid functional latexes can be cross-linked with β-(3,4-epoxycyclohexyl)ethyltriethoxysilane (19). A combination of amine-functional and epoxy-functional latexes gives stable one package coatings (20). A latex with allylic substitution cross-links on exposure to air (21). Hybrid alkyd/acrylic latexes are prepared by dissolving an oxidizing alkyd in the monomers used in emulsion polymerization (22). Stable thermosetting latexes can be prepared using triisobutoxysilylpropyl methacrylate as a comonomer (19).

Powder coatings form films by coalescence. Because the powder must not sinter during storage, the free volume at storage temperature must be sufficiently low to avoid coalescence at this stage. The T_g of powder coating particles is commonly of the order of 50–55°C. Higher T_g must be avoided because rapid coalescence after application requires that the $(T - T_g)$ under baking conditions be as large as possible without requiring excessively high baking temperatures. The problem is even more complex in thermosetting powder coatings where overly rapid cross-linking can impede coalescence and leveling. Other examples of coalescing systems include nonaqueous dispersion, plastisol, “water-reducible” resin, and electrodeposition coatings.

3. Flow

Rheological properties, ie, flow and deformation, of coatings have significant impacts on application and performance properties. The application and film formation of liquid coatings require control of the flow properties at all stages. The mechanical properties of the applied coating films are controlled by the viscoelastic responses of the films to stress and strain. A good overview of the field of rheology in coatings is available (23); a more extensive but somewhat dated discussion of the flow of coatings is also available (24).

3.1. Viscosity of Resin Solutions. The viscosity of coatings must be adjusted to the application method to be used. It is usually between 50 and 1000 $\mathrm{mPa \cdot s} (= \mathrm{cP})$, at the shear rate involved in the application method used.

The viscosity of the coating is controlled by the viscosity of the resin solution, which is in turn controlled mainly by the free volume. The factors controlling free volume are temperature, resin structure, solvent structure, concentration, and solvent–resin interactions.

The temperature dependence of viscosity of resin solutions can be expressed by the WLF equation (eq. 3) where the reference temperature T_r is taken as the lowest temperature for which data are available and e_1, and e_2 are adjustable parameters (25).

$$\ln\eta = \ln \eta_{T_r} - \frac{c_1(T - T_g)}{c_2 + (T - T_g)} \tag{3}$$

This relationship has been shown to hold for a wide variety of coating resins and resin solutions over a wide range of concentrations. A simplification of equation 3, where T_g is the reference temperature is given in equation 4, which assumes that the viscosity at T_g is 10^{12} Pa·s and A and B are adjustable parameters.

$$\ln\eta = 27.6 - \frac{A(T - T_g)}{B + (T - T_g)} \tag{4}$$

Equation 4 does not model the relationship of viscosity with temperature quite as well as equation 3, but it is useful because it shows the relationship to T_g of the resin solution. The T_g of the resin solution is an important, but not singular, factor in controlling viscosity. The T_g of the resin solution depends on the T_g of the resin, the T_g of the solvent, the concentration of the resin solution, and the effects of resin–solvent interactions. The T_g of the resin depends on the molecular weight and the structure of the resin. The flow of solutions of coatings resins in good solvents in the viscosity range of 50–10,000 mPa·s(=cP) is Newtonian and log viscosity increases as the square root of the molecular weight. Much further work is needed to elucidate the solvent–resin interaction effects, but it appears that low viscosity hydrogen bond acceptor solvents give the greatest reduction in viscosity for polar substituted low molecular weight resins.

The viscosity of high solids coatings in the range of application varies more rapidly with temperature than is the case for conventional lower solids coatings (26). Hence, the viscosity is reduced more by using hot-spray systems that permit a further increase in solids. Within the range of 0.05–10 Pa·s, log viscosity varies approximately directly with concentration. The viscosity of higher viscosity solutions varies more steeply with concentration.

3.2. Viscosity of Systems with Dispersed Phases. A large proportion of coatings are pigmented and, therefore, have dispersed phases. In latex paints, both the pigments and the principal polymer are in dispersed phases. The viscosity of a coating having dispersed phases is a function of the volume concentration of the dispersed phase and can be expressed mathematically by the Mooney equation (eq. 5):

$$\ln \eta = \ln \eta_e + \frac{K_E V_i}{1 - V_i/\phi} \tag{5}$$

where η_e is the viscosity of the external phase, K_E is a shape constant (2.5 for spheres), V_i is the volume fraction of internal phase, and ϕ is the packing factor, ie, the volume fraction of internal phase when the V_i is at the maximum close-packed state possible for the system. The Mooney equation assumes rigid particles having no particle–particle interaction. It fits pigment dispersions and latexes that exhibit Newtonian flow.

If there is particle–particle interaction, as is the case for flocculated systems, the viscosity is higher than in the absence of flocculation. Furthermore, a flocculated dispersion is shear thinning and possibly thixotropic because the floccules break down to the individual particles when shear stress is applied. Considered in terms of the Mooney equation, at low shear rates in a flocculated system some continuous phase is trapped between the particles in the floccules. This effectively increases the internal phase volume, and hence the viscosity of the system. Under sufficiently high stress, the floccules break up, reducing the effective internal phase volume and the viscosity. If, as is commonly the case, the extent of floccule separation increases with shearing time, the system is thixotropic as well as shear thinning.

Shear thinning systems that are generally also thixotropic, also result if the disperse phase particles are not rigid. In the shear field, the nonrigid particles are distorted, resulting in less crowding, and therefore lower viscosity. In terms of equation 5, K_E becomes smaller and the packing factor becomes larger. Hence, the viscosity of the system is lower as the shear rate increases and as the time at a given higher shear rate is extended. Emulsions, ie, dispersions of liquids in liquids, show thixotropic flow because the dispersed phase particles are fluid and can be distorted.

4. Mechanical Properties

Coating films should withstand use without damage. The coating on the outside of an automobile should not break when hit by a piece of flying gravel. The coating on the outside of a beer can must not abrade when cans rub against each other during shipment. The coating on wood furniture should not crack when the wood expands and contracts as a result of changing temperatures or swelling and shrinkage from changes in moisture content of the wood. The coating on aluminum siding must be flexible enough for fabrication of the siding and resist scratching during installation on a house. Reference (27) gives a methodology for considering the factors involved in service life prediction. A monograph discusses problems of predicting service lives and proposes reliability theory methodology for database collection and analysis (28).

Understanding relationships between composition and basic mechanical properties of films can provide a basis for more intelligent formulation. Reference (29) is a good review paper. In ideal elastic deformation a material elongates under a tensile stress in direct proportion to the stress applied. When the stress is released, the material returns to its original dimensions essentially instantaneously. An ideal viscous material elongates when a stress is applied in direct proportion to the stress, but does not return to its original dimensions when the stress is released. Almost all coating films are viscoelastic—they exhibit intermediate behavior.

Elastic deformation is almost independent of time and temperature. Viscous flow is time and temperature dependent; the flow continues as long as a stress is applied. Viscoelastic deformation is dependent on the temperature and the rate at which a stress is applied. If the rate of application of stress is rapid, the response can be primarily elastic; if the rate of application of stress is low, the viscous component of the response increases and the elastic response is lower. Similarly, if the temperature is low, the response can be primarily elastic, at a higher temperature, the viscous response is greater.

By dynamic mechanical analysis the elastic and viscous components of modulus can be separated. The higher the frequency of oscillation, the greater the elastic response—the smaller the phase angle; the lower the frequency, the greater the viscous response—the larger the phase angle.

Many coated products are subjected to mechanical forces either to make a product, as in forming bottle caps or metal siding, or in use, as when a piece of gravel strikes the surface of a car with sufficient force to deform the steel substrate. To avoid film cracking, the elongation-at-break must be greater than the extension of the film. Cross-linked coatings have low elongations-at-break when below T_g. Properties are affected by the extent to which cross-linking has been carried to completion. Incomplete reaction leads to lower XLD and, hence, lower storage modulus above T_g. The extent of reaction can be followed by determining storage modulus as a function of time (30). Thus, one can, at least in theory, design a cross-linked network to have a desired storage modulus above T_g by selecting an appropriate ratio of reactants of appropriate functionality.

An additional factor that can affect the mechanical properties of polymeric materials is the breadth of the T_g transition region (31). The same effect can be seen in tan δ plots, which exhibit various breadths. Broad tan δ peaks are frequently associated with heterogeneous polymeric materials. For thermosetting polymers, the T_g transition region is generally broader than for thermoplastics. Breadth of the distribution of chain lengths between cross-links is a factor, and blends of thermosetting resins such as acrylics and polyesters often display a single, broad T_g transition. Materials with broad and/or multiple T_g values have better impact resistance than comparable polymers with a sharp, single T_g.

When a cross-linked film on a metal substrate is deformed by fabrication, it is held in the deformed state by the metal substrate. As a result, there is a stress within the film acting to pull the film off the substrate. Stress within films can also arise during the last stages of solvent loss and/or cross-linking of films (32). It is common for coatings to become less flexible as time goes on. Particularly in air dry coatings, loss of the last of the solvent may be slow. If the cross-linking reaction was not complete, the reaction may continue decreasing flexibility. Another possible factor with baked films is densification. If a coating is heated above its T_g and then cooled rapidly, the density is commonly found to be lower than if the sample had been cooled slowly (33). During rapid cooling, more and/or larger free volume holes are frozen into the matrix. On storage, the molecules slowly move and free volume decreases, causing densification; it is also called physical aging.

Abrasion is the wearing away of a surface, marring is a disturbance of a surface that alters its appearance. A study of the mechanical properties of a series of floor coatings with known wear life concluded that work-to-break values best represented the relative wear lives (34). Studies of automobile clear coats have shown that wear resistance increases as energy-to-break of films increases (35). The coefficient of friction of a coating can affect abrasion resistance. Abrasion of the coating on the exterior of beer cans during shipment can be minimized by incorporation of a small amount of incompatible wax or fluorosurfactant in the coating. Another variable is surface contact area. Incorporation of a small amount of a small particle size SiO_2 pigment in a thin silicone coating applied to plastic eyeglasses reduces abrasion. The pigment particles reduce contact area, permitting the glasses to slide more easily over a surface.

Marring is a near-surface phenomenon; even scratches <0.5 μm deep can degrade appearance. Marring is a major problem with automobile clear topcoats. In going through automatic car washes, the surfaces of some clear coats are visibly marred and lose gloss (36). Plastic deformation and fracture lead to marring. The responses can be quantitatively measured by scanning probe microscopy (37). In general, MF cross-linked acrylic clear coats are more resistant to marring than isocyanate cross-linked coatings, but MF cross-linked coatings have poorer environmental etch resistance. Coatings can be made hard enough that the marring object does not penetrate into the surface, or they can be made elastic enough to bounce back after the marring stress is removed. If the hardness strategy is chosen, the coating must have a minimum hardness, however, such coatings may fail by fracture.

Field applications on a small scale and under especially stringent conditions accelerate possible failure. Traffic paints are tested by painting stripes across the lanes of traffic instead of parallel to traffic flow. Automobiles are driven on torture tracks with stretches of gravel, through water, under different climate conditions. Sample packs of canned goods are made; the linings are examined for failure and the contents evaluated for flavor after storage.

Many tests have been developed to simulate use conditions in the laboratory. An example is a gravelometer to evaluate resistance of coatings to chipping of automotive coatings when struck by flying gravel. Pieces of standard shot are propelled at the coated surface by compressed air under standard conditions. The tests have been standardized by comparison to a range of actual results and give reasonably good predictions of actual performance. A more sophisticated instrument, a precision paint collider, which permits variations in angle and velocity of impact and temperature has been described (38).

Many empirical tests are used to test coatings. In most cases, they are more appropriate for quality control than performance prediction. American Society for Testing and Materials (ASTM) tests are widely used (39). An excellent summary of the tests and discussion of their applications and significance is available (40).

5. Exterior Durability

For many coatings, an important performance requirement is exterior durability. There are many potential modes of failure when coatings are exposed outdoors. Commonly, the first indication of failure is reduction in gloss resulting from surface embrittlement and erosion leading to the development of roughness and cracks in the surface of the coating. In some cases, the next step is “chalking”, ie, the erosion of resin from the surface of the coating leaving loose pigment particles on the surface. Chalking reduces gloss and, as chalking proceeds, can lead to complete film erosion and also to color change caused by the increased surface reflectance, which makes colors shift to light shades. Colors can also change if the pigment or pigment–resin combination undergoes photochemical degradation on exterior exposure. Photochemical oxidation and hydrolysis of the resins in coatings are common causes of failure. On exterior exposure, films may crack or check as a result of embrittlement, reducing the elongation-to-break. Such films crack as they undergo expansion and contraction. These changes may be caused by temperature changes, especially when the substrate and the coating have different coefficients of thermal expansion. Similar stresses on coatings can be caused by expansion and contraction of wood substrates with changes in moisture content of the wood.

Various kinds of chemical attack, such as those resulting from acid rain and bird droppings, can result in film degradation and discoloration. Retention of dirt from the atmosphere on the coating surface can lead to drastic color changes and blotchy appearance. Mildew can grow on the surface of many coating films, again leading to blotches of gray discoloration. In view of the large variety of exposure conditions and possible modes of failure, no laboratory test has been devised to predict field performance of coatings on exterior exposure. However, careful accumulation of actual field use results correlated with environmental, compositional, and application variables is the most useful way of understanding the causes of failures and, hence, of being able to forecast the possible performance of a new coating material.

Although many failure mechanisms are involved, the two most common modes are hydrolysis and photochemical oxidation by free-radical chain reactions. In general, resins that have backbone linkages that cannot hydrolyze provide better exterior durability than systems having, eg, ester groups in the backbone. Some esters are more resistant to hydrolysis than others. In general, esters of highly hindered alcohols such as neopentyl glycol (NPG) (2,2-dimethyl-1,3-propanediol) [126-30-7] are less easily hydrolyzed than those of less hindered alcohols such as ethylene glycol (1,2-ethanediol) [107-21-1]. Esters of isophthalic acid (1,3-benzenedicarboxylic acid) [121-91-5] are more resistant to hydrolysis in the range of pH 4–8 than esters of phthalic acid. Ester groups on acrylic polymers are highly resistant to hydrolysis.

Susceptibility to free-radical induced photoxidation varies with structure of the resins and pigments and, in some cases, with the interactions between pigment and resin. In general terms, resistance of resins to photochemical failure is related to the ease of abstraction of hydrogens from the resin molecules by free radicals. The greatest resistance is shown by fluorinated resins and silicone resins, especially methyl-substituted silicone resins. The greatest sensitivity to degradation is shown by resins having methylene groups between two double bonds; methylene groups adjacent to amine nitrogens, ether oxygens, or double bonds; and methine groups. Resins containing aromatic rings substituted with a heteroatom directly on the ring, such as bisphenol A epoxy resins and urethane resins based on aromatic isocyanates, are very susceptible to photochemical failure.

Pigment selection can also be critical in formulating for high exterior durability. Some pigments are more susceptible to color change on exposure than others. Some pigments act as photosensitizers to accelerate degradation of resins in the presence of uv and water. For example, anatase TiO_2 accelerates the chalking of coatings during exterior exposure. Rutile TiO_2 pigments with appropriate surface treatments, on the other hand, lead to little, if any, increase in chalking. It cannot be concluded that because one colored pigment gives greater exterior life in one resin system compared to another colored pigment the order of durability is the same in other resins systems. Reversals are fairly common.

The exterior durability of relatively stable coatings can be enhanced by use of additives. Ultraviolet absorbers reduce the absorption of uv by the resins, and hence decrease the rate of photodegradation. Further improvements can be gained by also adding free-radical trap antioxidants such as hindered phenols and especially hindered amine light stabilizers (HALS). A discussion of various types of additives is available (41).

It has also been found that there can be interactions between hydrolytic degradation and photochemical degradation. Especially in the case of melamine–formaldehyde cross-linked systems, photochemical effects on hydrolysis have been observed.

Although many variations in methods have been tried, no reliable laboratory test is available to predict exterior durability. Reference (42) recommends use of reliability theory using statistical distribution functions of material, process, and exposure parameters for predicting exterior durabilitty. For predicting performance of automotive base coat/clear coat systems four performance measurements: clear coat uva performance, clear coat and base coat HALS performance, ability of all coating layers to resist photoxidation, and clear coat fracture energy (43).

Exterior exposure of panels in various locations such as Florida is widely used to forecast performance with reasonable success. However, coatings that are sensitive to acid rain or to cracking on rapid temperature change might not perform as well in actual use as predicted by Florida exposure results. In the EMMAQUA tests (DSET Laboratories, Inc.), panels are exposed in Arizona on a machine that turns to keep mirrors that reflect the sunlight to the panel surface approximately normal to the sun. The machine increases the radiation intensity shining on the panels about sevenfold over direct exposure of panels in the same location. To simulate the effect of rain, the panels are sprayed with water each night. The test can provide useful guidance in a few weeks, especially if comparisons are based on exposure to equal intensities of uv radiation rather than for equal periods of time. Many other accelerated laboratory tests have been devised. However, reversals in performance between pairs of coatings in the field as compared with the laboratory results indicate that frequently these tests are not reliable predictors.

The most promising approach to laboratory techniques for predicting performance is to understand the mechanism of failure and then use instrumental methods to study the susceptibility of a coating to failure. The most powerful tool available now is the use of electron spin resonance (esr) spectrometry to monitor the rate of free-radical appearance and disappearance.

6. Adhesion

In most cases, it is desirable to have a coating that is difficult to remove from the substrate to which it has been applied. An important factor controlling this property is the adhesion between the substrate and the coating. The difficulty in removing a coating also can be affected by how difficult it is to penetrate through the coating and how much force is required to push the coating out of the way as the coating is being removed from the substrate as well as the actual force holding the coating onto the substrate. Furthermore, the difficulty of removing the coating can be strongly affected by the roughness of the substrate. If the substrate has undercut areas that are filled with cured coating, a mechanical component makes removal of the coating more difficult. This is analogous to holding two dovetailed pieces of wood together.

Surface roughness affects the interfacial area between the coating and the substrate. The force required to remove a coating is related to the geometric surface area, whereas the forces holding the coating onto the substrate are related to the actual interfacial contact area. Thus the difficulty of removing a coating can be increased by increasing the surface roughness. However, greater surface roughness is only of advantage if the coating penetrates completely into all irregularities, pores, and crevices of the surface. Failure to penetrate completely can lead to less coating-to-substrate interface contact than the corresponding geometric area and leave voids between the coating and the substrate, which can cause problems.

6.1. Adhesion to Metals. For interaction between coating and substrate to occur, it is necessary for the coating to wet the substrate. Somewhat oversimplified, the surface tension of the coating must be lower than the surface tension of the substrate. In the case of metal substrates, clean metal surfaces have very high surface tensions and any coating wets a clean metal substrate.

Penetration of the vehicle of the coating as completely as possible into all surface pores and crevices is critical to achieving good adhesion. This requires that the surface tension of the coating be low enough for wetting, but the extent of penetration is controlled by the viscosity of the continuous phase of the coating. Although broad rigorous scientific studies of the relationship between continuous-phase viscosity and adhesion have not been published, the importance of this relationship is evident from the formulating decisions made over many years in the manufacture of coatings having good adhesion performance. The critical viscosity is that of the continuous phase because many of the crevices in the surface of metal are small compared to the size of pigment particles. Because penetration takes time, the initial viscosity of the external phase should be low and the viscosity should be kept as low as possible for as long as possible. Slow evaporating solvents are best for coatings that are to be applied directly on metal. Systems that cross-link slowly minimize the increase of viscosity of the continuous phase. Because viscosity of the vehicle drops with increasing temperature, baking coatings can be expected to provide better adhesion than a similar composition coating applied and cured at room temperature.

Adhesion is strongly affected by the interaction between coating and substrate. On a clean steel substrate, hydrogen bond or weak acid–weak base interactions between the surface layer of hydrated iron oxide that is present on any clean steel surface and polar groups on the resin of the coating provide such interaction. It has been suggested that several polar groups spaced along a resin backbone, having some flexible units to permit facile orientation of the groups to the interface during coating application, and some rigid segments to promote only partial adsorption of the groups so that there can be interaction with the balance of the coating resin, can provide cooperative interactions that enhance adhesion. Conversely, adhesion can be adversely affected if additives having single-polar groups and long nonpolar tails are present in a coating. For example, dodecylbenzenesulfonic acid is a catalyst for MF resins. However, its use in coatings directly applied on steel can adversely affect adhesion. Presumably, the sulfonic acid groups interact strongly with the steel surface leading to a monolayer having a surface of long hydrocarbon chains. The effect is similar to trying to achieve adhesion to oily steel or polyethylene.

Fracture mechanics affect adhesion. Fractures can result from imperfections in a coating film that act to concentrate stresses. In some cases, stress concentration results in the propagation of a crack through the film, leading to cohesive failure with less total stress application. Propagating cracks can proceed to the coating–substrate interface, then the coating may peel off the interface, which may require much less force than a normal force pull would require.

Adhesion of coatings is also affected by the development of stresses as a result of shrinkage during drying of the film. For example, in the case of uv-cure coatings, where curing is achieved by photoinitiated free-radical polymerization of acrylic double bonds, a substantial volume reduction occurs in the fraction of a second required. This loss in volume leads to stresses in the film that partly supply the force needed to pull the film from the substrate. Hence, less external force must be applied to remove the film. Sometimes such stresses can be relieved by heating the coating to anneal it. Internal stresses can also result from solvent loss from a film and other polymerization reactions, as well as changes in temperature and relative humidity, particularly at temperatures below T_g. These stresses can affect coating durability, especially adhesion (44).

The formation of covalent bonds between resin molecules in a coating and the surface of the substrate can enhance adhesion. Thus, adhesion to glass is promoted by reactive silanes having a trimethoxysilyl group on one end that reacts with a hydroxyl group on the glass surface. The silanes have various functional groups that react with the cross-linking agent in the coating on the other end of the molecule (45).

6.2. Adhesion to Plastics and Coatings. Wetting can be a serious problem for adhesion of coatings to plastics. Some plastic substrates have such low surface tension that it may be difficult to formulate coatings having a sufficiently low surface tension to wet the substrate. Polyolefin plastics, in particular, are difficult to wet. Frequently, the surface of the polyolefin plastic must be oxidized to increase surface tension and provide groups to interact with polar groups on the coating resin. The surface can be treated using an oxidizing solution, by flame treatment or by exposure to a corona discharge. Difficulties in wetting plastics can also result from residual mold release agents on the surface of the plastic. See Ref. 46 for further discussion.

Adhesion to plastics can be enhanced if resin molecules from the coating can penetrate into the surface layers of the plastic. Maleic anhydride modified chlorinated polyolefin in xylene primers enhance the adhesion of coatings on thermoplastic polyolefins (TPO) automobile bumpers (47). Penetration would take place through free-volume holes; hence, raising the temperature above the T_g of the plastic substrate generally promotes adhesion. The T_g of the plastic can be lowered by penetration of solvent from the coating into the surface of the plastic. Solvent selection in formulating a coating can be critical. In selecting coatings solvents for application to articles fabricated from high T_g thermoplastics such as polystyrene and poly(methyl methacrylate), a solvent system having too high a rate of evaporation should not be used in order to avoid crazing, ie, cracking of the surface.

The same considerations apply to intercoat adhesion to other coatings as to plastics. A further design parameter is available in formulating primers. Because adhesion to rough surfaces is better than to gloss surfaces, primers are usually highly pigmented, and hence have a rough surface to promote adhesion of the topcoat to the primer surface. Adhesion of topcoats can be further enhanced if the primer is formulated using a Pigment Volume Concentration (PVC) higher than Critical PVC (CPVC) (see Section 11.2). A film from such a primer has voids into which resin solution from the topcoat can flow, providing a mechanical anchor between the topcoat and the primer. Because the voids in the primer coat are thus filled with vehicle from the topcoat, the effective PVC of the final primer layer of the overall coating is approximately equal to CPVC. The PVC of the primer should be only a little above CPVC. Loss of significant amounts of vehicle from the topcoat into the pores of the primer can increase the PVC of the topcoat, and hence reduce its gloss.

6.3. Testing for Adhesion. Because of the wide range of exposures to stresses in actual use, there is no really satisfactory laboratory test for the adhesion of a coating film to the substrate during use. A useful guide for an experienced coatings formulator is the use of a penknife to see how difficult it is to remove the coating and to observe its mode of failure. Many tests for adhesion have been devised (48,49). From the standpoint of obtaining a measurement related to the work required to separate the coating from the substrate, the direct pull test is probably the most widely used. The accuracy of the test is subject to considerable doubt and the precision is not very good. Even for experienced personnel, reproducibility variations of 15% or more must be expected. A compressive shear delamination test has proven to be useful in studying the adhesion and cohesion properties of clear coat–base coat–primer coatings on TPO (47). The most common specification test, cross-hatch adhesion, is of little value beyond separating systems having very poor adhesion from others.

7. Corrosion Control

An important function of many coatings is to protect metals, especially steel, against corrosion. Corrosion protection is required to protect steel against corrosion with intact coating films. Another objective is to protect the steel against corrosion even when the film has been ruptured.

7.1. Protection by Intact Films. In the case of intact films, the key factors responsible for corrosion protection are adhesion of the coating to the steel in the presence of water, oxygen and water permeability, and the resistance of the resins in the film to saponification (50). If the resins in the coating are adsorbed to cover the steel surface completely and if the adsorbed groups cannot be displaced by water, oxygen and water permeating through the film cannot contact the steel and corrosion does not occur. Only a monolayer is required to protect against corrosion, if the monolayer stays in place over the period of exposure.

The factors affecting adhesion are critical in controlling corrosion. Clean surfaces are critical. Sandblasting to white metal provides a good surface for application of corrosion-protective coatings if the coating is applied over the sand-blasted surface before it can become contaminated. Conversion coating having insoluble phosphate crystals improves adhesion, and hence corrosion protection. It has been found that in automobiles the quality of the conversion coating, which is affected by the quality of the steel, is the most important variable in corrosion control. Viscosity of the external phase of the coating applied to the steel surface can be a critical factor. Because viscosity drops as temperature increases in greater penetration of vehicles, superior corrosion protection observed with baking coatings. In the case of corrosion control, penetration into the micropores and crevices is especially critical because if those surfaces do not have resin adsorbed on them when the water and oxygen permeate through the film, corrosion begins. Corrosion leads to a solution of ionic materials in water under the coating film, establishing an osmotic cell. The osmotic driving force accelerates the permeation of water and the osmotic pressure provides a further force to displace the film from the surface to form blisters.

Because water permeates through any coating film, it is desirable to have groups adsorbed on the surface that cannot be displaced by water. Although there is some controversy as to the mode of action, it is a common observation that resins having multiple amine groups along the chain give better corrosion protection than those having multiple hydroxy groups, perhaps because amines are less readily displaced from the surface of steel by water. Even though a particular interaction between a polar group on a resin molecule and the surface of the steel or the phosphate groups of the conversion coating is displaced by water, if there are multiple groups from the same resin molecule adsorbed, there can be a cooperative enhancement of adhesion. If one group desorbs, other groups that can do so readsorb the molecule onto the substrate surface. Phosphoric acid partial esters, as in epoxy phosphates, give enhanced adhesion and resistance to displacement by water. Resins that have saponifiable groups in the backbones are particularly likely to show poor wet adhesion.

If a coating had perfect wet adhesion, no other factors would affect corrosion protection, but frequently in practice such a high degree of wet adhesion cannot be attained. Corrosion protection is enhanced if the permeability of the film to oxygen and water is low. A significant factor controlling these permeabilities is the free-volume availability in the film, which is in turn related to T_g. From the point of view of corrosion protection, it is desirable to have the T_g of films at least 50°C higher than the service temperatures of the coatings. This condition is difficult, if not impossible, to achieve using ambient cure coatings and for the highest corrosion protection, baking coatings are desirable whenever it is feasible to use them.

Permeability is controlled not only by the diffusion rate but also by the solubility of the diffusing molecules. There can be significant variations of the solubility of water in various films. Films containing highly polar groups have the highest tendency to dissolve water. Films made with chlorinated polymers such as chlorinated rubber, vinyl chloride copolymers, and vinylidene chloride copolymers dissolve very small amounts of water and are widely used as vehicles for topcoats for corrosion protection coating systems. Permeability of coatings to oxygen and water is also reduced by pigmentation. Lowest permeability results from having a PVC close to but not above CPVC. Platelet pigments such as leafing aluminum pigments and mica can orient parallel to the surface of a film during solvent evaporation, and therefore act to improve the barrier properties of coatings.

7.2. Protection by Nonintact Films. It is also possible to achieve corrosion control by coatings after a film has been ruptured. Because the coatings used to achieve this control generally give poorer protection when their films are not ruptured, such systems should be used only when film rupture must be anticipated or when complete coverage of the steel interface cannot be achieved. There are two techniques used on a large scale: primers containing corrosion inhibiting pigments and zinc-rich primers.

The mechanism of action of corrosion inhibiting pigments is not completely understood, but it is generally agreed that they promote oxidation at the surface of anodic areas of the steel to form a barrier layer. This action is called passivation. For the pigments to be effective, they must have a minimum solubility in water. If the solubility is too high, however, they would be rapidly lost from the film by leaching with water and thus provide only short-term protection. Because the pigments are somewhat water soluble, their presence in an intact film can lead to blistering and loss of adhesion. Therefore, it is undesirable to use such pigments except when the need for protection by nonintact films is important.

The oldest corrosion inhibiting pigments are red lead Pb_3O_4 [1314-41-6], containing ~15% PbO, and zinc yellow $3ZnCrO_4 \cdot K_2CrO_4 \cdot Zn(OH)_2 \cdot 2H_2O$, [85497-55-8], commonly, but mistakenly, called zinc chromate. There is concern about toxic hazard with red lead. Even more serious, soluble chromates, such as are present in zinc yellow, are carcinogenic. Because there are no satisfactory laboratory tests to predict the effectiveness of coatings containing corrosion-inhibiting pigments, extended field experience is necessary to determine the utility of new pigments. Zinc–calcium molybdates, surface-treated barium metaborate, zinc phosphate, zinc salts of nitrophthalic acid, and calcium–barium phosphosilicates, and phosphoborates are pigments that have been recommended as corrosion inhibitors.

Zinc-rich primers can be very effective in protecting steel with nonintact films against corrosion. High contents of zinc metal powder are required in the primers; PVC of the zinc powder must exceed CPVC to permit the necessary electrical contact between the zinc particles and between zinc and steel. Also having the PVC above CPVC makes the coating porous so that water can enter the film permitting completion of the electrical circuit. The zinc becomes the anode and the steel the cathode of an electrolytic cell, the zinc acts as a sacrificial metal to protect the steel. Because a base, $Zn(OH)_2$, is generated, saponification-resistant binders are required. The most widely used systems are inorganic zinc-rich primers, also called zinc silicate primers. The vehicle is an alcoholic solution of partially polymermized tetraethyl orthosilicate (silicic acid tetraethyl ester) [78-10-4]. After application, atmospheric moisture continues the hydrolysis and completes the polymerization of the tetraethyl orthosilicate and zinc salts of the polysilicic acid form. In applying topcoats, penetration into the pores of the primer must be avoided. Increasingly, latex paints are being used as topcoats because they do not permit vehicle penetration into the pores.

It is desirable to clean a steel surface thoroughly before applying a coating, but it is not always possible. Sometimes it is necessary to apply coatings over oily, rusty steel. In this case, it is essential to have a vehicle that can displace and dissolve the oily contamination from the surface and have sufficiently low viscosity for a sufficiently long time after application for penetration through the rusty areas down to the surface of the steel. Drying oil primers pigmented with red lead are still widely used for this purpose. They have the very low surface tension necessary for wetting, and can dissolve the oil and penetrate through the rust. Although their wet adhesion to steel and saponification resistance are inferior to those of many other primers, it is better to have some vehicle on the surface of the steel rather than having no vehicle penetrate down through the rust to the steel surface. This inadequacy is partly offset by the use of red lead as a corrosion-inhibiting pigment.

Formulation of effective corrosion-resistant coatings is made difficult by the lack of a laboratory test that can provide reliable predictions of field performance. The most widely used test is exposure in a salt fog chamber. It has been shown repeatedly, however, that the results of such tests do not correlate with actual performance (51). Outdoor exposure of panels can provide useful data, especially in locations where salt spray occurs, but predictions of performance are not always satisfactory.

Useful guidance in evaluating wet adhesion can be obtained by checking adhesion after exposure in a humidity chamber. In some cases, cathodic disbonding tests may provide useful data (ASTM Standards G8-79, G19-83, and G42-80). Another approach to testing for delamination is the use of electrochemical impedance spectroscopy (eis) (52). Impedance is the apparent opposition to flow of an alternating electrical current, and is the inverse of apparent coating capacitance. When a film begins to delaminate there is an increase in apparent capacitance. The rate of increase of capacitance is proportional to the amount of surface area delaminated by loss of wet adhesion. High performance systems show slow rates of increase of capacitance so tests must be continued for long time periods. This method can be a powerful tool for study of the effect of variables on delamination.

An extensive survey of accelerated test methods for anticorrosive coating performance that emphasizes the need to develop more meaningful methods of testing has been published (53). The most powerful tool available is the accumulated material in data banks correlating substrate, composition, application conditions, and specifics of exposure environments with performance.

8. Resins for Coatings

8.1. Latexes. Latexes are aqueous dispersions of solid polymer particles, generally made by emulsion polymerization. Latex paints are sometimes called emulsion paints but that terminology should be avoided since there are paints made with emulsions of resin solutions. Reference (54) provides a broad discussion of latexes. Molecular weights of latex polymers is generally high, >1,000,000. However, the high molecular weight of the latex polymer does not affect the viscosity of the latex, making it possible to formulate relatively high solids coatings. Thus, film properties of thermoplastic coatings can be good. Latex coatings have low VOCs. Aqueous solvent free polyurethane dispersions are latexes but almost always called polyurethane dispersions, they are discussed in the section on waterborne urethanes.

Latexes are the principal vehicle of a large fraction of architectural coatings and a small but rapidly growing fraction of industrial and special purpose coatings. The largest volume of latexes are polymers of acrylic esters and almost all will form films at ambient temperatures. Minimum film forming temperatures (MFFT) are primarily determined by $(T - T_g)$ but are usually lower than the T_g because of plasticizing by water. By changing the monomer feed during emulsion polymerization it is possible to make latexes whose particles have higher T_g values in the center of the particles and lower T_g values in the outer shell. This permits making latexes that will form films at lower temperature related to the shell T_g polymer but after film formation exhibit properties intermediate to those from the low T_g shell and the higher T_g core (55).

Acrylic latexes are widely used in exterior latex coatings and in higher performance interior coatings. Vinyl acetate based latexes are widely used in interior coatings such as flat wall paint because of their lower cost. These latexes are copolymers to reduce MFFT, eg, vinyl acetate–butyl acrylate copolymers. Latex coatings form films by coalescence (see the section on Film Formation from Polymer Dispersions). It has been common to reduce film formation temperature by including a coalescing solvent in a formula. That is a solvent that dissolves in the latex particles reducing their T_g that slowly diffuses and evaporates out of the film after application.

There is increasing use of thermosetting latexes, ie, latexes having functional groups that can be cross-linked after application. Such latexes are prepared with lower T_g to permit lower temperature film formation and then cross-linked after application to increase their modulus. Some are used in two package coatings, eg, hydroxy-functional latexes with urea–formaldehyde or melamine–formaldehyde resins. Carboxylic-functional latexes can be cross-linked with carbodiimides (16) or polyimines (56). Use of β-(3,4-epoxycyclohexyl)-ethyltriethoxysilane as a cross-linker for carboxylic acid funtional latexes gives formulations that are stable for one year and films that cure at 115° (19).

Thermosetting latexes stable enough at ambient temperature for use in architectural coatings are more difficult to make. Several workers have prepared latexes with allylic substiutents that cure by autoxidation, for an example, see (22). Latexes made using triisobutoxysilylpropyl methacrylate as a coomonomer cross-link in 1 week with a tin catalyst and package stable for over 1 year (22).

8.2. Amino Resins. Melamine–formaldehyde (MF) resins are the most widely used cross-linking agents for baking enamels. They are made by reacting melamine (1,3,5-triazine-2,4,6-triamine) [108-78-1] and formaldehyde[50-00-0] followed by etherification of the methylol groups using an alcohol. Two classes of MF resins are used. Class I resins are made using excess formaldehyde and a high fraction of the methylol groups are etherified with alcohol. Commercial resins contain a range of compounds having a large fraction of the amine groups substituted with two alkoxymethyl groups; some oligomers have two or more triazine rings coupled with methylene ether groups. Various alcohols can be used. The largest volume Class I resins contain a high proportion of hexamethoxymethylmelamine (HMMM) (N,N',N''-hexamethoxymelamine).

Class II MF resins are made using a lower ratio of formaldehyde to melamine and a significant fraction of the nitrogens have one alkoxymethyl group and a hydrogen. An example of one compound present is N,N',N''-trimethoxymethylmelamine (TMMM). Class II resins have a larger fraction of oligomers.

The MF resins react with both hydroxyl and carboxylic acid groups and are used to cross-link any resins having such substituents. They also undergo self-condensation reactions, the Class II more rapidly than Class I. Class I resins tend to give cross-linked films having greater toughness and flexibility but Class II resins tend to cure at lower temperatures. Class I resins require strong acid catalysts such as sulfonic acids whereas Class II resin reactions are catalyzed by weaker acids such as carboxylic acids.

Work has been concentrated on increasing the solids content of coatings. Class I resins have lower molecular weights than Class II resins and provide higher solids. Lowest molecular weight resins are produced under conditions that minimize self-condensation and maximize HMMM content. Mixed methyl butyl ether Class I MF resins have lower T_g and viscosity and lead to coatings having somewhat lower VOC emissions. A further emphasis in research is to minimize emission of free formaldehyde and generally Class I resins are superior in this respect.

In high solids coatings, especially those made with low average functionality polyester resins, good film properties require closer control of curing time and temperature, catalyst concentration, and ratio of reactants than do the older, lower solids, higher average functionality systems. The potential problem is especially notable using Class II MF resins; there is greater latitude using the higher functionality Class I MF resins. Although it had been believed that steric hindrance limited the reaction of Class I resins so that only about one-half of the potential functional groups reacted, complete reaction has been demonstrated (57). Stoichiometric amounts of Class I MF resin and hydroxyl groups react, but it is frequently desirable to use a higher ratio of MF resin. The excess MF resin gives coatings having a higher modulus above T_g, apparently by increasing the extent of self-condensation. Another consideration is that in many cases the MF resin is less expensive than the coreactant.

In water-borne coatings, methyl ether MF resins are preferred because of greater water solubility compared to that of higher alcohol derivatives. Although either Class I or II MF resins can be used in water-borne coatings, Class I resins are preferred because of better storage stability. In anionic electrodeposition coatings, mixed methyl ethyl ether resins are commonly used for cross-linking the epoxy ester or other binder resin. The water solubility of these mixed ether MF resins is high enough for them to be incorporated into the system but sufficiently limited that essentially all of the MF resin dissolves in the epoxy ester aggregates rather than staying in solution in the continuous phase. This is essential to maintain balanced composition during application by electrodeposition.

Because of the high content of nitrogens having two alkoxymethyl groups, Class I MF resins require strong acid catalysts such as *p*-toluenesulfonic acid (*p*TSA) (4-methylbenzenesulfonic acid) [104-15-4]. The higher the concentration of catalyst the lower the curing temperature of the coating. However, the catalyst remains in the film and can catalyze hydrolysis of the cross-link bonds on exterior exposure, leading to film failure. Addition of sulfonic acid decreases storage stability. In order to avoid this problem, it is common to use blocked catalysts that are generally salts of a sulfonic acid and a volatile amine. It has been found that some grades of titanium dioxide pigment neutralize the catalyst and slow down curing as the coating is stored for longer times.

The choice of sulfonic acid can be critical in affecting film performance. Dinonylnapthalenedisulfonic acid [60223-95-2] gives superior film properties as compared to *p*TSA, perhaps because of greater solubility in the coating. Dodecylbenzenesulfonic acid [27176-87-0], which is also more soluble, gives superior properties when the coating is applied over primer, but poor adhesion results when applied directly to steel. Apparently the sulfonic acid is strongly adsorbed on the steel surface and the adhesion of the coating to this monolayer of catalyst is poor.

Other amino resins are used to a lesser degree in coatings. Urea–formaldehyde (UF) resins are used in some coatings for wood furniture because these resins cross-link at lower temperatures than MF resins and the higher water resistance and exterior durability that can be obtained using MF resins are not needed. Ethers of formaldehyde derivatives of 6-phenyl-1,3,5-triazine-2,4-diamine (benzoguanamine resins) [91-76-9] give coatings having superior resistance to alkalies and detergents and are used as cross-linkers for coatings used on home laundry machines and dishwashers. Ethers of formaldehyde derivatives of glycoluril (tetrahydroimidazo[4,5-*d*]imidazole-2,5-(1*H*,3*H*)-dione) [496-46-8] are useful for coatings requiring outstanding extensibility during forming. Amides react with formaldehyde to give methylol derivatives that in turn react with alcohols to give reactive ethers. Thermosetting acrylics having such reactive groups derived from acrylamide were among the first thermosetting acrylic resins.

8.3. Urethane Systems. Isocyanates react with a wide variety of functional groups to give cross-links. The most widely used coreactants are hydroxy-functional polyester and acrylic resins. The isocyanate group reacts with the hydroxyl group to generate a urethane cross-link. The reaction proceeds relatively rapidly at ambient or modestly elevated temperatures. In addition to the low curing temperatures, significant advantages of urethane coatings are generally excellent abrasion and impact resistance combined with solvent resistance.

A variety of polyisocyanates are commercially available; those most widely used in coatings are toluene diisocyanate (TDI) (2,4-diisocyanato-1-methylbenzene) [584-84-9], 4, 4′-di(isocyanatophenyl)methane (MDI)(bis(4-isocyanatophenyl)-methane); HDI; isophorone diisocyanate (IPDI) (1-isocyanato-3-(isocyanatomethyl)-3,5,5-trimethylcyclohexane) [4098-71-9]; 4,4′-di(isocyanatocyclohexyl) methane (HMDI)[bis(4-isocyanatocyclohexyl)methane]; and TMXDI. Aromatic isocyanates such as TDI give films that discolor rapidly on exterior exposure. Aliphatic isocyanates give coatings having excellent exterior durability. TMXDI is classified as an aliphatic isocyanate because the NCO group is not directly on an aromatic ring.

Most diisocyanates are toxic, therefore many times it is safer to use polyisocyanates. The lower vapor pressure and skin permeability of trifunctional and polyfunctional isocyanates reduces the toxic hazard but, as for any other reactive coating, caution should still be exercised, especially when coatings are applied by spray techniques.

TDI and TMXDI are available as prepolymers derived by reaction of excess TDI or TMXDI with TMP and removing the excess diisocyanate by vacuum thin-film evaporation. The average NCO functionality is a little over 3. The polyisocyanates TDI, HDI, and IPDI are available as trimers having an isocyanurate ring, ie, substituted 1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-triones. The average functionality is somewhat over 3. HDI is also available as a biuret derivative having an average functionality of ~3. Polyisocyanates can also be made by the copolymerization of TMI [1-(1-isocyanto-1-methylethyl)-3-(1-methylethenyl)benzene] [2094-99-7] and acrylic esters (58).

The reaction of isocyanates and alcohols is too rapid to permit formulation of one-package stable coatings from polyols and polyisocyanates. Thus two-package coating systems are used on a large scale: one package contains the polyisocyanate and the other a polyhydroxy resin and the pigment(s). Reaction rates are controlled by catalysts. The most widely used catalysts are organotin compounds, most commonly dibutyltin dilaurate (DBTDL) [dibutyl bis[1-(oxododecyl)oxy]-stannate] [77-58-7]. Highly catalyzed systems cure rapidly at moderate temperature but have pot lives so short that they must be used in proportioning mixing spray guns so that the two packages are mixed just before spraying. Slower cure systems may have pot lives of several hours. Any polyhydroxy resin can be used; the most widely used are polyesters and acrylics.

A principal challenge is formulating to maximize pot life while still curing in a short time at low temperature, which is an increasing problem as coatings are formulated to higher and higher solids. The difficulty can be severe because in uncatalyzed systems, reaction rates are second order in respect to alcohol, so that the reaction rate slows down dramatically as the concentration of alcohol groups decreases. Use of tin catalysts like DBTDL is especially desirable because the catalyzed reaction rate with respect to alcohol has been shown to be one-half (59). By using DBTDL, pot life can be extended by including a volatile carboxylic acid, such as acetic acid [64-19-7], in the formula. After application the acetic acid evaporates and cure rate approaches that without the acetic acid. Similarly, 2,4-pentanedione increases pot life. The reaction rate of isocyanates and alcohols is affected by the media. Rates are slowest in strong hydrogen bond acceptor solvents and most rapid in hydrocarbon, especially aliphatic hydrocarbon, solvents. Therefore, hydrogen-bonding solvents and resins having as low hydrogen bond potential as possible are used (60).

In formulating air-dry coatings, one should select combinations of polyol and polyisocyanate such that the T_g permits complete reaction at curing temperature. Usually, some excess isocyanate is used because some isocyanate also reacts with water from the atmosphere. In aircraft coatings, it is common to use a 2:1 ratio of isocyanate to hydroxyl. The excess isocyanate reacts with water to yield an amine that reacts very rapidly with another molecule of isocyanate to give a urea cross-link.

Aliphatic amines in general react to rapidly with isocyanates to be used even in 2K coatings. However, sterically hindered amines have been developed that are useful. Michael addition products of diethyl maleate with a diamine such as bis(4-amino-3-methylcyclohexyl)methane, a diaspartate, is an example. They permit formulation of very high solid 2K coatings with excellent pot life, cure rate, and film properties (61). The reaction is catalyzed by carboxylic acids and water, organotin compounds retard the reaction. Dialdimines can also be used in 2K coatings. The aldimine groups are sufficiently stable to hydolysis that they react directly with isocyanates to give cyclic unsaturated substituted ureas (61).

Another class of urethane coatings is known as moisture cure coatings. These are stable 1K coatings based on isocyanate-terminated resins as the sole vehicle. The cross-links formed are urea groups. Because pigments have water adsorbed on the surface of the particles, these coatings are almost always clears, because the cost of drying pigment is usually prohibitive. Moisture cure clear coatings are used where high abrasion resistance is needed, such as on floors, bowling alleys, and pins.

Isocyanates are also used to make coating resins that do not cross-link through reactions of the isocyanate groups. These have the advantage that the toxic hazards associated with isocyanates are handled in the resin factory rather than by the coatings applicator. One class of such products is urethane oils, also called urethane alkyds and uralkyds. A diiosocyanate such as TDI reacts with partial glycerol esters of drying oils to yield polyurethanes analogous to alkyd resins. Like alkyds, urethane oils form dry films by autoxidation. The dry films exhibit superior resistance to hydrolysis and abrasion as compared to alkyd films. Many coating products for the do-it-yourself market labeled as varnish are urethane oils. Their properties are generally superior to varnishes as well as alkyds.

Carbamate-functional resins made by non-isocyanate processes are also used. Carbamate-functional acrylic resins cross-linked with MF resins are used in automotive clear coats that combine the environmental etch resistance of urethane coatings and the mar resistance of MF cross-linked hydroxy-functional acrylic resins coatings (62). In another approach, a carbamate-functional oligomer was synthesized by reacting a hyrdoxy acid, such as dimethylolpropionic acid (DMPA), with glycidyl neodecanate (63). Automotive clear coats formulated with Class I MF resin showed excellent performance. 85% NVV (non-volatile volume %) coatings could be applied with hot spray.

High molecular weight, linear, hydroxy-terminated polyurethanes are used in lacquers for topcoats for coated fabrics. Low molecular weight, hydroxy-terminated polyurethanes can be used with MF resins to replace polyesters to take advantage of the greater hydrolytic stability of the urethane groups as compared to ester groups and the greater abrasion resistance of the urethane coatings. These coatings are more expensive than polyesters, especially when made with aliphatic diisocyanates, and tend to give higher viscosity solutions than polyesters.

Blocked Isocyanates. Another important class of urethane coatings is based on blocked isocyanates. See (64) for an extensive review of the chemistry and applications for blocked isocyanates. Blocked isocyanates are made by reaction of a diisocyanate and a blocking agent giving a product that is quite stable in the presence of alcohols and water at ambient temperature, but reacts with hydroxyl or amine groups at elevated temperatures. Using blocked isocyanates and hydroxy-functional acrylic or polyester resins, stable one-package coatings can be formulated without need for moisture-free pigments and solvents and with substantially reduced toxic hazard. However, the coatings require relatively high temperature cures and, in some cases, the blocking agent that evolves during cure presents a pollution problem.

MEK oxime (MEKO) (2-butanone oxime) [96-29-7], phenols, alcohols, and caprolactam (hexahydro-2H-azepin-2-one) [105-60-2] are widely used as blocking agents. Phenol blocked isocyanates are used in wire coatings, curing temperatures are high. Alcohols are particularly useful in electrodeposition coatings since they provide excellent hydrolytic stability in the coating bath. The MEKO blocked isocyanates react with alcohols at 130–140°C in the presence of a catalyst, but still give reasonable storage stability.

Caprolactam blocked IPDI is widely used in powder coatings. Oligomeric uretdiones are increasingly used in powder coatings because there are no volatile by products. The reaction products of diisocyanates and diethyl malonate (propanedioic acid diethyl ester) [105-53-3] act as cross-linking agents for polyols at the lowest temperature of any commercial blocked isocyanates but they are not truly blocked isocyanates. Rather, they react with alcohols by transesterification to yield films cross-linked with ester and amide bonds instead of urethane cross-linked coatings (65).

Polyamines react with blocked isocyanates at lower temperatures than polyols. Oximes are used as blocking agents with polyamines in applications such as magnetic tape coatings where the curing temperature must be kept low to avoid heat distortion of the plastic tape substrate. The reactivity is too high to permit one-package coatings but the combination of amine and blocked isocyanate provides an adequate pot life to permit application by roll coating. Alcohol-blocked isocyanates are sufficiently stable at ambient temperatures in the presence of amines to be used in one-package coatings. They are used in cationic electrodeposition coatings where there is also need for long term stability in the presence of large amounts of water.

Waterborne Urethane Systems. There has been increasing effort to use waterborne urethane coatings. One approach is preparation of aqueous dispersions of polyurethanes. These materials are latexes but they are almost always called polurethane dispersions (PUDs). Most of them are acid substituted resins neutralized with an amine such as triethyl amine. Reference (66) reviews various approaches. Both thermoplastic and thermosetting PUDs are used. In such applications as fabric coatings and chip resistant primers for automobiles.

In recent years, increasing effort has been devoted to 2K waterborne urethane coatings. It had been assumed for many years that using free polyisocyanates in a waterborne coating was not feasible due to the high reactivity of isocyanates with water. Selection of components, formulation, and application methods are critical. They are now commercial on a large scale. Thermosetting

PUDs have hydroxyl groups as cross-link sites. For example, hydroxy-terminated PUDs using DMPA as one of the polyols in the reaction. The carboxylic acid DMPA is so hindered that it reacts very slowly with the isocyanate. They have excellent hydrolytic stability compared to water-reducible polyesters and superior abrasion resistance. They can be cross-linked with polyisocyanates or MF resins. Bayer Corporation was awarded a Presidential Green Achievement Award in 2000 for their work with the systems. Reference (67) reviews the literature.

8.4. Epoxy Resins.

Epoxy resins are used to cross-link other resins with amine, hydroxyl, carboxylic acid, and anhydride groups. The epoxy group, properly called an oxirane, is a cyclic three-membered ether group. By far the most widely used epoxy resins are bisphenol A (BPA) [4,4-(1-methylethylidene)-bisphenol] [80-05-7], epoxy resins.

An important use for epoxy resins is as a component in two-package primers for steel. One package contains the epoxy resin and the other a polyfunctional amine. In coatings, generally low molecular weight polyamines are not useful because the equivalent weight is so low that the ratio of the two components would be very high, increasing the probability of mixing ratio errors; furthermore, low molecular weight amines tend to have greater toxic hazards. Amine-terminated polyamides are widely used, they are sometimes called amido-amines but frequently just polyamides. Amide groups do not react readily with epoxy groups. Polyamides are made from long chain dibasic acids, such as dimer acids, and a stoichiometric excess of a polyamine, such as diethylenetriamine (DETA) [*N*-(2-aminoethyl)-1,2-ethanediamine] [111-40-0]. The long aliphatic chain contributes flexibility to the cross-linked film. If more rigid films are needed, so-called amine adducts are used. Amine adducts are the reaction products of a low molecular weight BPA epoxy resin and a large excess of polyamine from which any unreacted polyamine is removed by vacuum thin-film evaporation. The product is a polyamine having substantially higher molecular and equivalent weight and rigid aromatic rings. In designing combinations of epoxy resin and amine for ambient temperature cure coatings, care must be taken so that the T_g of the fully cured coating is not too much over the temperature at which the film is to be cured, otherwise, the cross-linking stops because of restricted mobility in the film. Epoxy–amine coatings are particularly effective as corrosion protective primers for steel because the amine groups resulting from the cross-linking reaction promote adhesion to the steel in the presence of water and because the cross-linked resins are completely resistant to hydrolysis.

Epoxy resins also are used to cross-link phenolic resins. Such coatings are used in interior can linings. The hydrolytic stability and adhesion of the coatings are critical. Adhesion is further improved by the incorporation of a small amount of epoxy phosphate in the coatings. Epoxy phosphates are made by reacting BPA epoxy resins and small amounts of phosphoric acid and water. Complex reactions occur including formation of partial phosphate esters of a primary alcohol from a ring opening reaction with an epoxy group (68).

Epoxy resins are widely used in powder coatings. Probably the largest volume usage is of BPA epoxy resins cross-linked with dicyanodiamide (cyanoguanidine) [461-58-5]. Because BPA epoxy resins are easily photoxidized, they are not useful in coatings requiring exterior exposure. Triglycidylisocyanurate (TGIC) [1,3,5-tris(oxiranylmethyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione] [2451-62-9] has been used carboxylic acid terminated polyesters in powder coatings that require exterior durability.

Epoxy resins are raw materials to make epoxy esters by reacting BPA epoxy resins and drying oil fatty acids; each epoxy ring can potentially react with two fatty acid molecules and hydroxyl groups on the backbone of the epoxy resin can also esterify. A low molecular weight BPA resin is initially reacted with BPA to make a higher molecular weight BPA resin and then the fatty acid is added directly to the reactor for the esterification step. Lower molecular weight resins give lower viscosity epoxy esters but the functionality is also low so that more rapid cross-linking is obtained for epoxy esters based on higher molecular-weight BPA resins. These synthetic drying oils provide coatings having better adhesion and substantially better saponification resistance than alkyd resins. Exterior durability of these materials is poor, and the principal use is in primers for steel.

Epoxy esters of fatty acids having some conjugated double bonds can be converted to water-reducible resins by reaction with maleic anhydride (2,5-furandione) [108-31-6] followed by amine neutralization. Baking primers made with such resins provide the same corrosion protection as conventional solvent-borne epoxy ester primers. For some years, this type of vehicle was used in anionic electrodeposition primers. However, for automobiles cationic electrodeposition primers are now preferred. The vehicles for cationic primers are proprietary but consist of the reaction product of epoxy resins and polyfunctional amines.

8.5. Acrylic Resins. Acrylic resins are the largest volume class of coatings resins. Thermosetting acrylic resins are copolymers of acrylic or methacrylic esters and a hydroxy-functional acrylic ester. Other monomers such as styrene (ethenylbenzene) [100-42-5], vinyl acetate, and others, may be included in the copolymer. There is increasing emphasis on high solids and water-reducible types. The main advantages of acrylic coatings involve the high degree of resistance to thermal and photoxidation and to hydrolysis, giving coatings that have superior color retention, resistance to embrittlement, and exterior durability.

Hydroxy-functional thermosetting acrylics are widely used in baking enamels for automobile and appliance topcoats, exterior can coatings, and coil coating. Research efforts have been directed at increasing the solids content of such coatings while maintaining the excellent properties. In contrast to polyesters, where virtually all molecules have at least two hydroxyl groups, synthesis of very low molecular weight acrylic resins having an average functionality of two to three and containing few molecules that are nonfunctional or only monofunctional is difficult. Free-radical polymerization, the usual method for synthesizing thermosetting acrylics, results in a random distribution of the 2-hydroxyethyl methacrylate (HEMA) (2-methyl-2-propenoic acid 2-hydroxyethyl ester) [868-77-9] comonomer in the oligomer chains, and hence significant fractions of nonfunctional and monofunctional molecules unless the number average molecular weight is on the order of 3500 or higher and the average functional monomers per molecule is on the order of three or higher.

Various techniques have been studied to increase solids content. Hydroxy-functional chain-transfer agents, such as 2-mercaptoethanol [60-24-2], reduce the probability of nonfunctional or monofunctional molecules, permitting lower molecular-weight and functional monomer ratios. Making low viscosity acrylic resins by free-radical initiated polymerization requires the narrowest possible molecular weight distribution. This requires careful control of temperature, initiator concentration, and monomer concentrations during polymerization. The initiator structure may be critical; it should yield radicals that are least active in hydrogen-abstraction reactions. Azo initiators have been widely used. Most so-called high solids acrylic resin coatings contain only 45–50 vol% solids. However, there are proprietary acrylic resins available that can be used to make coatings having as high as 70 vol% solids.

Other functional groups than hydroxyls are also used. Carboxy acid functional acrylic resins are used with epoxy compounds as cross-linkers. Epoxy-functional acrylic resins are being used in powder clear coats for automobiles cross-linked with dicarboxylic acids such as dodecane dicarboxylic acid (69). Carbamate-functional acrylic resins are being used in automotive clear coats are cross-linked with MF resins, such coatings combine the mar resistance of urethane coatings and the environmental etch resistance of MF cross-linked resins (62).

Acrylic resins are, in general, more appropriate than polyesters for water-reducible baking coatings. Acrylic copolymers using acrylic acid(2-propenoic acid) [79-10-7] and HEMA as functional comonomers, prepared in an ether–alcohol solvent and partially neutralized with an amine, such as dimethylaminoethanol (DMAE) [108-01-0], are stable against both hydrolysis and alcoholysis. After pigmenting and adding MF resin, the coatings can be diluted with water and applied with relatively low VOC. Although such systems are commonly called water soluble, these acrylic resins are not truly soluble in water. On dilution with water, adequately stable dispersions of aggregates swollen with solvent and water are formed. As a result of the formation of these aggregates, the change in viscosity on dilution with water is abnormal. Initially the viscosity decreases; however, on further dilution, the viscosity increases. On still further dilution, the viscosity decreases rapidly. The pH after dilution is also abnormal, being on the order of 9 even with only 75% of the amount of amine required to neutralize the carboxylic acid groups on the resin. The viscosity at application solids is essentially independent of molecular weight. The morphology of such systems and the effects of variables on the abnormal viscosity and pH profiles obtained on dilution with water have been studied (70,71). Class I MF resins or polyisocyanates are used as cross-linking agents.

Another type of water-reducible acrylic resins is used in the interior linings of two-piece beverage cans. A graft copolymer of styrene, ethyl acrylate(2-propenoic acid ethyl ester) [140-88-5], and acrylic acid on a BPA epoxy resin is prepared in an ether–alcohol solvent (72). Benzoyl peroxide(dibenzoyl peroxide) [94-36-0] is used as the initiator that maximizes the opportunity for grafting. The product is a mixture of graft copolymer, unreacted epoxy resin, and ungrafted acrylic copolymer. The resin is partially neutralized with DMAE and diluted with water to spray application viscosity. Dilution with water gives a stable dispersion of resin aggregates swollen with solvent and water.

8.6. Polyester Resins. The term polyester is used in the coatings field almost entirely for low molecular weight hydroxy, or sometimes carboxylic acid, terminated oil-free polyesters. Polyesters have been a class of replacements for alkyd resins in MF cross-linked baking enamels. Hydroxy-terminated polyesters are also used with polyfunctional isocyanates in making air-dry and force-dry coatings as well as with blocked isocyanates in coatings for higher baking temperature and in powder coatings. Carboxylic acid-terminated polyesters are used predominantly with epoxy cross-linkers in powder coatings.

When adhesion directly to metal is required, polyesters are generally preferred over acrylic resins. When highest exterior durability is needed over primers, acrylic resins are generally preferred over polyesters because of the greater hydrolytic stability of acrylic resin coatings. In order to maximize the hydrolytic stability of polyesters for exterior durability, isophthalic acid (IPA) is commonly used instead of phthalic anhydride (PA) (1,3-isobenzofurandione) [85-44-0] in making these resins. An aliphatic acid, such as adipic acid (AA) (1,6-hexanedioic acid) [124-04-9] or dimer acids, is commonly used. The flexibility of the final film is partly controlled by the ratio of aromatic to aliphatic dibasic acids. The esters of highly substituted polyols such as neopentyl glycol (NPG), 1,4-dimethylolcyclohexane (cyclohexanedimethanol) (CHDM) [27193-25-5] and TMP are more hydrolytically stable than esters of simple polyols such as ethylene glycol. Mixtures of diol and triol are used to give an average functionality >2. The cross-link density of the final film is controlled by the equivalent weight, which is related to the average functionality and the number average molecular weight.

There has been significant progress in the development of polyesters for high solids coatings. In contrast to acrylic resins, the preparation of low molecular weight, and hence high solids polyesters, where substantially all of the molecules have a minimum of two hydroxyl groups is straightforward. The lower limit of the average molecular weight that is useful in baking systems is controlled by the volatility of the lowest molecular weight fractions. For conventionally prepared polyesters, the optimum number average molecular weight for baking enamels has been reported to be 800–1000 (73). Further improvements are achieved by synthetic techniques that give narrower molecular weight distributions (74). Because viscosity is increased by increasing the average number of functional groups per molecule, high solids polyesters are usually made with an average number of hydroxyl groups only a little over two. Low molecular weight, hydroxy terminated polyester diols and triols derived from the reaction of caprolactone (2-oxepanone) [502-44-3] and a diol or triol are commercially available, eg, Tone Polyols (75). Linear polyesters made by transesterification of 1,4-butanediol with a mixture of glutarate, adipate, and azeleate methyl esters give low viscosity, hydroxy-terminated polyesters with an average molecular weight of 680 (76). Such polyesters are used in mixtures having hydroxy-functional acrylic resins or somewhat higher molecular weight polyesters to increase solids.

Water-reducible polyester resins have terminal hydroxyl and carboxylic acid groups and an acid number of 40–60. To make such a resin reproducibly with a minimum risk of gelation, the reactivity of the different carboxylic acid groups must vary. The use of trimellitic anhydride (TMA) (1,3-dihydro-1,3-dioxo-5-isobenzofurancarboxylic acid) [552-30-7] near the end of the reaction at a lower temperature takes advantage of the higher reactivity of the anhydride group. Another method uses DMPA [3-hydroxy-2(hydroxymethyl)-2-methylpropanoic acid] [4767-03-7] as part of the diol in making a polyester. The highly hindered carboxylic acid esterfies more slowly than the carboxylic acid groups from isophthalic and adipic acids.

The polyester is dissolved in an ether–alcohol such as 1-propoxy-2-propanol [1569-01-3]. A secondary alcohol should be used because primary alcohols lead to more rapid transesterification than secondary alcohols. An amine such as DMAE is used to neutralize the acid, pigment is dispersed in the resin solution, MF resin is added as are additives, and the coating is reduced to application viscosity with water. The resin forms aggregates swollen with solvent and water as a reasonably stable dispersion. Use of cyclohexane dicarboxylic acid instead of isophthalic acid and 2-butyl-2-ethyl-1,3-propanediol instead of NPG gives a resin with somewhat better hydrolytic stability (77). The storage life of such systems is adequate with careful invenory control. The problem of hydrolysis can be minimized by use of a powdered solid polyester. For example, a powdered solid ester prepared from IPA, AA, NPG, CHDM, hydrogenated BPA, and TMA can be stored and stirred into a hot aqueous solution of DMAE shortly before the coating is required (78).

Another potential problem with water-reducible polyesters is formation of some low molecular weight nonfunctional cyclic molecules. In baking ovens, small amounts of such polyesters gradually accumulate by condensation in cool spots in the oven and eventually sufficient resin can accumulate to drip on products passing through the ovens. Water-reducible acrylic resins are used in much greater volumes because of the problems with water-reducible polyesters.

8.7. Alkyd Resins. Although no longer the principal class of resins in coatings, alkyds are still important and a wide range of types of alkyds are manufactured. Whereas some nonoxidizing alkyds are used as plasticizers in lacquers and cross-linked with MF resins in baking enamels, the majority are oxidizing alkyds for use in coatings for air-dry and force-dry applications. The principal advantages of alkyds are low cost and relatively foolproof application characteristics, resulting from low surface tensions. The principal shortcomings of these resins are embrittlement and discoloration upon aging and relatively poor hydrolytic stability.

Emphasis is being placed on developing high solids alkyd systems, eg, by using longer oil alkyds. However, as oil length increases, air drying slows for two reasons: the average number of functional groups, ie, activated methylene groups between two double bonds, eg, $\text{—CH=CHCH}_2\text{CH=CH—}$, per molecule decreases because the molecular weight decreases, and the ratio of aromatic rings to long aliphatic chains is reduced, resulting in lower T_g. Solids can be increased at the same average molecular weight by reducing polydispersity, ie, the breadth of molecular weight distribution. However, the properties of films from such narrow molecular weight distribution alkyds are inferior to those of broader molecular weight distribution resins of similar composition (79). One approach to high solids alkyds is the partial replacement of solvent in a with a reactive diluent. For example, dicyclopentenyloxyethyl methacrylate [70191-60-5] (80), mixed amides from the condensation of acrylamide (2-propeneamide) [79-06-1], drying oil acid amides with hexamethoxymethylmelamine [3089-11-0], and trimethylolpropane triacrylate [37275-47-1] have been recommended.

Water-reducible alkyds give aqueous dispersions by neutralizing the free carboxylic acid groups with an amine or ammonia. Comparable drying performance to solvent-borne alkyds can be obtained. However, they are not widely used because of limited hydrolytic stability that reduces the storage life of coatings. Also, film properties tend to be poorer than those of solvent-borne alkyds, especially in air-dry systems. The slow loss of amine or ammonia leads to short term high sensitivity to water. Even in the fully dry films, the presence of unreacted carboxylic acid groups leads to films having comparatively poor water resistance limiting their usefulness.

Another approach to waterborne alkyds, more widely used in Europe than in the United States, is to emulsify alkyds (81). The emulsions are stabilized with surfactants and can be prepared with little, if any solvent.

8.8. Other Coatings Resins. A wide variety of other resin types are used in coatings. Phenolic resins, ie, resins based on reaction of phenols and formaldehyde, have been used in coatings for many years. Use has been declining but there are still significant applications, particularly with epoxy resins in interior can coatings.

Silicone resins provide coatings having outstanding heat resistance and exterior durability. The cost is relatively high but for specialized applications these resins are important binders (82). Silicone-modified acrylic and polyester resins provide binders having intermediate durability properties and cost. Fluorinated polymers also exhibit outstanding durability properties. High cost, however, limits applicability.

Polyfunctional 2-hydroxyalkylamides serve as cross-linkers for carboxylic acid-terminated polyester or acrylic resins (83). The hydroxyl group is activated by the neighboring amide linkage. Solid grades of hydroxyamides are used as cross-linkers for powder coatings.

A range of acetoacetylated resins has been introduced (84). The acetoacetoxy functionality can be cross-linked with melamine–formaldehyde resins, isocyanates, polyacrylates, and polyamines. There is particular interest for possible corrosion protection on steel because the acetoacetoxy group can form coordination compounds with iron, perhaps enhancing the adhesion to steel surfaces.

9. Volatile Components

In most coatings, solvents are used to adjust the viscosity to the level required for the application process and to provide for proper flow after application (85). Most methods of application require coating viscosities of 50–1000 $\mathrm{mPa \cdot s} (= \mathrm{cP})$. Many factors must be considered in the selection of the solvent or, more commonly, solvent mixtures. Except for water-borne systems, solvents are usually chosen that dissolve the resins in the coating formulation. Solubility parameters have been recommended as a tool for selecting solvents that can dissolve the resins. However, the concept of solubility parameters for the prediction of polymer solubility is an oversimplification and the old principle that like dissolves like is the most useful selection criterion. The problem of solvent selection is most difficult for high molecular weight polymers such as thermoplastic acrylics and nitrocellulose in lacquers. As molecular weight decreases, the range of solvents in which resins are soluble broadens. Even though solubility parameters are inadequate for predicting all solubilities, they can be very useful in performing computer calculations to determine possible solvent mixtures as replacements for a solvent mixture that is known to be satisfactory for a formulation. For resins that are soluble in esters and ketones, costs can generally be decreased by using mixtures that contain hydrocarbons and alcohols to replace part of the esters and ketones.

An important characteristic of solvents is rate of evaporation. Rates of solvent loss are controlled by vapor pressure and temperature, partial pressure of the solvent over the surface, and thus the air-flow rate over the surface, and the ratio of surface area to volume. Tables of relative evaporation rates, in which *n*-butyl acetate is the standard, are widely used in selecting solvents. These relative rates are determined experimentally by comparing the times required to evaporate 90% of a weighed amount of solvent from filter paper under standard conditions as compared to the time for *n*-butyl acetate. Most tables of relative evaporation rates are said to be at 25°C. This, however, means that the air temperature was 25°C, not that the temperature of the evaporating solvent was 25°C. As solvents evaporate, temperature drops; the drop in temperature is greatest for solvents that evaporate most rapidly.

When coatings are applied by spray gun the atomized particles have a very high ratio of surface area to volume, and hence solvent evaporation is much more rapid during the time when the atomized particles are traveling from the orifice of the spray gun to the surface being coated than from the film of the coating on the surface. Except in the case of some high solids coatings, this rapid evaporation of solvent during the atomized stage permits formulation and spray application of coatings that level well yet do not sag on vertical surfaces. By adjusting the combination of solvents to the particle size of the droplets obtained with a particular spray gun and the distance between the spray gun and the object being sprayed, the viscosity of the coating arriving at the surface can be adjusted to stay low enough to permit leveling, yet increase rapidly enough to avoid, or at least minimize, sagging. The control of sagging and leveling is also affected by film thickness. Because a thin film has a higher surface area to volume ratio than a thicker film, the concentration of solvent left in a thin film decreases more rapidly with time than the concentration in a thick film. The variations in solvent evaporation are so dependent on the particular application conditions that tables of relative evaporation rate are only useful as general guidelines. Final adjustment of solvent selection must be done under actual field conditions.

The loss of solvent during spray application of high solids coatings is usually less than that from conventional lower solids coatings. As a result, it is difficult to control sagging during spray application of many high solids coatings. The lower rate of solvent loss has not been fully explained. Because of the lower molecular weight and higher concentrations of resins in high solids coatings, the ratio of numbers of solvent molecules to resin molecules is lower than in lower solids coatings. Hence, vapor pressure depression is greater in the case of high solids coatings. However, this difference would not seem to be large enough to account for the very large differences in solvent losses that have been reported. Another factor may be that high solids coatings may reach a stage where solvent loss is controlled by diffusion rate much earlier than is the case in low solids coatings.

Toxic hazards, environmental considerations, flammability, odor, surface tension, and viscosity also affect solvent selection. In high solids coatings, the effect of solvent choice on viscosity can be critical. Because the resins used in high solids coatings tend to have polar functional groups, it is usually desirable to use hydrogen bond acceptor solvents so as to minimize hydrogen bonding between resin molecules, which tends to increase viscosity. Because VOC emission regulations are based on mass of solvent per unit volume of coating, it is important to take solvent density into consideration in comparing the effect of solvent selection on viscosity and choice of solvents.

10. Color and Appearance

Color and the related property of gloss are important to the decorative and, sometimes, functional aspects of coatings. Discusssion of the interrelationships between the three major variables, the object, the light, and the observer, that affect color is beyond the scope of this article. See (86) and the references cited therein for a broad discussion. The discussion of color here is limited to color matching.

10.1. Color Matching.

Most pigmented coatings must be color matched to a standard. Poor color matching is a common source of customer complaints and problems and costs can be minimized if established specifications for the initial color match and for judging the acceptability of production batches are made. Acceptance of a color recommendation made by the coatings supplier effectively eliminates the time and cost involved in an initial color match and ensures selection of a pigment combination appropriate to the coating use. If, however, a coatings user provides a sample or standard for a color match, formulators need the following information.

1. *Possibility of a Spectral (Nonmetameric) Match*. Only if exactly the same pigments, including white and black if needed, can be used in establishing the new coating as were used in the customer's sample, can the fraction of light absorbed at each wavelength be identical to the sample. Although a color can usually be matched under one light source using different pigment combinations, it is only possible to match the color under all light sources if chemical compositions are identical. If this is not possible, the user must accept a metameric match; ie, the colors match under some light source but not under others. For example, if the coatings user has been using a coating that has lead-containing pigments and wishes to have a lead-free paint, only a metameric match is possible.
2. *Light Sources*. If the match is to be metameric, the coatings user and the supplier must agree on the light source(s) under which the color is to be evaluated. Furthermore, a decision should be made whether it is more desirable to have a close match under one light source without regard to how far off that match might be under other light sources, or to have only a fair match under several light sources.

3. *Gloss and Texture.* The color of a coating depends in part on gloss and surface texture. The light reaching the eye of an observer has been reflected both from the inside and the surface of the coating film. The light from within the film is "colored light", whereas the light reflected from the surface of the film is "white light". The color seen by the observer varies with the ratio of light from within and that from the surface of the film. At most angles of viewing, more light is reflected from a low gloss surface than from a high gloss surface. Therefore, at most angles of viewing, a low gloss coating having exactly the same colorant combination as a high gloss coating has a lighter color than the high gloss coating. It is impossible to match the colors of high gloss and low gloss coatings at all angles of viewing. Therefore, there must be agreement as to the gloss, and if the gloss of the color standard is different from the gloss desired for the new coating, the angles of illumination and viewing must be agreed upon. It is not possible to make even a metameric match of the color of some fabric samples with a coating under all angles of viewing because the colorants as well as the surface texture must be different. Claims to the contrary are misleading.
4. *Color Properties Required.* Colorants must be chosen that can meet performance requirements such as exterior durability and resistance to solvents, chemicals, and heat. Health and safety regulations may also affect colorant choice.
5. *Film Thickness and Substrate.* In most cases, a coating does not completely hide the substrate, and the color of the substrate affects the color of the applied coating. The extent of substrate effect depends on film thickness and is particularly important in applications such as can and coil coatings that are commonly <25 μm thick. A thin coating where the color was established over a gray primer does not match a standard applied over a red primer; a coating designed for a one-coat application on aluminum does not match the color standard when applied on steel.
6. *Baking Schedule.* Because resin color can be affected by heating, the color of the coating is affected by the time and temperature of baking, and the baking schedule must be specified. Color requirements for overbaking must also be established.
7. *Cost.* The color matcher should know any cost limitations. An important element affecting cost is the tolerance limits permitted in production.
8. *Tolerances.* The closeness of the color match required is important. In some cases, such as coatings for exterior siding or automotive topcoats, very close matches are required. In many other applications, users set tight tolerance limits even if they are not needed. Overly tight tolerance requirements raise costs without performance benefits. For coatings that are produced over time and have many repeat batches, the most appropriate way to set tolerances is by a series of limit panels. For example, for a deep yellow coating, the greenness and redness limits and limits of brightness and darkness are needed. Because colors may change on aging, spectrophotometric measurements need to be made of both the standard and limit panels, and Commission Internationale d'Eclairage (CIE) tristimulus values

> should be calculated. Any coating giving a color that fell within this color space should acceptable. Attempts have been made to assign numerical values to color differences permitting specifications that would give a numerical definition of the allowable tolerance in a single number. This objective has not been attained, although progress has been made in developing equations that permit calculation of color difference numbers ΔE in which the scale is equal for all colors. The use of ΔE specifications is not desirable except for single colors, because a ΔE value of 1 is a tighter specification for some part of the color range than for other parts, even with 1976 CIE color difference equations. Furthermore, ΔE color difference specifications permit variation around the standard equally in any direction. In practice, coatings users are more concerned about color variation in one specific direction. For example, whites that are too blue are more acceptable, in general, than whites that are too yellow.

Once the laboratory establishes a color match, the factory should match the color in spite of the fact that batch-to-batch color variations are to be expected in the pigments as manufactured. Whenever possible, the color match should be made using at least four colorants, including black and/or white, if they are needed. Four colorants give the four degrees of freedom necessary to move in any direction in three-dimensional color space. Sometimes this is not possible. For example, because the type of color mixing involved in using mixtures of pigments is subtractive color mixing, if a bright color is desired that can be made only from a single pigment, eg, phthalocyanine green, there is no pigment available that could make a batch of phthalocyanine green that was grayer than the standard less gray. A large fraction of color matching, particularly when repeated production batches are made of the same color, is now performed using instrumental measurements and color matching computer programs.

Metallic colors for automotive topcoats are an example of critical formulation and color matching problems. These colors owe their popularity to the “color flop” as the viewing angle is changed. The change is in the opposite direction and larger than is the case when viewing ordinary high gloss coatings. The depth of the color is light when viewed from near normal, ie, perpendicular to the surface (face color), and darker when viewed from a wide angle from normal (flop color). A high degree of flop, ie, a large color change with a change in viewing angle, requires that three conditions be met: the gloss of the coatings must be high, the coating matrix in which the aluminum pigment is suspended must be essentially transparent, and the nonleafing aluminum pigment used must be oriented parallel or nearly parallel to the surface of the film. In order to have a transparent matrix, the pigment-free dry film must be completely transparent and the color pigment selection and dispersion must be such that there is no light scattering from the pigment. The aluminum pigment is oriented in the film as it is forming by film shrinkage because of evaporation of volatiles in the applied coating. The upper layers of the film increase in viscosity more rapidly than the lower layers. The extent of shrinkage and, hence, the degree of orientation decreases as the solids of the coating increase. The highest degree of orientation has been achieved for lacquers having volume solids on the order of 10%. Similar results were obtained using water-reducible acrylic coatings applied at ~18% volume solids. Conventional thermosetting acrylic enamels having a volume solids >30% give noticeably less flop. About 45% volume solids is the highest solids content that gives a significant degree of orientation of the aluminum pigment particles. The considerations in obtaining a pleasing appearance using the increasingly popular pearlescent pigments in automotive coatings are similar, because pearlescent pigments are flake pigments that must be oriented approximately parallel to the surface of the film.

10.2. Gloss. Gloss is a complex phenomenon. See (87) for discussion of gloss and gloss measurement; (88) is an old but useful review of gloss of coatings. People commonly think that high gloss results from high reflectance of incident light from the surface but low gloss surfaces reflect more total light than high gloss surfaces. The high gloss surface, however, reflects most of the light at the specular angle and low gloss surfaces reflect at all angles. A rough surface has many small facets oriented randomly whereas a high gloss surface is more nearly planar. Most commonly, a rough surface is obtained by incorporation of a large fraction of pigment in the formula. Lower gloss will also result from a hazy pigment free film since light is also reflected back out of the film from the incompatible areas in the film with different refractive indices. Gloss is affected by the distance between the observer and the surface. For example, a coating with a fine wrinkle will have a low gloss when observed visually but under a microscope can be seen to be a wavy high gloss surface.

No fully satisfactory method of gloss measurement is available and no satisfactory rating scale for visual gloss has been developed. All people will agree as to which film is glossier if the differences are large but frequently disagree in ranking if the differences are small. Widely used gloss meters are limited because the reflection is only measured at the specular angle, the distance from the surface to the light meter is fixed. Furthermore, color affect the reflectance, dark colors absorb more light and therefore reflect less than light colors. To partially overcome this problem meters can be calibrated with white and black standards. Jet black gloss coatings reflect primarily at the specular angle because light is reflected only from the surface whereas in a white coating light is reflected from the surface but there is also diffuse reflectance from the white pigment in the coating. Colors of intermediated depths give intermediate reflectance results. The standards for the measurement are standardized with a sophisticated goniophotometer at NISH (89).

Distinctness-of-image gloss meters are more reliable for high gloss surfaces. The film is used as a mirror and distortion and blurring the image is compared to that of a mirror. New instruments are now available to measure reflectance at small angle increments without using an aperture in front of the detector (90). This permits separation of reflection from micro- and macroroughness giving a separate rating for gloss and the effect of surface variations such as orange peel or texture.

11. Pigments

Pigments in coatings provide opacity and color. Pigment content governs the gloss of the final films and can have important effects on mechanical properties.

Some pigments inhibit corrosion. Pigmentation affects the viscosity, and hence the application properties of coatings. Pigment manufacturing processes are designed to afford the particle size and particle size distribution that provide the best compromise of properties for that pigment. In the process of drying the pigment, the particles generally aggregate. The coatings manufacturer must disperse these dry pigment aggregates in such a way as to achieve a stable dispersion where most, if not all, of the pigment is present as individual particles. An excellent treatise on the chemistry, properties, and uses of pigments is available (91).

Pigments can be divided into four broad classes: white, color, inert, and functional pigments. The ideal white pigment, when dispersed in the coating, would absorb no visible light and would efficiently scatter light entering the film. Scattering leads to reflection of diffuse light back out of the film. The opacity of the film increases as light scattering increases. Light scattering increases rapidly as the difference in refractive index between the pigment particles and the binder increases. Light scattering is also affected by the particle size of the pigment and its concentration. Efficient scattering of light permits hiding the substrate under a film of coating by the thinnest film. Hiding is also increased by light absorption.

Because of its high refractive index and relatively low absorption of light, rutile TiO_2 [1317-80-2], a form of titanium dioxideTiO_2, [13463-67-7], is the most widely used white pigment. The optimum particle size of rutile TiO_2 for scattering visible light is 0.19 μm at 560 nm. Because light scattering drops off faster on the lower side of the optimum than on the higher side, commercial rutile TiO_2 is made with an average particle size of 0.22–0.25 μm. If aggregates of TiO_2 particles are not separated and stabilized as a dispersion of individual particles, light scattering is low. In the case of rutile TiO_2, hiding increases linearly with concentration in a dry coating film until the PVC exceeds $\sim$10%. For a further increase in concentration, hiding increases less than proportionally. Finally, above $\sim$22% PVC, hiding actually decreases because of less light scattering. Whereas the exact pigment content is system dependent, the most cost-efficient level of pigmentation using TiO_2 for white coatings is $\sim$18%. Another crystal type of TiO_2, anatase [1317-70-0], is available; it absorbs even less visible light than rutile, and hence gives whiter films but has a lower refractive index so that it does not scatter light as efficiently. Titanium dioxide can promote the photodegradation of coatings on exterior exposure, leading to erosion of binder from the surface exposing loose pigment particles. This phenomenon is called chalking. Surface treatment using alumina and silica gives pigments that lead to minimal chalking.

Small air bubbles also scatter light because the refractive index of air is $\sim$1.0, whereas the refractive index of most polymers is $\sim$1.5. Air bubbles in films are sometimes useful in increasing opacity but the efficiency in scattering light is much less than for rutile TiO_2.

Color pigments selectively absorb some wavelengths of light more strongly than others. A wide variety of color pigments are used in coatings. The selection of pigments for a coating formulation is based among other factors on color, cost, transparency or opacity, durability, and resistance to heat, chemicals, and bleeding, ie, solubility in solvents. In contrast to white pigments, where there is an optimum particle size for scattering, in the case of color pigments, smaller particle size leads to stronger light absorption. However, other properties are commonly adversely affected if the particle size is too small. For example, exterior durability commonly decreases and solubility increases as particle size is decreased. Pigments are produced having average particle sizes that provide the best compromise of color strength and other properties.

Aluminum-flake pigments are used. There are two important classes: leafing and nonleafing aluminum pigments. Leafing aluminum pigments are surface treated so that when a coating is applied, the platelets come to the surface of the drying film, resulting in a barrier to permeation of water and oxygen and giving high light reflectance so that the appearance approaches that of aluminum metal. The nonleafing grade does not behave in this manner but tends to orient within the film parallel to the surface.

Inert pigments, also called extenders and fillers, do not exhibit significant absorption or scattering of light when incorporated into coatings. In most cases, inert pigments are used to occupy volume in the coating composition. The viscosity and flow properties of coatings can be substantially affected by increasing the volume of pigments dispersed in a coating. Many properties of the dried film depend on the pigment volume concentration in the film. Although such effects could be obtained using higher volumes of white and color pigments than needed for opacity and color, the volume effects can generally be obtained by using less expensive inert pigment and just sufficient white and color pigments required for the opacity and color. A wide variety of clays, silica, and carbonates are used as inert pigments.

The most widely used functional pigments are the corrosion-control pigments. These pigments inhibit the corrosion of steel.

11.1. Pigment Dispersion. The dispersion of pigments involves wetting, separation, and stabilization. Wetting, ie, displacement of air and water from the surface of the pigment by the vehicle, requires that the surface tension of the dispersion medium be lower than that of the pigment surface. Except when the vehicle is water, wetting is rarely a problem. Wetting agents are required for dispersion of low polarity surface pigments such as organics, in water, and occasionally for dispersion of pigments in organic media. The rate of wetting of pigment is fastest when the viscosity of the vehicle is low.

Pigment aggregates are separated into individual particles by a variety of dispersion equipment (24), which transmit shear stress of sufficient magnitude to break up the aggregates. If little force is required, low viscosity dispersions can be made using equipment that provides low shear stresses. The most widely used equipment of this type is a high speed impeller in a tank. Pigments where the aggregates are not easily separated require equipment that exerts a higher shear stress on the aggregates, such as ball mills, sand mills, shot mills, attritor mills, extruders, and others. For pigment aggregates that are even more difficult to separate, equipment imparting even higher shear stress is needed, eg, dough mixers and two-roll mills. Because this last type of equipment is expensive and labor costs are high, use is limited to the preparation of dispersions from expensive pigments where ultimate color strength is important. This class of dispersion equipment is especially useful when the aggregates must be reduced to the ultimate particle size in order to minimize light scattering, such as in transparent pigment dispersions for use in metallic coatings for automobiles.

Stabilization of the pigment dispersion is usually the most critical aspect of the process. If the dispersion is not fully stabilized, the separated pigment particles flocculate, ie, reagglomerate. Although flocculates are easily separated again by low shear stresses, flocculated dispersions are not desirable because the hiding and color strength are lower, reflecting the larger effective particle size of the flocculates in the film. Flocculation of the pigment in gloss coatings generally leads to reduction in gloss. Furthermore, at low shear rates the viscosity of flocculated systems is much higher than that of nonflocculated systems.

Pigment dispersions are stabilized by charge repulsion and entropic repulsion. Although both types of stabilization force may be present in most cases, for pigment dispersions in solvent-borne coatings entropic repulsion is usually the most important mechanism for stabilization. In solvent-borne coatings, entropic stabilization can generally be achieved by adsorption of resin on the pigment surfaces. The adsorbed layer of resin swells with solvent. It has been shown for a wide variety of pigments and binders, that a stable dispersion is obtained if the thickness of the adsorbed layer is at least 8–10 nm. If the thickness is less, flocculation occurs (92). The reduction in entropy involved in the compression of an adsorbed layer having an average layer thickness >10 nm requires a force greater than that imparted by the Brownian motion of the pigment particles. The principal factors controlling adsorbed layer thickness are molecular weight of the resin and the presence of multiple, but limited numbers of adsorbable groups scattered along the resin chain.

Solvent selection can sometimes affect the stability of a pigment dispersion. A change in solvent may swell the adsorbed layer further and promote stabilization. On the other hand, some solvents might be so strongly adsorbed on the pigment surface that the resin could not successfully compete with it despite having multiple interaction sites. Such a system would not lead to a stable dispersion because the adsorbed layer thickness of a solvent layer is <1 nm. Most conventional coatings are stabilized using the same resin system that has been selected for the coating binder. In some cases, a related resin having more functional groups or higher molecular weight has to be designed.

However, in high solids coatings, low molecular weight resins having a limited number of functional groups must be used, leading to thinner adsorbed layers.Therefore, flocculation is a more common problem than for conventional coatings. Dispersing agents have been designed having a low molecular weight, so there is a minimum effect on viscosity while stabilizing the dispersions. They have multiple functional groups are absorbed more strongly than conventional surfactants. Reference (93) discusses the design parameters for such dispersants.

Experimental determination of adsorbed layer thickness requires a laboratory effort appropriate for research studies but not for day-to-day formulation development. The Daniels flow point method (24) is a simple procedure that permits determination of whether a resin–solvent–pigment combination can give a stable dispersion and, if so, approximately what concentration of resin in the solvent is required to prevent flocculation. The procedure permits use of the lowest possible viscosity vehicle for pigment dispersion. This permits more rapid wetting by the vehicle and also permits higher pigment loading at the same viscosity. The most expensive equipment in a coatings factory is the dispersion equipment. Therefore, it is desirable to disperse as high a volume of pigment per unit time as possible.

Determination of the extent of dispersion is not a simple task. Color strength of colored pigment dispersions and scattering efficiency of white pigment dispersions are determined by comparing the tinting strength to a standard. Flocculation can be detected by color changes on application of low shear stress, rapid settling, or centrifugation to a bulky sediment, and by the presence of shear thinning flow. A steel bar having a tapered groove called a Hegman gauge is widely used for testing the degree of dispersion. A sample is placed in front of the deep end of the groove and the dispersion is drawn down to see at what gauge reading particles can be detected. The scale is 0–8 for a groove depth varying from 100 μm to 0 μm. The diameter of most white and color pigments is <1 μm. The procedure is of little practical value because it detects only the presence of relatively large-size aggregates and does not give any indication of whether most particles are present in their ultimate particle size. Furthermore, the Hegman gauge cannot detect the presence of flocculation. For research purposes, the most accurate technique available for quantifying pigment dispersion is infrared back scattering (94).

Dispersion of pigments for latex paints is the principal application of aqueous dispersions. Commonly, three surfactants are used in preparing the dispersion of the white and inert pigments: potassium tripolyphosphate, an anionic surfactant, and a nonionic surfactant. The final colored latex paint formulations, which are very complex, commonly contain seven pigments, some having high surface energies (inorganic pigments) and some having low surface energies (organic pigments). The latex polymer is present as a dispersion that must be stabilized against coalescence and flocculation, and latexes themselves commonly contain two or more surfactants and a water-soluble polymer. Generally, but not always, the latex particles have a low surface tension. Complexity is increased by the use of at least one and sometimes two water-soluble polymers in the latex paint formula that can adsorb on the surface of some of the pigment particles and the latex particles. Although wetting inorganic pigments with water usually presents no problem, many organic pigments require a wetting agent to displace the air from the surface of the pigment particles. All dispersions must be stabilized against flocculation. The appropriate surfactants, wetting agents, and water-soluble polymers are selected largely by trial and error. Accumulation of data banks of successful and unsuccessful combinations provides a valuable tool for more efficient formulation.

11.2. Pigment Volume Relationships. Pigmentation can have profound effects on the properties of coating films depending on the level of pigmentation of these films (95). Variations in these effects are best interpreted in terms of volume relationships rather than weight relationships. Pigment volume concentration is defined as the volume of pigment in a dry film divided by the total volume of the dry film, commonly expressed as a percentage.

As the volume of pigment in a series of formulations is increased, properties change, and at some PVC there is a fairly drastic change in a series of properties.

This PVC is defined as the critical pigment volume concentration (CPVC) for that system. The CPVC is the maximum PVC that can be present in a dry film of that system, having sufficient solvent-free resin to adsorb on all the pigment surfaces and fill all the interstices between the pigment particles. In other words, when the PVC is above the CPVC, there are voids in the film. Gloss decreases as PVC increases. Hiding generally increases as PVC increases but above CPVC there is a rapid increase in the rate of increase of hiding because of the presence of voids. In the unique case of rutile TiO_2, hiding passes through a maximum at $\sim$22%. If the PVC of rutile pigmented coatings were increased above CPVC, the hiding would again start to increase rapidly. Tinting strength of white paints increases rapidly above CPVC. Tensile strength of films increases with increasing PVC, passing through a maximum at CPVC. Stain resistance is poorer and the ease of removing stains becomes more difficult for coatings above CPVC. Blistering of films on wood is less likely to occur above CPVC. The intercoat adhesion to a primer is improved when the primer has a PVC $>$ CPVC.

CPVC depends on the pigment and pigment combinations. Pigment density is an important variable in comparing weight data with volume data. The CPVC of dense pigments tends to be lower than might be expected looking at weight data. The CPVC is lower for smaller particle size pigments, because these have a higher volume proportion of adsorbed resin than larger particle size pigments. Broad particle size distribution systems pack more efficiently and have higher CPVC values. Flocculation results in lower CPVC in a dry film as compared to the same pigment combination having a well-stabilized dispersion. Each coating application has a PVC/CPVC ratio that provides the best compromise of properties for the use involved. By determining the appropriate PVC/CPVC ratio for some application, this ratio can be used as a starting point for formulation of other pigment combinations for that application.

Experimental determination of CPVC is time consuming. A reasonable approximation can be obtained by determining the pigment loading that gives a viscosity approaching infinity in a 100% solids system, such as linseed oil with a pigment or combination of pigments. When expressed as grams of linseed oil required per 100 g of pigment, this infinite viscosity value is called the oil absorption of the pigment. Oil absorption values can be converted to CPVC values using the densities of the pigment(s) and the oil. Because different pigments have different particle size distributions, mixtures give CPVC values that are higher than the average based on the CPVC values of the individual pigments. Equations have been developed to calculate CPVC of pigment mixtures from a combination of oil absorption values and particle size distributions of the individual pigments (96). Even if CPVC data are not available, a formulator can still make use of the concept by thinking in terms of volume rather than weight relationships. Volume relationships are particularly useful in maximizing the volume of inert pigment that can be used in a coating, which in turn minimizes cost while retaining the required physical properties.

Application of CPVC concepts to latex paints is controversial. Reference (97) provides a review of the literature. However, most workers agree that for a particular pigment combination the CPVC of a latex paint is always lower than that for the same pigment combination in a solution-based paint (98). This may result from the alignment of pigment and latex particles as the water evaporates in forming a film. Latexes of low T_g and small particle size give coatings having higher CPVCs than when higher T_g and/or larger particle size latexes are used. The addition of a coalescing agent to the formula tends to increase CPVC. To reduce cost of low gloss latex paints, the formula having the highest possible CPVC permits the incorporation of the largest volumes of low cost inert pigments.

12. Application Methods

Many methods are used to apply coatings. Many factors affect the choice of method: capital and operating costs, film thickness, appearance requirements, the structure of the object being coated, and VOC emissions. Reference (99) gives a review. Brushes and hand rollers are widely used for architectural coatings by do-it-yourselfers. Spray application is used for some architectural coatings but particularly for irregularly shaped industrial products. Several types of spray systems are used. Hand-held air spray guns are the least expensive and are most often used for objects not made on an assembly line. They are low cost but the transfer efficiency (fraction of the coating applied that goes on to the object) is low. Newer high volme, low pressure (HVLP) guns give much higher transfer efficiency and are increasingly required for refinishing automobiles to reduce VOC emissions. Airless spray systems cost more but apply coatings more rapidly and permit spraying into closed recesses. Electrostatic spray systems have higher transfer efficiencies and better wrap-around at a higher cost. There are two broad types of the spray systems: spray guns and spinning bells. Spray guns can be hand held or robot held. Bell systems are generally fixed or robot systems. The trend is to higher speed bells because they permit spraying higher viscosity coatings, hence reducing VOC emissions. Hot spray systems are also used to reduce VOC emissions. The coating is heated to 65°C, permitting a roughly 50% reduction in VOC emissions. The newest approach is supercritical fluid spraying (100). Supercritical liquid CO_2 is a solvent roughly comparable to xylene and is used to replace part of the solvent for spraying with airless guns. VOC emission reductions of 30–90% have been reported.

Dip coating gives very high transfer efficiency and complete coverage of all surfaces including those inaccessible to spraying and has a high capital cost but a very low operating cost. Film thicknesses at the top of the object are lower than at the bottom. Coatings must be very stable. The method is only applicable to long runs of the same coating. Waterborne coatings are desirable to reduce VOC and flammability. Flow coating is a variation in which the coating is squirted on the object and the excess is recirculated. Production line speeds can be higher and loss of solvent in minimized. This increases coating turnover reducing stability requirements and inventory cost. A related method is curtain coating. Coating is run through a slot while flat sheets are run under the slot and excess coating is recirculated. Film thickness is controlled by the rate of movement of the sheets under the slot. Capital cost is high but operating cost is low. Leveling is superior to that obtainable with roller coating.

Roll coating is also widely used for flat objects. There are two types: direct roll coating and reverse roll coating. Direct coating is applicable to sheets and reverse roll coating is applicable to continuous webs. Reverse roll coating is desirable where applicable since it gives superior leveling. The largest single use is for applying coil coatings.

13. Film Defects

Many kinds of defects can develop in a film during or after application. Reference (101) is a monograph about film defects.

13.1. Leveling.

The most widely studied leveling problem has been leveling of brush marks. One proposal is that the driving force for leveling is surface tension (102). The formulator has little control over the variables except viscosity. This model provides satisfactory correlation between experimental data and predictions when the liquid film has Newtonian flow properties and sufficiently low volatility such that viscosity does not change. In most cases, viscosity changes due to solvent evaporation and the equation is not applicable. It has also been proposed that the surface tension differential is the major driving force for leveling in coatings with volatile solvents (103). Wet film thickness in valleys of brush marks is less than in the ridges; when the same amount of solvent evaporates per unit area of surface, the fraction of solvent that evaporates in the valleys is larger than in the ridges. As a result, the surface tension in the valleys is higher than on the ridges and surface tension differential flow drives coating from the ridges into the valleys. The extent of the flow driven by surface tension differential depends on the rate of evaporation of the solvent.

In spray application, surface roughness is called orange peel, which consists of bumps surrounded by valleys. Orange peel is encountered when spraying coatings that have solvents with high evaporation rates. Leveling of sprayed films can often be improved by addition of small amounts of silicone fluid that reduces surface tension. When one sprays a coating, initially the surface is fairly smooth then orange peel grows. The growth of orange peel results from a surface tension differential driven flow. The last atomized spray particles to arrive on the wet coating surface have traveled for a longer distance between the spray gun and the surface; hence, have lost more solvent, have a higher resin concentration and, therefore, a higher surface tension than the main bulk of the wet film. The lower surface tension wet coating flows up the sides of these last particles to minimize overall surface free energy. With the silicone fluid, the surface tension of the wet coating surface and the surface tension of the last atomized particles are uniformly low, there is no differential to promote growth of orange peel.

Electrostatically sprayed coatings are likely to show surface roughness. It has been suggested that the greater surface roughness results from arrival of the last charged particles on a coated surface that is quite well electrically insulated from the ground. These later arrivals may retain their charges sufficiently long to repel each other and thereby reduce the opportunity for leveling. It has also been suggested that when coatings are applied by high-speed bell electrostatic spray guns, differentials in the pigment concentration within the spray droplets may result from the centrifugal forces (104). These pigment concentration differences lead to rougher surfaces and reduction in gloss of the final films.

Leveling problems are particularly severe with latex paints. Latex paints, in general, exhibit shear thinning and rapid recovery of viscosity after exposure to high shear rates. Due to their higher dispersed phase content, the viscosity of latex paints changes more rapidly with loss of volatile materials than the viscosity of solventborne paints. The leveling is primarily surface tension driven, since surfactants give low surface tension to latex paints that is almost unchanged as water evaporates.

13.2. Sagging. When a wet coating is applied to a vertical surface, gravity causes it to flow downward (sagging). Sagging increases with increasing film thickness and decreases with increasing viscosity. The commonly used test is a sag-index blade. A drawdown, which is a series of stripes of coating of various thickness, is made on a chart and placed in a vertical position. Sag resistance is rated by observing the thickest stripe that does not sag down to the next stripe. For research purposes, a sag balance gives more quantitative information (105).

In spray applied solvent solution coatings, sagging can generally be minimized while achieving adequate leveling by a combination of proper use of the spray gun and control of the rate of evaporation of solvents. Sagging of high solids solvent borne coatings is more difficult to control than with conventional solids coatings. While other factors may be involved, less solvent evaporates while atomized droplets are traveling between a spray gun and the object being coated (106). A factor is the colligative effect of the lower mole fractions of solvent(s) in a high solids coatings. While this effect slows solvent evaporation from a high solids coating, it is not large enough to account for the large differences in solvent loss that have been reported. High solids coatings may undergo transition from first to second-stage solvent loss with relatively little solvent loss as compared to conventional coatings (107). High solids polyesters are formulated at concentrations above the transition concentration where solvent loss rate becomes diffusion controlled (108). Also the transition points occur at higher solids with linear molecules such as *n*-octane [111-65-9] versus isooctane (2,2,4-trimethylpentane) [540-84-1], and *n*-butyl acetate [123-86-4] as compared to isobutyl acetate. It is necessary to make the systems thixotropic. For example, dispersions of fine particle size silicon dioxide, precipitated silicon dioxide, bentonite clay treated with a quaternary ammonium compound, or polyamide gels can be added to impart thixotropy. The problem of sagging in high solids automotive metallic coatings can be particularly severe. Even a small degree of sagging is very evident in a metallic coating, since it affects the orientation of the metal flakes. Use of SiO_2 to impart thixotropy is undesirable, since even the low scattering efficiency of SiO_2 is enough to reduce color flop in the coatings. Acrylic microgels have been developed that impart thixotropic flow using the swollen gel particles. Reference (109) discusses the rheological properties of the systems. In the final film, the index of refraction of the polymer from the microgel is nearly identical with that of the cross-linked acrylic binder polymer so that light scattering does not interfere with color flop.

Hot spraying helps control sagging. The coating cools on striking the object and the viscosity increase reduces sagging. Use of carbon dioxide under supercritical conditions is helpful in controlling sagging, since the CO_2 flashes off almost instantaneously when the coating leaves the orifice of the spray gun increasing viscosity. High-speed electrostatic bell application permits application of coatings at higher viscosity, which helps control sagging.

13.3. Crawling, Cratering, and Related Defects. If a coating is applied to a substrate that has a lower surface free energy, the coating will not wet the substrate. The mechanical forces involved in application spread the coating on the substrate surface, but since the surface is not wetted, surface tension forces tend to draw the liquid coating toward a spherical shape. Meanwhile, solvent is evaporating, and viscosity is increasing and flow stops resulting in uneven film thickness with areas having little, if any, coating adjoining areas of excessive film thickness. This behavior is called crawling. Crawling can result from applying a coating to steel with oil contamination on the surface. It is especially common in coating plastics. Crawling can also result from the presence in the coating of surfactant-type molecules that can orient rapidly on a highly polar substrate surface. Even though the surface tension of the coating is lower than the surface free energy of the substrate, it could be higher than the surface free energy of the substrate after a surfactant in the coating orients on the substrate surface. If one adds excess silicone fluid to a coating to correct a problem like orange peel, small droplets of insoluble fractions of the poly(dimethylsiloxane) can migrate to the substrate surface and spread on it, and the film crawls. Modified silicone fluids, such as polysiloxane–polyether block copolymers, have been developed that are compatible with a wider variety of coatings and are less likely to cause undesirable side effects. The effect of a series of additives on crawling and other film defects has been reported (110).

Cratering is the appearance of small round defects that look somewhat like volcanic craters on the surface of coatings. Cratering results from a small particle or droplet of low surface tension contaminant landing on the wet surface of a freshly applied film. Some of the low surface tension material dissolves in the adjacent film, creating a localized surface tension differential. This low surface tension part of the film flows away from the particle to cover the surrounding higher surface tension liquid coating. Loss of solvent increases viscosity, leading to formation of a characteristic crest around the pit of the crater. The user applying the coating should minimize the probability of low surface tension contaminants arriving on the wet coating surface. Spraying lubricating oils or silicone fluids on or near the conveyor causes craters. Presence of some contaminating particles cannot be avoided; so coatings must be designed to minimize the probability of cratering. Lower surface tension coatings are less likely to form craters. Alkyd coatings have low surface tensions and seldom give cratering problems. In general, polyester coatings are more likely to give cratering problems than acrylic coatings. Additives can be used to minimize cratering. Small amounts of silicone fluid generally eliminate cratering, excess silicone must be avoided. Octyl acrylate copolymer additives usually reduce cratering. A comparison of effects of additives on the control of defects such as cratering is available (111).

In roll coating tin plate sheets, the coated sheets are passed on to warm wickets that carry the sheets through an oven. In some cases, one can see a pattern of the wicket as a thin area on the final coated sheet. The heat transfer to the sheet is fastest where it is leaning against the metal wicket. The surface tension of the liquid coating on the opposite side drops locally because of the higher temperature. This lower surface tension material flows toward the higher surface tension surrounding coating. In spraying flat sheets as solvent evaporates, the coating is thickest at the edges and just in from the edge the coating is thinner than average. Solvent evaporates most rapidly from the coating near the edge, where the air flow is greatest. This leads to an increase in resin concentration at the edge and to a lower temperature. Both factors increase the surface tension there, causing the lower surface tension coating adjacent to the edge to flow out to the edge to cover the higher surface tension coating. Surface tension differential driven flow can also result when overspray from spraying a coating lands on the wet surface of a different coating. If the overspray has lower surface tension than the wet surface, cratering occurs. If the overspray has high surface tension compared to the wet film, local orange peeling results.

When coatings are applied on plastic sheets that are adhered to steel supports in an automobile, surface tension driven flow leads to defects at the boundary line above the steel supports called bondline readout (BLRO). A study has been published reporting an investigation of parameters affecting BLRO (112).

13.4. Floating and Flooding. Floating is most evident in coatings pigmented with two pigments. A light blue gloss enamel panel can show a mottled pattern of darker blue lines on a lighter blue background. With a different light blue coating, the color pattern might be reversed. These effects result from pigment segregations that occur as a result of convection current flows driven by surface tension differentials while a film is drying. Rapid loss of solvent from a film during drying leads to considerable turbulence. Convection patterns are established whereby coating material flows up from lower layers of the film and circulates back down into the film. The flow patterns are roughly circular, but as they expand, they encounter other flow patterns and the convection currents are compressed. As solvent evaporation continues, viscosity increases and it becomes more difficult for the pigment particles to move. The smallest particle size, lowest density particles continue moving longest; the segregated pattern of floating results. Floating is particularly likely to occur if one pigment is flocculated and the other is a nonflocculated dispersion of fine particle size. If, in a light blue coating, the white pigment is flocculated and the blue is not, one will find darker blue lines on a lighter blue background. If the blue one is flocculated and not the white, there will be lighter blue lines on a darker blue background. Floating can occur without flocculation using of a combination of pigments with very different particle sizes and densities. When a fine particle size carbon black and TiO_2 are used to make a gray coating; the particle size of the TiO_2 is several times that of the carbon black and TiO_2 has about a fourfold higher density. A larger particle size black, such as lamp black, can be used to make a gray with a lower probability of floating. As with other flow phenomena driven by surface tension differentials, floating can be prevented by adding a small amount of a silicone fluid.

In flooding, the color of the surface is uniform but different than should have been obtained from the pigment combination used. One might have a uniform gray coating, but a darker gray than that expected from the ratio of black-to-white pigments. The extent of flooding can vary with the conditions encountered during application, leading to different colors on articles coated with the same coating. Flooding results from surface enrichment by one or more of the pigments in the coating. The stratification is thought to occur as a result of different rates of pigment settling within the film, which are caused by differences in pigment density and size or flocculation of one of the pigments. Flooding is accentuated by thick films, low vehicle viscosity, and low evaporation rate solvents. The remedies are to avoid flocculation and low density fine particle size pigments.

13.5. Wrinkling. A wrinkled coating shrivels or wrinkles into many small hills and valleys. Some wrinkle patterns are so fine that to the unaided eye, the film appears to have low gloss rather than to look wrinkled. However, under magnification, the surface can be seen to be glossy but wrinkled. In other cases, the wrinkle patterns are broad or bold and are readily visible. Wrinkling results when the surface of a film becomes high in viscosity while the bottom of the film is still relatively fluid. It can result from rapid solvent loss from the surface, followed by later solvent loss from the lower layers. It can also result from more rapid cross-linking at the surface of the film than in the lower layers of the film. Subsequent solvent loss or cure in the lower layers results in shrinkage, which pulls the surface layer into a wrinkled pattern. Wrinkling is more apt to occur with thick films than with thin films because the possibility of different reaction rates and differential solvent loss within the film increases with thickness.

Wrinkling can occur in uv curing of pigmented acrylate coatings with free-radical photoinitiators. High concentrations of photoinitiator are required to compete with absorption by the pigment. Penetration of uv through the film is reduced by absorption by the pigment as well as by the photoinitiator. There is rapid cross-linking at the surface and slower cross-linking in the lower layers of the film, resulting in wrinkling. The uv curing of pigmented cationic coatings, which are not air inhibited, is even more prone to surface wrinkling.

13.6. Popping. Popping is the formation of broken bubbles at the surface of a film that do not flow out. Popping results from rapid loss of solvent at the surface of a film during initial flash off. When the coated object is put into an oven, solvent volatilizes in the lower layers of the film, creating bubbles that do not readily pass through the high viscosity surface. As the temperature increases further, the bubbles expand, finally bursting through the top layer resulting in popping. The viscosity of the film meanwhile has increased enough so that the coating cannot flow together to heal the eruption. Popping can also result from entrapment of air bubbles in a coating. Popping can result from solvent that remains in primer coats when the topcoat is applied. In coating plastics, solvents can dissolve in the plastic, and then cause popping when a coating is applied over the plastic and then baked. Another potential cause of popping is evolution of volatile by-products of cross-linking.

Popping can be minimized by spraying more slowly in more passes, by longer flash-off times before the object is put into the oven, and by zoning the oven so that the first stages are relatively low in temperature. The probability of popping can also be reduced by having a slow evaporating, good solvent in the solvent mixture. This tends to keep the surface viscosity low enough for bubbles to pass through and heal before the viscosity at the surface becomes too high. Popping can be particularly severe with water-reducible baking enamels because slow loss of water during baking, especially with high T_g resins. In contrast to increased probability of popping with higher T_g water-reducible coatings, popping is more likely to occur with lower T_g latex polymers. Coalescence of the surface before the water has completely evaporated is more likely with a lower T_g latex.

13.7. Foaming. During manufacture and application, a coating is subjected to agitation and mixing with air, creating the opportunity for foam formation. In formulating a latex paint, an important criterion in selecting surfactants and water-soluble polymers as thickeners is their effect on foam stabilization (113). Acetylene glycol surfactants such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol are reported to be effective surfactants that do not increase the viscosity of the surface of bubbles as much as surfactants such as alkylphenol ethoxylates (114).

A variety of additives can be used to break foam bubbles. Most depend on creating surface tension differential driven flow on the surface of bubbles. Silicone fluids, are effective in breaking a variety of foams, since their surface tension is low compared to almost any foam surface. Small particle size hydrophobic SiO_2 can also act as a defoamer and/or a carrier for active defoaming agents (114). Also, a small amount of immiscible hydrocarbon will often reduce foaming of an aqueous coating. Several companies sell lines of proprietary antifoam products and offer test kits with small samples of their products. The formulator evaluates the antifoam products in a coating with foaming problems to find one that overcomes the problem. While it is possible to predict which additive will break a foam in a relatively simple system, such predictions are difficult for latex paints because of the variety of components that could potentially be at the foam interface. The combination of surfactants, wetting agents, water-soluble polymers, and antifoam can be critical.

14. Product Coatings

About 30% of the total volume of coatings produced in the United States in 1999 (1.45×10^9 L) applied in factories to a very large variety of products ranging from automobiles to toys (1). They are often called original equipment market (OEM) coatings.

14.1. Coatings for Metal. A large fraction of the product coatings are applied to metal. The essential first step in metal coating is the preparation of the metal. Oil and related contaminants must be removed by detergent or solvent washing. Solvent degreasing is the most effective. In detergent washing, the last trace of detergent must be rinsed off before drying preparatory to painting. For best adhesion and corrosion resistance, the surface of the metal should be treated. For steel, phosphate conversion coating treatments are used. Aluminum, for applications when the product will not be exposed to salt, needs no treatment. Chromate conversion treatments have been used when salt exposure is possible but proprietary chromate-free treatments are now being used because of toxic hazards with chromates. The surface should be carefully rinsed before applying paint. Surface contaminants can result in crawling and/or blistering of the coating. Treated surfaces should not be touched. Water-soluble contaminants such as salts can lead to blistering after the coated product is put into service. Oils can lead to crawling of the wet coating film applied on top of the oil.

Primers. If reasonably high performance is required in the end product and unless cost is of paramount importance, a minimum of two coats, usually a primer and a topcoat, should be applied to metal. For highest performance, primer vehicles should provide good wet adhesion, be saponification resistant, and have low viscosity to permit penetration of the vehicle into microsurface irregularities in the substrate. Color, color retention, exterior durability, and other such properties are generally not important in primers. Resin systems such as those including BPA epoxy resins that provide superior wet adhesion can thus be used in spite of their poor exterior durability.

In order to provide a suitable surface for adhesion of the topcoat, the gloss of the primer should be low and the cross-link density should be as low as handling characteristics permit. In some cases, it is desirable to have the PVC > CPVC permitting good intercoat adhesion with the topcoat and relatively easy sanding. After penetration by the topcoat vehicle, the PVC becomes approximately equal to CPVC. High pigmentation is desirable because the least expensive component is inert pigment. Furthermore, high pigmentation reduces oxygen and water permeability of the final combined film as long as highly hydrophilic pigments are avoided. One drawback for high solids is that highly pigmented, high solids coatings have higher viscosities. Waterborne primers are replacing solventborne primers in many applications.

When feasible, baking primers are preferable since they provide better adhesion. A primer should be designed for baking at as high a temperature as possible because this promotes penetration into the conversion coating and micropores on the surface of the metal. The primer vehicle should be designed to provide maximum resistance to displacement by water, ie, to have good wet adhesion. Multiple polar groups spaced along the polymer backbone tend to promote wet adhesion and resins substituted with amine groups or phosphoric acid partial esters show enhanced wet adhesion. Cost is sometimes the dominant factor on composition and alkyds are still widely used as primer vehicles even though epoxy esters, epoxy/amine, or epoxy-phenolic-based primers generally provide better performance.

Electrodeposition Primers. Primers for automobiles and a significant part of primers for household appliances are applied by electrodeposition. Almost all electrodeposition primers are now cationic. The compositions are proprietary, but the vehicles in some primers are epoxy/amine resins neutralized with volatile organic acids such as lactic acid; an alcohol-blocked isocyanate is used as a cross-linking agent. The pigments are dispersed in the resin system and the coating is reduced with water. The amount of amine salt is such that a stable dispersion, not a solution, results in the aqueous phase. All of the resin, cross-linking agents, and pigments must be located in the dispersed phase aggregates, so that all components deposit at equal rates.

Recent emphasis has been directed to lowering baking temperatures. The two major approaches to the problem have been selection of blocking agents for the isocyanate cross-linking agents that unblock at lower temperatures and catalysts that reduce the temperature while retaining excellent hydrolytic stability. See (115) for a review.

In application, the automobile or other article to be coated is made the cathode in an electrodeposition system. A current differential on the order of 250–400 V is applied, which attracts the positively charged coating aggregates to the cathode. At the cathode, hydroxide ions from the electrolysis of water precipitate the aggregates on the surface of the metal. As the conveyor removes the coated product from the bath, residual liquid is rinsed off with water and the article is conveyed into a baking oven for a high temperature bake.

As the coating operation continues, acid accumulates in the electrodeposition bath. Thus pH must be controlled by the addition of acid-deficient make-up coating and by the removal of excess acid from the bath. Other soluble materials also tend to accumulate in the bath. These must be removed by continuous passage through ultrafiltration units. Additionally, the temperature must be closely controlled. Highly automated electrodeposition tanks are used. The high voltage application is required in order to have high throw power, ie, deposition on internal surfaces of the metal article in the short time that it is in the tank. High throw power without film rupture at the readily accessible coated surfaces requires a limited conductivity of the applied film and low conductivity of the continuous water phase. The low conductivity requirement is another reason that the efficient operation of the ultrafiltration process is essential. The voltage that can be used varies with the type of metal being coated. Whereas film rupture has been attributed to gas evolution under the film from the electrolysis of water, it appears that electric discharges through the film may be more important.

Cationic electrodeposition primers show substantially better corrosion protection than anionic ones. In anionic electrodeposition, the phosphate conversion coating on the steel partially dissolves with the hydrogen ions generated at the anode surface. However, in the case of cationic primers, if zinc–iron phosphate conversion coatings are used on steel and zinc–manganese–nickel conversion coatings are used on zinc-coated steels, the conversion coatings do not dissolve. Furthermore, the resin used in the cationic electrodeposition primer is generally saponification resistant and promotes good wet adhesion, which are critical requirements for corrosion protection.

Electrodeposition primers offer substantial advantages in some applications over conventional primers: The highly automated lines permit low operating costs; the VOC emissions are lower than from other primer systems; and areas not reached by spray application are coated, giving superior corrosion protection. There is also the advantage of essentially 100% utilization of the coating and no waste from overspray. Furthermore, electrodeposition gives uniform film thickness to the coating on all areas of the article, avoiding thin spots, fatty edges, sagging, etc.

The capital cost of application facilities is high for electrodeposition limiting this technique to high production articles. Because the film thickness of the electrodeposited primer is uniform, the surface of the coating in effect replicates any irregularities in the surface of the metal. If high gloss topcoats are to be applied over the primer, care must be taken in selecting steel and steel treatment procedures that permit adequate smoothness or a coat of primer-surfacer over the electrodeposited primer may be required.

It is more difficult to obtain adequate intercoat adhesion of a topcoat to an electrodeposited primer than to a spray-applied primer. This adhesion problem is partially because the PVC must be lower than CPVC. The lower pigment content gives a higher gloss surface, which reduces the opportunity for intercoat adhesion. Commonly, this problem is overcome by applying a coat of primer-surfacer to provide intercoat adhesion between the primer and topcoats, before application of the topcoat. A recent innovation has been the introduction of the use of two electrodeposition coatings for priming of automobiles. The first coat is an electroconductive coating. With this conductive primer another electrocoating can be applied as a second coat. The second is formulated to replace a spray coating of a primer-surfacer, which reduces application cost.

Topcoats. The selection of a topcoat depends on cost, method of application, product use and performance requirements, among other factors. As a result of increasingly stringent air quality standards and increased solvent costs, approaches to reduction of solvent emissions are being sought. Three approaches are being followed: high solids coatings, waterborne coatings, and powder coatings (for discussion of powder coatings see the section on Powder Coatings).

High Solids. There is no agreement on a definition of high solids coatings. For any particular use, it means higher solids than previously used in that application. In automotive acrylic metallic coatings, high solids usually is taken to be ~45 vol%. This limit results from the solvent level required to give sufficient shrinkage during film formation to orient the aluminum pigment to give the desired color effect. In the case of clear coats, ~70 vol% can be achieved with reasonable film properties. Urethane based coatings can be formulated with higher solids and generally give superior abrasion resistance than acrylic–MF coatings. For applications in which outstanding exterior durability is not required polyester coatings give satisfactory performance and can be formulated with up to ~70 vol% solids.

Whereas the main driving force behind the development of higher and higher solids coatings has been the reduction of VOC emissions, solvent cost is also a factor. A further advantage is that the same dry film thickness can be applied in less time. High solids coatings are made using lower molecular weight resins having fewer average functional groups per molecule as compared to conventional coatings. As a result, more complete reaction of the functional groups is necessary to achieve good film properties. Greater care is necessary for high solids coatings manufacturers to maintain close adherence to quality control standards. Additionally, application techniques, baking times, and temperatures for which the coating is designed, must be carefully adhered to. There is a relatively small window of cure. Shorter times or lower temperatures can result in undercure and the properties are more affected by overcure, in general, than conventional coatings (116). High solids coatings are likely to have high surface tensions, and hence are more likely to give film defects such as crawling and cratering than conventional coatings. Sagging of spray-applied high solids coatings is more difficult to control than for conventional coatings. See Section on Sagging.

Waterborne Coatings. Two classes of waterborne systems are used: water-reducible and latex systems. Water-reducible systems are used on a larger scale but the consumption of latex product coatings is increasing. When the coating is reduced with water, the polymer separates into relatively stable aggregates containing the pigment and cross-linking agent and these are swollen by solvent and water. In anionic systems, the resin is sufficiently substituted with

COOH groups to give the desired water dilutability after partially neutralizing with an amine. Acid numbers are in the range of 40–80. The coatings are cross-linked with MF resins or blocked isocyanates. Water-reducible urethane resins can be used with MF cross-linkers or as 2K clear coats with polyisocyanates to give coatings having superior abrasion resistance (117).

Because the molecular weight and average functionality of the resins used in water-reducible coatings are comparable to those of conventional solution thermosetting coatings, film properties obtained after curing are fully equivalent. Similarly, and in contrast to high solids coatings, they have tolerances to variations in cure conditions comparable to those of conventional solution coatings. Surface tensions are relatively low, and few problems with crawling and cratering are encountered. Because the solids are low, good orientation of aluminum pigment can be obtained and such water-reducible coatings are being used increasingly in base coats for automobiles along with a high solids clear coat (118).

There are disadvantages to the water-reducible coatings. Solids contents at application viscosities are relatively low, 18–25 vol%. Because most of the volatile material is water, VOC emissions are still lower than from most high solids coatings. The evaporation rate of water depends on the relative humidity, which can lead to inconsistent flow behavior during flash off. Above a critical relative humidity, water evaporates more slowly than the solvent; below this critical value the solvent evaporates more slowly than water. The viscosity of the coating depends strongly on the ratio of solvent-to-water as well as on the concentration, thus abnormal viscosity changes can occur when flash-off occurs above the critical relative humidity. Popping is more difficult to control in water-reducible baking enamels than in solvent-based counterparts, even when the relative humidity in the flash-off zone is well controlled. See the section on Popping.

Acrylic coatings of fairly similar composition can also be applied as topcoats directly on metal by anionic electrodeposition. Performance on aluminum is excellent, over steel some iron is dissolved at the anode, and anionic electrodeposition coatings tend to become discolored. Cationic electrodeposition topcoats can be made for use on steel, using, eg, 2-(dimethylamino)ethyl acrylate as a comonomer and a blocked aliphatic diisocyanate as the cross-linking agent for hydroxy-functional groups. Electrodeposition topcoats are particularly useful where it is difficult to achieve full, uniform coverage by other means such as on articles having sharp edges, eg, finned heat exchange units. The highly automated electrodeposition process can lead to significant cost reduction. It has been reported for cationic electrodeposition coating of air conditioners that replacing a former system of flow-coated primer and spray-applied topcoat required only one operator. In the former system, 50 people, including those doing the required touch up and repair were needed (119).

Until the 1980s, latex-based coatings were infrequently used in product coating applications. High gloss coatings cannot be made using latexes and transparent coatings are difficult if not impossible to make. Furthermore, the rheological properties of the coatings limit utility. Flow problems are least severe when coatings are applied by curtain coating or reverse roll coating because these two methods do not involve film splitting. The availability of associative thickeners that minimize flocculation of latex particles permits formulation of industrial coatings that are less thixotropic, and hence level better after application. Popping can cause difficult problems in applying thick coats of latex-based coatings. Low VOC emissions and excellent film properties resulting from the high molecular weight of the polymer are expected to lead to increases in the use of latexes in product coatings.

Coil Coatings. An important segment of the product coatings market is sold for application to coiled metal, both steel and aluminum (120). In this process, the metal is first coated and then fabricated into the final product rather than fabricating first into product. The method offers considerable economic advantages because coatings are applied by direct or reverse roll-coating at high (up to 400 m/min) speeds to wide (up to 3 m) coils in a continuous process. The metal is cleaned, conversion coated, and coated with primer (if desired) and topcoat in an in-line operation. Coatings can be applied to both sides of the metal during the same run through the coil coating line. The labor cost of coating application is much less than for application to a previously fabricated product. There is essentially 100% effective utilization of coating, and the loss by overspray involved in coating fabricated products is avoided.

Use of coil-coated stock reduces fire risk, and hence insurance costs for the metal fabricator. The problem of controlling VOC emissions is also avoided because no coating is done in the factory. The VOC emission control problems for the coil coater are minimal. The oven exhaust is used for the air needed for the gas heaters for the oven. The solvents are used as fuel rather than being allowed to escape into the atmosphere. Film thickness of the coatings is more uniform than can be applied by spray, dip, or brush coating of the final product. The coatings are all baked coatings, and when coil-coated metal is used, substantially greater exterior durability and corrosion protection can be achieved as compared with field-applied air-dry coatings.

There are limitations to the applicability of the process. The metal must be flat. Coil coating is economical only for long runs of the same color and quality of coated metal. Offsetting the economic advantages of coil coating is the higher cost of maintaining inventories of coated metal coils. Additionally, because the films must sometimes withstand extreme extensions in fabricating a final product, they must generally have long elongations-to-break, which may limit the range of other film properties that can be designed into the coating. For example, it may be difficult to achieve a high modulus at a low rate of application of stress while still having adequate elongation-to-break to permit fabrication without film cracking. Although some coating may be smeared over the cut edge of the metal when the coil is cut, the cut edge of the metal usually has little, if any, coating on it. These cut edges can be a weak spot for corrosion protection and can present an appearance problem if the edges are visible in the fabricated product. Although coatings can be made that can be welded through, they char from the intense heat and have, therefore, an unacceptable appearance if the weld marks are visible. Design of a final fabricated product must take the cut edge and weld marks into account, hiding and/or locating them in positions least likely to cause corrosion problems.

In order to have reasonable oven lengths for curing at high speeds, the coatings must cure in short times, <1 min. Therefore, the ovens are operated at high temperatures, >290°C. The short-time, high temperature cure schedules are difficult to duplicate in a coatings development laboratory. Substantial experience is required to make informed estimates of how to translate laboratory cure response to coating line cure response. This problem can be particularly acute for color matching. The ability to do satisfactory color matching for coil lines is a prerequisite to commercial success in supplying coil coatings. Because during start up, and sometimes in splicing a new coil onto the previous coil, the line must be slowed down, it is essential that there be a minimum change in color and film properties when the standard curing time is exceeded.

A wide range of resin compositions are used in coil coatings, depending on the product performance requirements and cost limitations. The lowest cost coatings are generally alkyd coatings. They are appropriate for indoor applications where color requirements are not stringent. Alkyd–MF coatings are sometimes used outdoors when long-term durability is not needed. Greater durability and better color retention on overbaking are obtained using polyester–MF. Polyesters usually provide better adhesion to unprimed metal than acrylic coatings. For two-coat systems, epoxy ester primers are widely used along with acrylic–MF topcoats. Blocked isocyanates can also be used for cross-linking the polyesters and acrylics but care is needed because urethanes decompose thermally and loss of film properties and discoloration on overbake may be severe. For this reason, it is necessary to use blocked diisocyanates that react at relatively low temperatures. Oximes are the most widely used blocking agents for coil-coating systems. Thermoplastic coatings based on vinyl plastisols and acrylic latexes resist severe deformation during fabrication and exhibit good exterior durability.

For greater exterior durability, silicone-modified polyesters or silicone-modified acrylic resins are used. Hydroxy-functional polyester or acrylic resins are partially reacted with a silicone intermediate having methoxy substituents on the siloxane resin chain. Cross-linking is completed during curing by reaction of the remaining methoxy substituents and hydroxyl groups on the polyester or acrylic resin. In order to avoid softening during prolonged exposure to high humidity, which can result in reversible hydrolysis of cross-links with groups having three oxygens on a silicone atom, it is common to use a small amount of an MF resin as a supplementary cross-linker. Silicone-modified coatings have longer exterior lifetimes than the corresponding unmodified polyester or acrylic coating. Silicone-modified coatings are more expensive. They are particularly useful in colored coatings where the color change can be substantial when chalking occurs. The white coated product in the same quality line may well be made without silicone modification to reduce cost, because color change resulting from the chalking of the white coating after exposure for a long period is less obvious. For still greater exterior durability, fluorinated polymer systems are used.

In the can industry, large-volume three-piece cans, used for packing many fruits and vegetables, are made from coil-coated stock. Oil-modified phenolic resins are used for coating tinplated steel coils on the side that becomes the interior of the can. Coil stock for making ends for two-piece beverage cans is coated with epoxy–MF, epoxy–phenolic, or a cationic uv cure epoxy coating.

14.2. Wood Products Coating. Furniture is an important class of wood products that is industrially coated. The appearance standards are set by the fine furniture industry where the flat areas are composed of plywood having high quality top veneer; the legs and rails are solid wood; and there are frequently carved wood decorative additions. The finishing process for fine furniture is long and requires significant artistic skill. If the final overall color of the furniture is lighter than the color of any part of the wood, the first step is bleaching using a solution of hydrogen peroxide in methanol [67-56-1]. The bleached wood, or unbleached for darker color finishes, is given a wash coat of size to stiffen the fibrils so they can be cleanly removed by sanding. The wood is then coated with stain, a solution of acid dyes in methanol, to give a desired overall color tone to the piece of furniture. A wash coat, generally a low solids vinyl chloride copolymer lacquer, is applied over the stain, partially to seal the stain in place but also to prepare the surface for the next operation, filling. The filler, a dispersion of pigments, usually in linseed oil with mineral spirits solvent, is sprayed over the whole piece of furniture. It is then wiped off, leaving filler only in the pores of the wood. The colors of fillers are commonly dark brown; the filler serves to emphasize the grain pattern in the hardwood veneer. Next, shading stains are selectively sprayed on the wood to give different colors to various sections. It is common to distress the surface to resemble antique furniture. For example, spots of black pigment stain can simulate India ink spots dropped from quill pens, and dark stains carefully applied into corners simulate dirt accumulated over many years. When this “art work” is completed, a sanding sealer is applied to immobilize the lower layers of the finish and to provide a surface that can be sanded smooth. Finally a topcoat is applied and polished smooth.

The primary binder that has been used for many years in the sanding sealer and the topcoat is nitrocellulose. Nitrocellulose lacquers supply a coating that brings out the natural beauty of the wood and gives a depth of finish that has not been matched with other systems. The film properties of the lacquers improve with increasing molecular weight of the nitrocellulose, whereas the solids of the lacquers decrease. Lacquers suitable for high quality furniture have volume solids $<20\%$. Other components of the lacquer are plasticizers and hard resins to provide a combination of flexibility and hardness for sanding and polishing while retaining flexibility to withstand cracking as the wood in the furniture expands and contracts. Zinc stearate [557-05-1] is incorporated in the sanding sealer to reduce clogging of sand paper.

Topcoats generally include fine particle size silicon dioxide to reduce the gloss. In making a low gloss topcoat, it is essential to retain the transparency. Low gloss can be achieved using a minimum amount of fine particle size SiO_2 pigment. When the solvent evaporates from the low solids lacquer, convection currents carry the fine particle size SiO_2 to the surface. Hence, the PVC of the surface layer is relatively high, giving the low gloss, whereas the PVC of the entire film is low (2–4%) in order to maintain transparency. As higher and higher solids lacquers while maintaining clarity are attempted, low gloss becomes more and more difficult. The convection currents are not as strong using the lesser amounts of solvent.

Nitrocellulose lacquers offer other important advantages for furniture. There is latitude as to when a complete piece of furniture is rubbed after finishing, whereas thermosetting systems must be rubbed after some cross-linking but before cross-linking has advanced to the point that it cannot be rubbed without leaving permanent scratches. Using lacquers, the production line can be shut down at the end of a shift and pieces on the line can be rubbed the next day or after a weekend; using thermoset systems, the line must be stopped early or an extra shift must be brought in just for the rubbing. Because of warehousing space problems for furniture, factories frequently prefer to load furniture onto trucks almost directly off the finishing line. The finish must therefore withstand print tests equivalent to the pressures that are going to be encountered in shipping very soon after they are applied. This is a problem for water-based topcoats because the rate of loss of water depends on humidity. The loss of the last of the water from an almost dry film can be slow, resulting in delay before the furniture can be wrapped and shipped.

This finished furniture is a beautiful product attained at a high cost. Most good furniture is made at substantially lower cost with as little sacrifice in appearance as possible. The expensive hardwood veneer plywood is replaced by printed, coated particleboard. The artists' work of filling, shading, distressing, glazing, and so on needs only to be done once on a carefully selected beautiful wood laid up meticulously into fine patterns. The finished panels are then photographed to make a series of three gravure printing plates of the finest through the boldest parts of the pattern. The particleboard is coated with a uv cure filler and sanded smooth. A lacquer base coat is sprayed on, in a color corresponding to the first coat of stain in fine furniture finishing. Then three prints are applied by offset gravure printing using three carefully selected color inks. The panel is assembled into the furniture and finished with lacquers as in the standard process. Only experts can distinguish the prints from real wood by just looking at the surface.

Conventional nitrocellulose lacquer finishing leads to the emission of large quantities of solvents into the atmosphere. An approach to reducing VOC emissions is the use of supercritical carbon dioxide as a component of the solvent mixture (121). VOC emission reductions of 50% or more result. See the section Application Methods.

Many alternatives to nitrocellulose lacquers for topcoats are being used increasingly. Especially for lower cost furniture exposed to hard use such as motel and institutional furniture, alkyd–UF topcoats are used. The UF resins, in contrast to MF resins, are used because the former can be cured using butyl acid phosphate [1623-15-0] catalyst at room temperature or force dried at 60–70°C. These resins are applied at ∼35 vol% solids and require about one-half of the spraying time of a nitrocellulose lacquer. They are also more difficult to repair and do not provide the depth of appearance of nitrocellulose lacquers.

Considerable efforts have been invested in developing waterborne coatings for wood furniture. The two approaches are water-reducible acrylic resins with UF cross-linkers and hydroxy-functional vinyl acetate copolymer latexes with UF cross-linking. The 2K waterborne urethane coatings with very low VOC are being increasingly adopted, especially for office furniture and kitchen cabinets (67). Waterborne systems would be used more widely if it were not for the effect of relative humidity on drying and the relatively long time for the coatings to develop print resistance. Because of grain raising caused by direct contact of water with wood, water systems are not suitable for the first layer of coating on the wood.

The uv-cure coatings are widely used in European furniture manufacture but have found more limited applications in the United States. Most U.S. furniture has a relatively low gloss finish, frequently has curved surfaces, and is finished after assembly; most European furniture has a relatively higher gloss finish with primarily flat surfaces, and the furniture is generally assembled after coating. The uv-cure coatings are more easily adapted to coating before assembly. Because of the pressure on the furniture industry to decrease VOC emissions, uv-cure coatings may become more widely adopted in the United States. The use of high pressure laminated plastics having wood grain reproductions can be expected to take a larger share of the furniture top market in response to VOC regulations.

The other principal component of industrial wood finishing is the panel industry. The highest cost segment of this industry, fine hardwood veneer paneling for executive office walls, is comparable to the fine furniture industry where similar nitrocellulose lacquer finishing systems are used. However, the bulk of the industry requires less expensive finishing operations. Some plywood is stained followed by roll coating with a low gloss nitrocellulose lacquer topcoat. It is common to print grain patterns from woods such as walnut onto inexpensive, relatively featureless veneers such as luan before applying a lacquer topcoat. Lacquer topcoats are being replaced by alkyd–UF coatings.

Large volumes of wood grain paneling are made from hardboard paneling. The coating systems are usually a base coat, three prints, and a clear topcoat. In higher style paneling, the hardboard is embossed in the pressing step involved in making the hardboard. For example, if a pecky cypress paneling is desired, the hardboard would be embossed with holes resembling those of pecky cypress. The first step in finishing such a board is to apply a so-called hole color with a brush roll rollercoater. Then the flat surfaces are precision coated with a base coat. The base coat color is the equivalent of the stain color if real wood were being used. Then three prints are applied from gravure rollers made by photographing carefully selected and finished real cypress. Finally, an overall low gloss topcoat is applied. Because hardboard can withstand contact with water and relatively high temperature baking, the coatings are most commonly water-reducible acrylic–MF coatings. Imitations can be made of any wood and also of brick paneling, marble paneling, and porcelain tile.

Factory coated hardboard is also used for exterior siding for homes. The largest volume of such hardboard is preprimed board. A primer is applied in the factory that is suitable for exterior exposures up to 6 months before painting with exterior house paint. While only one coat of latex paint need be applied, it has been reported that greater durability is obtained if a primer is applied after house construction using an acrylic latex topcoat (122). Fully prefinished hardboard is also sold commercially. The exterior durability of this paneling is superior to that of the field painted paneling, but the styling is more limited; it is used primarily in commercial buildings.

14.3. Radiation Curing. Radiation has several significant advantages over heat as the source of energy to carry out cross-linking reactions (123). Coatings can be designed that cure rapidly, in a second or less, at room temperature yet have relatively long storage lives. The energy requirements for curing are much lower than for thermal baking systems. Reactive monomers are used to provide the low viscosities for application. In some cases, the energy source is high energy electrons, but more commonly uv, radiation curing systems are used.

In uv-curing coatings, a photoinitiator is required in the formula, whereas in electron-cured coatings the energy is directly absorbed by the reacting molecules. Both free-radical and cationic initiated polymerization systems are employed for uv cures. Benzoin derivatives, benzil ketals, acetophenone derivatives, α-hydroxyalkylphenones, *O*-acyl-α-oximinoketones, and benzophenone (diphenylmethanone) [119-61-9] and 2-(dimethylamino)ethanol combinations are examples of photoinitiators (124).Vehicle systems are oligomers substituted with several acrylic ester groups mixed with low molecular weight difunctional or trifunctional acrylates and a monofunctional acrylate. Acrylic ester systems provide a much more reactive cure than methacrylate systems. Styrene is sometimes used as a monomer with unsaturated polyesters. However, cure is slower than for acrylic esters and significant amounts of styrene evaporate. Many pigments absorb uv radiation, thus most commercial uv-cure coatings are unpigmented, clear coatings. Printing inks, which are applied as very thin films, and particle board filler, where only inert pigments that absorb little uv are used, are examples of uv-cure pigmented systems.

Photoinitiators for cationic polymerization generate reactive electrophiles (acids). Three classes of cationic photoinitiators have been used commercially: triarysulfonium, diaryliodonium, and ferrocenium salts of very strong acids, such as hexafluorophosphoric acid (125). When the uv absorption of a potential photoinitiator is low, a strongly absorbing photosensitizer can also be used. The most widely used vehicles are epoxy resins diluted with monofunctional and difunctional epoxy compounds to adjust the viscosity. An important advantage of this type of system is that shrinkage is substantially less than in systems where acrylic double bonds are polymerized. Furthermore, the protons generated by the photoinitiator are more stable than the free radicals generated in radical systems. Hence, curing can continue after the article being coated has passed beyond the uv source. However, reaction rates are slower than for free-radical polymerized acrylate coatings. High speed curing can be carried out by combining uv exposure to release the acid catalyst and baking to give a rapid cross-linking reaction.

Cationic systems have fewer limitations. They are not air inhibited, the photoinitiators do not initiate photodegradation reactions, there is less shrinkage during curing, and the stability of the acids generated permits migration if the initiator through a pigmented film, allowing cure of somewhat thicker pigmented films. However, commercial adoption has been slow, possibly because of higher costs and slower cure rates at ambient temperatures.

There are many advantages to radiation curing, but there are also limitations. Only flat surfaces that can be passed under the focused uv source, or cylindrical surfaces that can be rotated under the source, can be practically cured by this method. Although it is desirable in many cases to make coatings that cure at low temperatures, in uv-cure systems, as in all other coatings, the T_g of the final cured film is limited to temperatures a little above the temperature of the film during curing by the limitation of available free volume on the cross-linking reactions. Radical initiated uv-cure systems are poor candidates for coatings requiring good exterior durability, because the residual photoinitiator initiate degradation reactions. Solvent-free pigmented uv-cure coatings are limited not only by the depth of penetration of the uv radiation but also by the effect of the pigmentation on flow properties. Even for gloss coatings, such as exterior white can coatings, the amount of pigmentation is sufficient to increase the viscosity enough to affect leveling adversely. As a result of the substantial shrinkage that occurs in a very short time in the uv curing of acrylate systems using radical photoinitiators, adhesion to smooth surfaces such as metals is generally reduced by the stresses in the film. Such stresses can frequently be relieved by heat treatment after curing. Also, costs tend to be relatively high.

Uses that have developed for uv curing reflect the special advantages of the system rather than replacement to reduce VOC emissions or energy consumption. Clear coatings on heat-sensitive flat plastic substrates, where rapid cure is needed, is an area where uv curing has found application, eg, uv-cure abrasion-resistant topcoats for vinyl plastic flooring. These coatings are made using acrylic ester-terminated polyurethanes as the oligomers. Other examples of application to heat-sensitive substrates are coatings for thin wood veneers used for door skins and coatings for paper.

The high solids of uv-cure systems can also be important in some cases. For example, uv curing fillers for particleboard for use in paneling and furniture has the advantage over conventional coatings that the high solids permit filling of the rough surface in one coat rather than using multiple coats of solvent-based systems. In printed circuit boards, uv-cure systems are widely used. Another application, which illustrates the advantages of high cure rates, is the use of uv cure clear coatings of glass optical fibers in waveguides.

14.4. Powder Coating. Another coating technique that substantially reduces VOC emissions is powder coating. Worldwide production of powder coatings in 1999 was ~527,000 metric tons (126). A variety of coating types and application methods are used and powder coatings have been the most rapidly growing part of the coatings industry. There are three methods of application: passing heated objects to be coated into a fluidized bed of powder particles suspended in air, electrostatically spraying grounded articles at ambient temperature with powder, and flame spraying.

Thermoplastic powders are frequently applied by a fluidized-bed process, which results in relatively thick films. As the coating builds up, the temperature at the surface drops. The last particles picked up stick to the surface but do not completely fuse into the film. A conveyor transfers the article into an oven when fusion and leveling are completed. The polymers are usually vinyl chloride copolymers, polyolefins, or polyesters, especially scrap poly(ethylene) terephthalate.

Thermosetting powders are generally applied by electrostatic spray. The sprayed parts are carried into an oven for fusion, leveling, and cross-linking. The T_g of the powder coating before curing must be above the storage temperature in order to avoid sintering. As a result, the range of physical properties of the final films is limited. The high T_g of the powder before application requires high baking temperatures. In order to coalesce after application, the temperature must be sufficiently above the T_g for the free volume to be adequate for ready coalescence. The T_g of the resins used in powder coatings is controlled by the monomers and molecular weight. It has been reported that, at least in one case, it is advantageous to use higher molecular weight, more flexible resins because these can have adequate package stability but flow more easily at higher temperatures than a lower molecular weight resin of similar T_g with more rigid chains. The problem of coalescence and flow is further compounded by the decrease in free volume and increase in viscosity resulting from the cross-linking reaction that is simultaneously proceeding. Although leveling is adequate for many applications, it can be a limitation for powder coatings.

The range of suitable resin compositions is much narrower than in liquid coatings. The T_g of the powder must be sufficiently high to prevent sintering during storage. The components are blended and the pigments are dispersed in the vehicle by passing through a heated extruder that subjects the material to high shear stress. The cross-linking reaction must proceed slowly enough under the conditions encountered in the extruder that very little polymerization occurs during the process. Because some cross-linking does occur, the number of times that the same material passes through the extruder must be limited as well as the fraction of recycled material that is incorporated in any batch. These considerations place a premium on raw material control for resins as well as pigments. In solvent coatings, the final viscosity and application properties can be adjusted by the additions of solvents and varying their evaporation rates. In powder coatings, on the other hand, the application properties are governed by the resins alone.

The BPA epoxy resins, with dicyandiamide as the cross-linking agent, are widely used in coatings where exterior durability is not required. Phenolic resins are used as cross-linkers for epoxy resins when greater chemical resistance is required. So-called hybrid polyester powder coatings are based on carboxylic acid terminated polyesters and BPA epoxy resins. These have superior color retention at lower cost but still inferior exterior durability. For applications where exterior durability is required, triglycidyl isocyanurate (TGIC) is used along with carboxylic acid functional polyesters. However, concern about possible toxic hazards of TGIC has led to work on alternate systems. Tetra-(2-hydroxyalkyl)bisamides are used as cross-linkers for carboxylic acid functional resins (127). Tetramethoxymethylglycoluril is also used as a cross-linker for hydroxy-functional polyesters (128).

Hydroxy-functional polyester or acrylic resins cross-linked with blocked isocyanates give powder coatings having superior exterior durability combined with abrasion resistance. Caprolactam blocked isophorone diisocyanate is the most widely used blocked isocyanate. Blocked isocyanate powder coatings tend to give better leveling than most other powder coatings perhaps because the caprolactam released by the unblocking reaction volatilizes only slowly. While the caprolactam is still present in the film, it can lower viscosity and may help promote coalescence and leveling. Polyfunctional uretdiones are increasingly used as blocking agents since there is no volatile blocking agents. See Ref. 129 for a review of blocked isocyanate powder coatings.

In flame spray powder coating, a thermoplastic powder is applied by propelling the powder through a flame in which it melts and is then deposited on the substrate to form a film. Poly(dimethyl terephthalate) powders are most commonly used. The largest advantage over other means of application is that it can be done in the field on objects like grain railcars. Also, since it is a nonelectrostatic application, nonconductors such as concrete, wood, and plastics can be coated (130).

Powder coatings have many advantages. The VOC emissions approach zero because no solvents are used. Compared to many solvent-borne baking coatings, fuel cost for heating ovens are low, even though the baking temperature may be higher. This results from the substantial increase in recirculation of the hot air in the ovens, because there is less need to exhaust air to keep the solvent concentration below the lower explosive limit. Lack of solvent permits even application of coatings to the inside of pipes without the solvent wash encountered when solvent coatings are applied to an enclosed area. As compared to electrostatic spray applied solvent-borne or waterborne coatings, utilization efficiency of powder coatings can be much higher because the oversprayed powder can be collected and reused. On the other hand, the overspray from liquid coatings must be caught in a water wash spray booth. This overspray cannot be directly recycled and generally the resulting sludge becomes a solid waste disposal problem.

There are disadvantages or limitations to powder coatings as well. Only substrates that can withstand the relatively high baking temperatures can be coated. Color changeover in the application line requires shutting down the line and cleaning the booth. Therefore, powder coating is most applicable to product lines where long runs of the same color are processed. Color matching is more difficult than with conventional coatings. Because the final coatings cannot be blended or shaded with tinting colors, the whole batch must be reworked if the color match is not satisfactory. By careful control of incoming raw materials and processing variables, satisfactory reproducibility of color matching for many applications is possible. Metallic colors showing the color change with angle of viewing such as are widely used in automotive topcoats cannot be made in powder coatings although other metallic colors can be obtained.

Examples of applications for powder coatings include pipe lining, coatings for rebars, clear coats and primer surfacers for automobiles, underbody automotive parts, wheels, garden tractors, home appliances, playground equipment, metal furniture, fire extinguishers, and many others. As VOC restrictions become more restrictive, powder coatings can be expected to increase in usage.

15. Architectural Coatings

About 45% of the volume of all coatings produced in the United States in 1999 were architectural coatings (2.16×10^9 L (1)). These coatings are designed to be applied to residences and offices, and for other light-duty building purposes. In contrast to most product coatings, they are designed to be applied in the field, in some cases by contractors but in large measure by do-it-yourself consumers. A wide range of products is involved.

15.1. Flat Wall Paint. The largest volume of architectural coatings is flat wall paint. In the United States, almost all flat wall paint is latex-based. Latex paints have the advantages of low odor, fast drying, easy clean-up when wet, durability of color and film properties, and lower VOC emissions as compared to oil- or alkyd-based paints. They are manufactured primarily as white base paints, which are tinted by the retailer to the color selected by the customer from large collections of color chips. Two or three base whites are made, one for pastel shades, one for deep shades, and sometimes one for medium color shades. This method of marketing has the advantage of being able to supply a wide choice of colors while carrying a relatively low inventory. It is critical to maintain the same level of hiding when formulating new white base paints. The tinting colors used by retail stores are designed to be used for a wide variety of formulas.

The performance of quality grades of latex flat wall paints is excellent in most respects, thus the emphasis in technical efforts is on cost reduction. In most cases, vinyl acetate copolymer latexes are used. When high scrub resistance is required a higher cost latex having a high content of acrylate ester monomers is used. The least expensive component in the paint, on a volume cost basis, is the inert pigment. Therefore, the inert pigment content is maximized. In order to have low gloss, flat paints have a PVC near the CPVC. In order to have the highest inert pigment content, formulas are developed having CPVC as high as possible by using a broad distribution of particle sizes.

In ceiling paint, paints having PVC higher than CPVC give excellent performance. The cost of such paints is lower because of the higher inert pigment content and, at the same time, hiding is better because the final film incorporates air voids. For ceiling paints, one coat hiding is particularly important. On a ceiling the reduction in stain and scrub resistances is not a significant disadvantage.

On a volume basis, the most expensive component of flat wall paints is the TiO_2. Therefore, significant efforts are applied to reach a standard hiding with the minimum possible level of TiO_2. The efficiency of hiding by TiO_2 decreases as the TiO_2 concentration is increased above $\sim$10 vol%; it becomes economically inefficient at roughly 18 vol% in the dry film. Above a PVC of $\sim$22, hiding actually decreases with increasing TiO_2 concentration. In the range of 15–18 vol% of TiO_2, the efficiency of hiding can be increased by using as part of the inert pigment some material having a particle size in the same range as that of the TiO_2. This permits substituting inexpensive inert pigment for some of the TiO_2 while maintaining hiding and tinting strength. A mathematical model has been developed to predict the optimum inert pigment size and concentration for a given formulation (131).

Another method of minimizing TiO_2 requirement is the use as pigments of high T_g latexes, the particles of which contain air voids, eg, Ropaque (Rohm and Haas Co.) (132). When used in paints having a PVC slightly lower than CPVC, the air voids inside the high T_g polymer particles in the film provide hiding and permit lower TiO_2 concentrations. Such paints can have stain and scrub resistances equal to other latex paints.

Most wall paints are applied by roller. During roller application, some latex paints give excess spatter, ie, small particles of paint are thrown into the air when the paint is applied. This is the result of the growth of the filaments that are produced by film splitting to the length where they break in two places rather than in one. Paints having high extensional viscosity exhibit this behavior (133). Extensional viscosity increases when high molecular weight water-soluble polymers with very flexible backbones are used as thickeners, leading to increased spattering. Minimum spattering is obtained with low molecular weight water-soluble thickeners having rigid segments in the polymer backbone, such as low molecular weight hydroxyethylcellulose.

A continuing challenge in latex paints of all kinds is to protect against the effects of bacteria in the can and mildew growth after application. Excellent housekeeping in a latex paint plant is essential to minimize the introduction of bacteria into the paint. A bacteriocide incorporated in the paint can kill the bacteria without destroying the enzyme, and viscosity can drop even using adequate bacteriocide in the paint. Bacteria can generate foul odors or, in extreme cases, sufficient gas pressure inside the cans to blow the can lids off. The more common problem is that bacteria feed on many water-soluble cellulosic thickeners used in latex paints. The enzymes split the cellulose molecules reducing the molecular weight, leading to a reduction in viscosity. It is also essential to avoid introducing enzymes that might have been generated through bacterial growth. Mildew can grow on almost any paint surface but latex paints are particularly susceptible, and therefore contain a fungicide. Many fungicides and bacteriocides are available. Testing is difficult because fungal and bacterial growth are so dependent on ambient conditions. See (134) for a review of additives.

15.2. Exterior House Paints. Latex paints dominate the exterior house paint market in the United States because of superior exterior durability of latex paints (resistance to chalking, checking, and cracking) compared to oil or alkyd paints. Another advantage of latex paints used on wood surfaces is that because of high moisture vapor permeability, they are much less likely to blister than oil or alkyd paints.

Another application where latex paints show outstanding performance is over masonry such as stucco or cinder block construction. This performance results from saponification resistance in the presence of the alkali from the cement. Because masonry surfaces are porous, having both small and large pores, the low viscosity external phase of a latex paint can penetrate rapidly into the small pores, causing a rapid increase in the viscosity of the remaining paint. The bulk paint, in turn, sinks into the larger holes more slowly than a solution-based paint. Thus, less latex paint is required to cover the same surface area as compared to alkyd paints. The penetration of various components of latex paint into such porous substrates has been studied (135).

There are limitations to the applicability of exterior latex house paints providing a continuing market for oil or alkyd exterior house paints. Because film formation from latex paints occurs by coalescence, there is a temperature limit, below which the paint should not be applied. This temperature can be varied by choice of the T_g of the latex polymer and the amount of coalescing agent in the formula. In the United States, most latex paints are formulated for application at temperatures $>5-7^\circ$C. If painting must be done when the temperature is $<5-7^\circ$C, oil or alkyd paint is preferable.

Another limitation is that latex paints do not give good adhesion when applied over a chalky surface such as weathered oil or alkyd paint. The latex particles are large compared to the pores between the "chalk" particles on the surface of the old paint. When a latex paint is applied, no vehicle penetrates between the chalk particles to the surface beneath and there is nothing to provide adhesion to the underlying substrate. This problem can be minimized by replacing part of the latex polymer solids with a modified drying oil emulsified into the latex paint. When the film dries, the emulsion breaks and the modified drying oil can penetrate between the chalk particles to the substrate. The exterior durability of the exterior latex paint is reduced by incorporating modified drying oil. It is common to use an oil- or alkyd-based primer over a chalky surface then apply a latex topcoat. The problem of adhesion to chalky surfaces is becoming less important with time because, as latex paints are more commonly used, there are fewer chalky surfaces to repaint.

Cost is an important factor in exterior house paints that are designed with low gloss because this permits higher pigment loading especially in high CPVC paints. Low gloss also reduces dirt pickup, which is a greater problem with latex paints than alkyd paints because they remain thermoplastic. Calcium carbonate pigments should be avoided. The latex paint film is permeable to water and carbon dioxide. Calcium carbonate can dissolve in the solution of carbonic acid and the soluble calcium bicarbonate leaches out to the surface of the film. The reaction is reversed when water evaporates, and the calcium bicarbonate decomposes depositing a frost of calcium carbonate on the surface of the film.

15.3. Gloss Enamels. About one-half of the gloss paint or enamels sold are based on alkyd resins. Professional painters particularly favor the continued use of alkyd gloss paints. The need for reduction of VOC emission levels, especially in California, has led to efforts to increase the solids content of alkyd paints or overcome the disadvantages of latex gloss paints. It is not possible to make latex enamels that have as high a gloss as solution-based coatings. In solution-based coatings, gloss is enhanced during the solvent evaporation by the formation of a thin surface layer that has a lower pigment content than the average PVC of the coating as a whole. In many cases, there is a layer of roughly 1 μm on the surface of the gloss paint film that contains essentially no pigment particles. In latex paints, formation of such a clear surface layer is not possible, and the gloss is lower. The ratio of pigment to binder at the surface of a latex paint film can be decreased somewhat by using a finer particle size latex.

Also reducing the gloss of latex paints is the haze resulting from the incompatibility of surfactants with the latex polymer film and blooming of surfactant to the surface. Whereas this can be ameliorated by making latexes with as low a surfactant concentration as possible, it probably can never be completely eliminated. On the other hand, the far superior resistance of the latex polymer to photoxidation as compared to any alkyd leads to superior gloss retention by latex paints. The difference in gloss retention is particularly large in exterior applications. Furthermore, the latex paint films are more resistant to cracking, checking, and blistering.

An important limitation of gloss latex paints is not gloss, rather it is the greater difficulty of getting adequate hiding from one coat. In professionally applied paint, the cost of labor is higher than the cost of the paint. Alkyd paints, which provide hiding in one coat, are favored by painting contractors in many cases over latex paints that commonly require two coats. There are several factors involved in the hiding differences that exist between gloss latex and gloss alkyd paints. The volume solids of latex gloss paints are substantially lower than the volume solids of alkyd gloss paints. The solids of latex paints are commonly $\sim$33% compared to $\sim$67% for an alkyd paint. In order to apply the same dry film thickness, twice as much wet paint has to be applied. The main factor controlling the wet film thickness initially applied is the viscosity of the paint at the high shear rates experienced during brush application. In order to apply a thicker wet film, latex paint should have a higher viscosity at high shear rate than is appropriate for an alkyd paint. For many years the high shear viscosity of most latex gloss paints was lower than that of a corresponding alkyd paint. The film thickness applied is also affected by the judgment of the painter and the fact that the wet hiding of latex paints is substantially higher than the dry hiding. When the water (refractive index 1.33) evaporates from the film, the latex particles (refractive index $\sim$1.5) coalesce. The number of interfaces for scattering light drops and hiding decreases. This effect is augmented by the larger difference in refractive index between rutile TiO_2 (refractive index 2.76) and water, which is the interface in the wet film, as compared to TiO_2 and the latex polymer that is the interface in the dry film. In the wet paint, the TiO_2 scatters light more efficiently because of the lower volume concentration as compared to the dry film. There is a similar difference in alkyd paints but the effect is smaller because the volume change during drying is less.

The largest factor affecting hiding by gloss latex paints is poor leveling. Assuming that a uniform dry film of 50 μm of a paint provides satisfactory hiding in some application, if the film has thinner areas of, eg, 35 μm, and thicker areas, eg, 65 μm, the hiding power of the uneven film is poor. Actually, the uneven film is even worse than a uniform 35-μm film, because the thick- and thin-film areas are right next to each other and the contrast in hiding is thus emphasized. The poorer leveling generally encountered for latex paints has several causes. First, in alkyd paints for brush application the solvent is very slow evaporating mineral spirits, whereas in latex paints the water evaporates more rapidly, unless the relative humidity is very high. As a result, the viscosity of the latex paint increases more rapidly after application. Second, the volume fraction of the internal phase in latex paints is much higher than in alkyd paints because for a latex paint both the binder and the pigment are in the dispersed phase. Therefore, the viscosity changes more rapidly with loss of volatiles than is the case for alkyd paints. In latex paint, leveling occurs only by flow driven by their low surface tension, whereas in the case of solvent-based brush applied paints the principal driving force is surface tension differential driven flow, which tends to lead to a more uniform film thickness (136).

The rheological properties of gloss latex paints influence leveling and hiding. Latex paints have exhibited a much higher degree of shear thinning than alkyd gloss paints, leading to paints having viscosity that is too low at high shear rate, and a subsequent applied film thickness that is too thin. At low shear rates, the viscosity is too high to permit adequate leveling. Latex paints recover viscosity rapidly after stopping a high shear rate. The reasons for the greater dependency of viscosity on shear rate in latex paints have not been fully elucidated. It appears, however, that it may at least partly result from flocculation of latex particles in the paint. Progress in minimizing this problem has been made by using associative thickeners in formulating latex paints. Many kinds of associative thickeners have been made that are all moderately low molecular weight, water-soluble polymers having occasional long-chain nonpolar hydrocarbon groups spaced along the backbone. Such thickeners reduce shear thinning of latex paints, perhaps by stabilizing the latex particles against flocculation. Latex paints formulated with associative thickeners have increased high shear viscosity allowing the application of thicker wet films. The thickeners afford reduced low shear rate viscosity and a slower rate of recovery of the low shear rate viscosity that improves leveling at the same time (137). The thicker wet film in itself also promotes leveling, because the leveling rate increases with the cube of wet film thickness.

Another shortcoming of latex paints, which is particularly evident in gloss paints, is the time required to develop full film properties. Latex paints dry to touch and even to handling much more rapidly than do alkyd paints, but the latex requires a much longer time to reach the full dry properties. For example, in blocking situations such as placing a heavy object on a newly painted shelf, or the problem of sticking windows and doors, latex paints require more time to develop block resistance than do alkyd paints. The initial coalescence of latex particles is rapid but the rate of coalescence is limited by free-volume availability. Because $(T - T_g)$ must be small, the free volume is small. This situation is helped by using coalescing solvents, but the loss of these solvents is diffusion rate controlled and the rate is affected strongly by free-volume availability.

Another important potential problem for use of gloss latex paints is adhesion to an old gloss paint surface when water is applied to the new dry paint film. Adequate adhesion to an old gloss paint surface is always a problem for any new coat of paint. It is essential to wash any grease off the surface to be painted and to roughen the surface by sanding. But after wetting with water, some latex paint films can be peeled off the old paint surface in sheets. The resistance to adhesion loss by wetting with water improves as the system ages, but for several weeks or even months wet adhesion can be a serious problem. Proprietary latexes have been developed that minimize this problem. It has been said that amine-substituted latex polymers exhibit greater resistance to loss of adhesion. Such polymers can be prepared using an amine-substituted acrylic monomer, such as 2-(dimethylamino)ethyl methacrylate, as a comonomer in preparing the latex or reacting the carboxylic acid groups on a latex polymer and hydroxyethylethyleneimine (1-aziridinoethanol) [1072-52-2].

16. Special Purpose Coatings

Special purpose coatings include those coatings that do not fit under the definition of architectural or product coatings. About 25% of the volume (1.22×10^9 L) of U.S. coatings production in 1999 falls into this category (1).

16.1. Maintenance Coatings.

Heavy-duty maintenance coatings are applied to bridges, off-shore drilling rigs, chemical or petroleum refinery tanks, and similar structures. The applications are usually over steel at ambient temperatures and the objective is corrosion protection. In choosing a system, many factors must be taken into consideration: cleaning of the steel surface, film integrity, temperature of the painting operation, environment, materials, costs, etc.

For applications where the surface can be thoroughly cleaned and where maintenance of film integrity can be reasonably expected, it is most appropriate to use a primer without passivating pigments but having excellent wet adhesion.

For example, a two-package epoxy–amine coating would serve. This combination of epoxy resin and polyamine should be designed in such a way that the T_g of the fully reacted coating permits the reaction to go to completion in a reasonable time period (commonly a week) at the temperatures that prevail during the curing period. Epoxy–amine coatings have the further advantage that they can cure underwater, and hence are suitable for piers and off-shore installations. The topcoats should be designed to minimize oxygen and water permeability. Chlorinated polymers such as vinyl chloride copolymers, vinylidene chloride (1,1-dichloroethene) [75-35-4] copolymers, or chlorinated rubber are used in topcoats. Urethane coatings based on aliphatic isocyanates are used because of good abrasion resistance. Where applicable, use of leafing aluminum pigment in the final coat is desirable to provide a further barrier to water and oxygen permeation.

In situations where complete cleaning of the steel is not possible and where film ruptures are to be expected, primers having passivating pigments or zinc-rich primers are used. Cost is generally lower and mechanical integrity of the films is generally greater using passivating pigment primers. On the other hand, corrosion protection can generally be extended for longer time periods using zinc-rich primers. The substrate should be cleaned as well as possible before painting, generally by sandblasting, and primer should be applied as soon as possible after the surface has been sandblasted. Topcoats for passivating pigment primers are the same as for epoxy–amine primers. When using zinc-rich primers the effectiveness of the primer depends on maintaining its porous structure, therefore, the next coating should not penetrate down into the pores of the primer coat. For solvent-based topcoats, this is generally accomplished by applying a very thin film on the primer surface. The viscosity of a thin film increases rapidly as a result of fast solvent evaporation, minimizing penetration into the primer pores. The application requires highly skilled workmanship and careful inspection. Further topcoat can then be applied without concern for penetration into the primer.

Application of latex paints directly over a zinc-rich primer essentially eliminates the penetration problem. The latex polymer particles are large compared to the primer pores, and after coalescence the viscosity of the polymer is so high that it does not penetrate into the pores. The water and oxygen permeability of latex paints is generally higher than that of solvent-based paints. Thus, it is especially desirable to incorporate platelet pigments such as mica or leafing aluminum. Use of vinylidene chloride–acrylate ester copolymer latexes has been recommended because of the lower water permeability. Field performance using latex paints over zinc-rich primers in such applications as highway bridges has been reported to equal solvent-borne paint performance.

Not only are latex paints being used over zinc-rich primer, they are also increasingly being used directly on steel for corrosion protection. The steel should be thoroughly cleaned, eg, by sandblasting, and the first coat of paint applied quickly. A sandblasted steel surface is highly activated and can flash rust when water contacts the surface, ie, a layer of hydrated iron oxide forms almost instantly. This can be avoided when a latex paint is applied by incorporating a low volatility amine such as 2-amino-2-methyl-1-propanol [124-68-65] in the formula. Latexes have been designed that have superior wet adhesion to metal, eg, by using a small amount of 2-(dimethylamino)ethyl methacrylate as a comonomer. Because the size of the latex particles is large compared to the cross-section of surface pores in steel and the viscosity of the polymer after coalescence is high, the vehicle of latex paints cannot fully penetrate the micropores on the steel surface. Therefore, passivating pigments should be incorporated in the primer formula to provide corrosion protection in these areas. Passivating pigments for latex paints must be carefully selected. Solubility of the pigment must be high enough to provide the desired passivating action, but low enough that the ions do not destabilize the latex dispersion. Recommendations are that latex paints should not be applied on highway bridges when the temperature is $<10^\circ$C and the relative humidity $>75\%$.

16.2. Marine Coatings. Many marine coatings play a key role in extending the life of ships by corrosion protection (138). Products are similar to those used for other heavy-duty maintenance applications. Ship bottom coatings, designed to delay the growth of barnacles, algae, and other marine life on underwater hulls, are widely called antifouling paints. Cuprous oxide has been used as a toxicant in antifouling coatings, but it was replaced in large measure by toxicant pigments based on tributyltin derivatives because of the longer service life of the latter. The service life of antifouling paints was substantially extended by the development of polymers having tributyltin groups covalently bonded to the polymer. The polymers were designed so that organotin compounds were slowly released by hydrolysis (139). Because of the toxicity of tin, analogous copper based with degradable organic toxicants as supplementary antifouling agents are being used (140).

All toxicants used to control fouling are toxic to marine life in harbors, and although there is considerable controversy with regard to environmental risk, regulations are becoming more restrictive. Efforts are now concentrated on means other than toxicants to control marine growths on ship bottoms. Some progress has been reported using silicone coatings that have such low surface tensions that marine growth has difficulty adhering to the surface. For example, a silicone elastomer system has been commercialized for the fast ferry market; their speeds of >30 knots per hour displace fouling organisms that manage to attach to the surface (141).

16.3. Automobile Refinish Paints. Paint for application to automobiles after they have left the assembly plant (refinish paints) is a significant market. Although some of this paint is used for full repainting, especially of commercial trucks, most is used for repairs after accidents, commonly just one door or part of a fender, etc. In order to be able to serve this market, it is necessary to supply paints that match the colors of all cars and trucks, both domestic and imported, that have been manufactured over the previous 10 years or so. Repair paints for the larger volume car colors are manufactured and stocked, but for the smaller volume colors formulas are supplied by the coatings manufacturer to the paint distributor that permit a color match for any car by mixing standard bases.

The nitrocellulose lacquers used for primers are being replaced with waterborne primers such as 2K waterborne urethane coatings (67). Topcoats were formerly nitrocellulose lacquers but are now almost exclusively thermosetting enamels. In the United States, many shops cure the enamels at room temperature; in Europe, cure is commonly carried out at temperatures of 60–75°C. Most cars now have a base coat over the primer and a clear coat as the topcoat. Most base coats are metallic colors that have been applied with enamels wth ~40% volume solids. Increasingly waterborne base coats such as 2K waterborne urethane coatings or latex-based coatings. Solvent borne 2K clear coats such as polyisocyanate/aldimine or diaspartates are frequently used (60). The 2K waterborne urethane clear coats are being introduced.

When solvent borne coatings are used, HVLP are being increasingly used. These guns give better transfer efficiency, and hence lower paint usage and lower VOC emissions.

16.4. Other Special Purpose Coatings. Large volumes of traffic paint are used to mark the center lines and edges of highways. The white paints are pigmented with TiO_2 and the yellow paints have been pigmented with chrome yellow. Concern about the toxic hazard of using chrome yellow is leading to its replacement with organic yellow pigments. The paint must dry fast enough after application so that a car can drive over it within minutes. The most widely used vehicles are alkyds with chlorinated rubber and fast evaporating solvents. Immediately after application, glass reflector beads are applied. To an increasing degree, hot melt coatings are being applied and, in high traffic areas where the lifetime of paint is short, paints are being replaced with thermoplastic tapes. Other examples of special purpose coatings include aerosol-packaged coatings, swimming pool paints, and nonstick coatings for cooking utensils.

17. Economic Aspects

The value of the international coatings market in 1999 was $68.6 billion of which $23.4 billion were in Europe, $19.0 billion in North America, $15.5 billion in Asia, and $10.4 billion in the rest of the world (142).

The value of coatings has been growing but the volume of coatings has been growing slowly or declining. Because there are very large differences in the prices per unit volume, changes in product mix can give distorted comparisons of value/volume totals. A primary factor affecting both price and volume has been changes resulting from the effect of reducing VOC. For any particular use, there is usually a required dry film thickness for the coating after application. High solids coatings require lesser volumes of coating to achieve the same film thickness than conventional solvent content coatings. Therefore, for the same amount of applied coating, the volume of coating sold decreases. Because solvents are usually the lowest cost components of the coating, cost per unit volume increases.

Coating volume is also affected by other technologies that can substantially reduce the need for coatings. For example, in many cases coatings are not required on molded plastics products that have replaced coated metal products. High pressure laminates are increasingly used as furniture tops. In some cases, the replacements have been from one kind of coating to another. For example, recoated siding for residential housing, both metal and hardboard, have substantially reduced the potential market for exterior house paint for two reasons. The initial coating is sold industrially rather than as architectural coating and also the durability of the coatings can be much greater than that of field applied paint increasing the time interval before repainting. Such coated siding has to a degree been replaced in turn by uncoated vinyl siding.

The effect of environmental regulation and the increasing recognition of immediate or potential toxicity hazards of coating components has led to a technical revolution in the coatings field and will continue as strictness of environmental regulations increases. The number of companies has been declining rapidly due to mergers. A substantial fraction of the industry is concentrated in chemical companies and a few large independent companies. However, there are still a number of small- and medium-sized companies that generally serve specialized segments of the business or restricted geographical areas. It is estimated that 45% of the companies have <20 employees.

Whereas the larger companies are international in scope, imports and exports are relatively small. In general, requirements in different countries are quite different and there is generally a need for relatively close contact between consumer and supplier so that the U.S. industry faces little competition from imported coatings and, conversely, exports play a minor role in the field.

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