

PAINT

1. Introduction

Paint has one of the most important roles in our economy. Its job is to protect homes, cars, and infrastructure from all adversities and at the same time add appearance and aesthetics to the painted item. The main functions of a paint are to protect and beautify the substrate it is applied to. Paint is a liquid coating that is pigmented to produce an opaque solid film after application.

Paints have been used for about 30,000 years. Ancient paintings have been found on the walls of caves in France. These early coatings were decorative and were made from naturally occurring materials. Over the years different technologies have evolved to meet the challenges. Alkyds were an early improvement over oil type paints. They dried faster and allowed doors to be closed in just a few days instead of weeks without the door sticking shut. This is termed block resistance. Latex technology came out of WWII and the search for a rubber replacement. Today higher solids coatings and solvent-free paints are a product of the environmental movement.

Coatings commonly encountered in architectural applications include primers, stains, varnishes, sealers, interior and exterior house paints. Today these coatings may be obtained in a variety of types including oil based, latex, urethane, and others. The choice of color is almost endless in most interior and exterior house paints thanks to the industries ability to tint and the advent of the color computer (spectrophotometer). The choice of pigment, resin, extender, solvents, and additives type, as well as the amount, all play an important role in the performance of a paint. The manufacturing of the paint requires the quantitative addition and mixing of components in the correct order to produce a consistent paint.

Paints have been a bargain over the years. The price of a gallon of paint has remained low even though the price of other goods have increased. The application of technology and economy of scale has allowed this savings over the years. Early latex paints were not good performers, today they out perform most oil based products. As technology continues to evolve, it will improve coatings even further.

2. Chemical and Physical Properties

Coatings used in architectural applications can be either pigmented or clear, water-borne, or solvent-borne. The term paint refers to a coating that is pigmented and produces hide or opacity. The most important component in all these coatings is the resin, which can also be called the polymer or binder. In almost all cases, part of the coating is volatile and is emitted from the coating. The material that remain on the surface is referred to as the solids content of the paint. The solids content of a typical liquid paint includes many of the additives, the pigments, and the resin. Modern paints use the term high or higher solids for many coatings which simply indicates that the new paint has more solids and less volatile material in it than the previous coatings of this type. Powder coatings are solid powders of approximately 40 micron which are melted on the

surface and become a uniform coating. Powder coatings have no volatile components and are mainly applied by an original equipment manufacturer, OEM. The formulator selects pigments, resins and additives to achieve the desired performance criteria as well as meet the volatile organic compound (VOC) level, safety, and cost criteria. Many factors must be considered during the formulation of a coating including manufacturing ease, method of application, storage stability, as well as future maintenance of the surface such as washability or repainting.

Two major classes of coatings are used in architectural coatings. The first class is the latex-type coatings which include the acrylics, vinyls and styrene-based resins and many co-polymer systems, all are water borne. These coatings have solids content generally between 35 and 60 wt%. The second type includes the alkyd and modified alkyd or oil-based resins. Most are solvent-borne, but a few are water-borne coatings. Alkyd systems can be 30 wt% to as high as 100 wt% solids. Very few systems have been formulated at the 100% solids level due to application viscosity.

2.1. Binders and Resins. The resin or binder is the single most important component of paint. It must adhere to the substrate as well as bind to the pigment. The resin must have the necessary physical properties for the intended purpose. These physical properties include flexibility, hardness, abrasion resistance, water resistance, gloss, stain resistance, bioresistance, washability, ultra-violet light stability, and chemical resistance. The major factor for performance is dependent upon end use, ie, for the interior, exterior, a floor, or as a water barrier.

Oil-based paint technology was the primary coatings technology until the 1950s when latex resins began to take hold. Many early coatings contained substantial amounts of lead as the primary pigment. Lead poses a health hazard if ingested, but not generally if left undisturbed. It is therefore critical to determine if a coating contains lead before it is sanded or disturbed. In 1978 coatings were no longer formulated with lead. Most coatings formulated from the 1950s on utilized titanium dioxide as the primary hiding pigment, but some alkyd or oil-based coatings still utilized lead-based driers. Today approximately 75% of the architectural coatings are latex-based products with the remainder being alkyd (oil)-based systems.

Alkyds are classified as long oil >60%, medium oil, or short oil <40% based upon the amount of unsaturated oil used in their manufacture. The oil is typically derived from unsaturated fats from soybean, linseed, tung, canola, sunflower, menhaden, and similar oils. The manufacturing process involves the condensation polymerization of the oil with a branching polyol such as pentaerythritol and a carboxylate such as phthalic anhydride or dimethyl phthalate. The oligomerized material is usually dissolved in mineral spirits or an aromatic solvent. The alkyd resin-based coating dries first by evaporation, then it cross-links by an oxidation, and is then catalyzed by chemical driers such as cobalt naphthenate.

The modified alkyds are another type. There are several different alkyd type including the silicone, urethane, styrene, VT (vinyl toluene), epoxy, and acrylic modified alkyds. The modification is basically a graft of the modification on the alkyd backbone structure. These modifications can enhance the properties

of the coating substantially. For example, silicone modified alkyds can extend the life of a coating on a metal storage tank from 5 years for a typical alkyd to 15 or more years. Each of the above modifications brings a specific benefit and usually an increase in price.

Urethane-modified alkyds are one of the most popular. These coatings are often referred to as polyurethane or urethane oil coatings. This type is typically used for clear wood finishes such as floor coatings and for use over stained wood. There are two types of urethanes, aliphatic and aromatic. Aliphatic urethanes can be used for interior or exterior finishes. The aromatic urethanes are used for interior finishes only. The aliphatic should be employed for all finishes exposed to the sun, including window trim. If aromatic urethanes are used on interior window trim, they will usually yellow and may crack in as little as three years. The aromatic urethanes are more abrasion resistant and are often used for coating gym floors.

Latex resins or polymers are often referred to as emulsions. Latex resins are prepared by emulsification of the monomers and subsequent polymerization to produce solid polymer particles of approximately 0.1 micron diameter. The term emulsion is incorrect for the latex since it is not a liquid polymer but a solid. A better term for this system is a dispersion. The monomers used to make the polymer determine its physical properties. The resin chemist utilizes as many as five or more different monomers to produce a polymer with the desired properties. Unlike solvent-borne coatings, the molecular weight of the latex resin does not affect the viscosity. Many latex resins have molecular weights over 200,000 g/mole. The particle size, however, is critical since the larger the particle size, the less pigment that can be utilized and the resultant hide will be less. However, if the particle size is smaller, the coatings will tend to be less water resistant due to the amount of surfactant used to make the latex. Each latex particle regardless of size contains the same amount of surfactant or soap. Therefore as the particle size decreases the percentage of soap in the resin solids increases. The typical size of the latex particle being 0.1 micron is a compromise between water sensitivity and pigment content.

Several major types of latex resins are typically used. The first is often referred to as vinyl or vinyl acetate-based resin. Here, vinyl acetate (85–90%) and either *n*-butyl acrylate or 2-ethylhexyl acrylate (10–15%) are copolymerized. These resins are usually used for interior flat paints and ceiling paint. These vinyl coatings are not very hydrolytically stable and therefore are targeted for dry application areas such as living rooms or bed rooms. The second type is the acrylates which are based mainly upon the various acrylate monomers and target bathrooms and kitchen coatings applications. The acrylates are more hydrolytically stable. The third group is the methacrylates which are used for increased hydrolytic stability applications and where a harder film is desired. These are usually used for exterior applications. The fourth group is the styrenated resins. The styrene monomer can be combined with acrylates, vinyls and methacrylates to produce coatings. These coatings can have a variety of applications from interior architectural coatings to roof coatings. The styrene content must be kept typically below 35% for exterior application or yellowing can occur. The yellowing is due to photooxidation of the styrene units.

2.2. Pigments and Extenders. The primary colored pigments are selected based upon their spectral characteristics, cost, stability, and performance characteristics. These pigments give the paint hide, color, and general quality appearance. The extender or filler pigments are not hiding, but help with the performance of a paint while lowering its cost. Pigment performance in general includes tint strength, dispersability, light stability, weatherability, chemical resistance, solvent resistance, and gloss effects.

Colored pigments may be either organic or inorganic. The organic pigments include phthalo blue, phthalo green, hansa yellow, and various red pigments. The most common inorganic pigments are red iron oxide, yellow iron oxide, the different umbers, and titanium dioxide a white pigment. Carbon black is the pigment of choice when a darkening of the coating is needed. Inorganic pigments are used in preference to the organic pigments due in part to cost and hide. Hide is primarily based upon refractive index differences between the resin and the pigments. Light, when it passes from one refractive index material into another, is refracted. This will result in light scatter for small particles if the difference in refractive index is large. Most resins have refractive indexes between 1.4 and 1.6. Titanium dioxide, the rutile form, has a refractive index of 2.7. Inorganic pigments, however, are usually more dull and less vivid, so organic pigments are available to produce very brilliant colors.

Titanium dioxide has been optimized for size to maximize scatter (0.24 micron) and whiteness. Titanium dioxide is a uv absorber and can photooxidize resins. To prevent this process, all titanium oxide pigment particles are coated with alumina, silica, or zirconia to prevent photooxidation of the resin. It should be noted that the coating does not prevent the titanium dioxide from absorbing uv light and dissipating the energy as heat. The use of titanium dioxide in coatings also has the advantage of preventing uv from passing through the coating by absorbing the uv. The amount of titanium dioxide used is dependent upon the degree of hide needed and the lightness of the color desired. Typically, about 2 pounds of TiO_2 per gallon are used for white and very light pastel, the mid tones may require only 1.5 pounds, and the dark colors may not contain any TiO_2 .

The amount of pigment is often expressed as the PVC which is the volume of pigment divided by the total volume solids in the paint.

$$\text{PVC} = V_{\text{Pigment}} / V_{\text{Total solids}} \quad (1)$$

A second important relationship is the CPVC which is the maximum amount of pigment which a given formulation can have. This is analogous to a mortar requirement of 1 bag of mortar per 40 bricks. If a certain amount of resin is needed to glue a certain volume of pigment together, any more pigment will result in poor performance. To lay 80 bricks, 2 bags of mortar are needed. The equation below relates the density, d , of the pigment and its oil adsorption value, OA as determined by ASTM D261 using raw linseed oil, to the CPVC for a given pigment. If more than one pigment is used, the volume average of each pigment's CPVC must be used.

$$CPVC = 1/(1 + ((d^*OA)/93.5)) \quad (2)$$

The amount of TiO_2 is generally far less than the CPVC. A PVC of about 20% is usually considered the most TiO_2 needed. This observation is related to non-Beers/Lambert behavior of high pigment concentrations. Additional TiO_2 does not improve hide, but does increase cost since it is a relatively expensive pigment. To decrease cost, extender pigments are used. These pigments are of similar refractive index to the resin so they do not cause hide. They can be added to the coating in an amount approaching the CPVC. Their size is typically 5 to 25 microns and they can have a marked effect on gloss. When a more glossy coating is desired, smaller particle size extenders are used and their amount is kept low. For flat or mat finishes, the particle size may be larger and the amount of extender is usually higher.

Extenders are chosen from a long list of ground minerals. Calcium carbonate, silica, clay, talc, and feldspar are some of the more common extenders. Others include glass microspheres, barrytes, gypsum, calcium sulfite, and mica.

Hide in most white paints and very light pastels is enhanced through the addition of a trace (0.25 lb), of a predispersed black, umber or similar dark pigment per 100 gallons of paint to slightly dirty the white. The result is an increase in the hide from the 95–97% range to 99.5% because the black or umber absorbs the light resulting in higher hide without significantly changing the hue of the paint. Seldom is a white paint truly white with a hide of almost 100%.

2.3. Solvents. Alkyds and latex paints are the two most popular paints. Alkyds are often referred to as solvent-borne paints; the latex paints are considered to be water-borne. The term “borne” refers to the solvent’s continuous phase. If the liquid phase is water, the paint is water borne, if the solvent is organic then it is said to be solvent-borne. The solvent is part of the coating’s delivery system, and along with the resin, it is often referred to as the vehicle. The solvent dissolves the resin or allows it to be a stable dispersion. Also, the solvent is used to create the correct application thickness or viscosity. Addition of more solvent will result in a lowering of the viscosity.

Alkyd coatings are usually dissolved in mineral spirits or aromatic solvents such as toluene or xylene. The amount of volatile organic solvent that a coating contains is referred to as its VOC.

$$VOC = \frac{\text{Weight of solvent} - \text{Weight of exempt solvent}}{\text{Volume of paint} - \text{volume of exempt solvent}} \quad (3)$$

Most coatings are limited in the amount of VOC they may contain by the EPA or the regional air quality control boards. Aromatic solvents are being targeted for elimination due to their ability to form smog, and the subsequent increase in the ozone level of atmosphere. Use of solvents considered as ozone depleting substances, ODS, which destroy the ozone layer, are limited and are to be avoided. They are mainly the fluorinated or chlorinated solvents of very low molecular weight. The Hazardous Air Pollutants, HAPs, are also generally being limited in their use or avoided. Water-borne coatings usually contain two solvents in addition to water. They can contain a glycol, either ethylene or propylene glycol,

which acts as an antifreeze and helps with wet-edge retention. Wet-edge retention is the ability to allow all the water to evaporate before the latex particles fuse into a continuous film. This is very important when a painter gets interrupted in the middle of a job and must return to finish it after 5–15 minutes. If the surface skins over, the roller will pick up the skin and re-deposit it in another area producing a very patchy surface. The second solvent is the coalescent aid, which generally is a volatile plasticizer that allows the latex beads to flow together after the water and glycol have left the film. The coalescent aid is usually a solvent that evaporates very slowly.

One of the main research efforts today is to eliminate solvents from all coatings. This effort is driven in part by governmental regulations which strive to reduce air pollution. A typical latex paint contains approximately 0.5 lb/gal of VOC. An alkyd can contain between 2.5 and 4.5 lb/gal. The end use and regulations in the area determine the allowable VOC levels.

Solvent selection must also match the resin. Solubility parameters can be used to match the resin with solvents. Hildebrand, Kauri butanol values or Hansen parameters can be used with the latter being the most predictive. The Hansen values uses hydrogen bonding contributions, polarity and cohesive parameters to match solvents. The use of eq. (4) results in better solvent matching (1).

$$\delta_T^2 = \delta_P^2 + \delta_H^2 + \delta_d^2 \quad (4)$$

2.4. Additives. Additives are designed to fix deficiencies with a paint. There are additives for stabilizing a dispersion (dispersants), wetting out the pigment (wetting aids), removing foam (defoamers), destroying the microbes (biocides), corrosion prevention (anti-corrosives), and many more. Some additives are predictably needed, while others are only selected after the paint has been found to have a problem. The combined amount used of these additives is usually small, typically less than 3% of the total formulation. Many paints have ten or more different additives. The cost of the additives can significantly affect the price of the paint. For example, costs for the resin and white pigment are on the order of \$1/lb, the extender, Ca \$0.10 /lb, surfactants can be \$2.50 to as high as \$40 /lb, and uv inhibitors are \$20–25 per pound. It is easy to see that the additives can rapidly raise the price of a coating. The manufacturer must weigh the benefits over the cost of the additive. An additive may kill algae, but if \$1.00 is added to the price of the paint, its sales price may become non-competitive (2).

2.5. Typical Paint Formulations. Paint formulations vary considerably depending on the end use, targeted quality, and sales price. Table 1 illustrates a typical alkyd semi-gloss paint formulation. Table 2 gives an example of an interior high quality flat latex paint formulation.

3. Application and Appearance Properties

3.1. Rheology and the Application Process. The application process for conventional coatings consists of three general stages, regardless of what type of application technique is used. First, the coating is transferred from the container to an applicator, such as a brush, roller, or spray gun. The coating is then, in turn, transferred from the applicator to the substrate to form a thin film. The flow-out of the film surface and the subsequent loss of the solvent through evaporation occurs last. These three application stages depend considerably on the coating's rheology, or flow, properties. Coatings rheology has three components: shear stress, shear rate, and viscosity. Given a rectangular body of liquid made up of many horizontal thin layers, shear stress is the force pulling the top layer sideways divided by the area of the top layer. Assuming that the bottom layer is stationary, but the intermediate layers are pulled along with the top, the shear rate is the velocity of the top layer divided by the depth of the liquid body. Viscosity is the ratio between the shear stress and the shear rate (3). Viscosity decreases in response to an increase in shear rate, and rebuilds as the shear rate drops. At low shear rates, coatings sag, level, and settle. The application processes of brushing, rolling, or spraying of a coating are high shear rate events.

A good coating has a low viscosity under application conditions and remains at a low viscosity for a short time to allow for leveling, but once the leveling has taken place, the viscosity rises enough to resist sag. If the viscosity remains low for too long, the coating will sag. If the viscosity is too high, the coating will not sag, but it will have little to no leveling, and brush and roller marks may consequently be visible on the dried coating.

Solvents, binders, extenders, pigments, and additives all contribute to the rheological properties of the coating. Solvents, binders, extenders, and pigments all affect the high shear rate viscosity of coatings; binders can also affect low shear rate viscosity. Additives usually influence moderate and low shear rate viscosity (4). The formulator adjusts the amount of different thickeners to produce a rheological curve that allows no settling in the can, a low shear condition, good shear thinning to allow for application and a controlled rebuild of viscosity with time to allow flow and prevent sag. The kinetic rebuilding property of viscosity described here is termed thixotropy and the coating is called a thixotropic coating.

3.2. Appearance Properties. The most important contributions to the appearance of a coating are color, opacity, and gloss. When light strikes a coating film, it encounters particles and is absorbed, scattered or transmitted in different proportions depending on the type of pigment.

The color of a coating is a function of the pigment's absorbance properties. The degree to which a coating pigment particle absorbs light depends on the extinction coefficient, or absorbance, of the pigment for that particular wavelength of light. It also depends on the path length of the light through the particle. Most pigments strongly absorb particular parts of the visible light spectrum and are transparent to all others (3). The components of the color of a coating are its hue, lightness, and saturation or chroma. Hue is the term used to describe a

coating as red, yellow, blue, etc. Different hues can be mixed to form new ones, resulting in the continuum of the color wheel. Lightness is an attribute independent of hue that describes the darkness or brightness of a coating. Saturation or chroma describes the vividness or dullness of a coating. This measure is independent of both hue and lightness.

Several conditions determine how a color appears to an observer. Different light sources such as the sun, incandescent or a fluorescent light will cause a difference in the appearance of a coating's color. The appearance change is due to the spectral output of the light source. If a light source does not emit any red light, a red apple will not appear red, but will appear black. The sensitivity of the observer's eyes also affects their perception of a color. The size of the area of the color makes a difference, as larger areas of color look more vivid and bright than smaller areas. The background that a color is placed against affects how it appears. A color sample placed in front of a bright background will appear darker than if it is placed in front of a darker background. The direction from which a color is being observed or illuminated can also change its appearance.

The primary determinant of the hide, or opacity, of paint is its particles' ability to scatter light. The major categories of light-scattering are reflection, refraction, and diffraction. Reflection is the scattering of light off the particles of a coating due to the difference in refractive indices between a particle and the resin. Refraction is the bending of the light that is not reflected off the particle as it enters and travels through the particle. Like reflection, it is caused by differences in refractive indices. Diffraction occurs when light waves pass close by a particle of a coating and are bent behind the particle. Light-scattering by diffraction increases with decreasing particle size until the optimum is reached at approximately half the wavelength of light (3).

The gloss of a coating is mainly evaluated in terms of its specular reflectance, which is measured as the amount of transmitted light that is reflected off of a coating at the angle equal to the incidence angle of a beam of light. As the proportion of light that is reflected increases, the coating film appears lighter.

4. Manufacturing: Milling/Dispersion and Tinting

When an architectural paint is manufactured, all of its raw materials are mixed together in a specific order so that a homogenous mixture is formed, much like a cake batter. This recipe of raw materials, such as the binder, pigments, and additives, must be carefully formulated to ensure that the components are compatible and mix well, and that the final desired appearance and properties of the dry paint will be achieved.

The manufacturing of paints is generally done in three main steps: premix, dispersion, and let down. In general, the premix includes part of the resin in some cases, solvent or water, dispersant, wetting aids, thickeners, biocides, pH modifiers, antifoaming agents and several other additives which are added before the pigments. Dispersion refers to the de-agglomeration of the pigments which is done at fairly high shear rate. Many resins are not stable to the high shear forces in the grind phase. The final phase is let down which refers to the adding in of all the components that remain. Some manufacturing processes can

do all these steps in one vessel, but some require multiple separate steps and pieces of equipment. It depends largely on the coating being manufactured. Some coatings may not require that the three steps are separate, while others do. For example, latex resins can often not withstand the high shear of the dispersion phase, so they are often added in the let down.

Dispersing, or de-agglomerating, the pigments can prove to be one of the most difficult stages of manufacturing paint. The difficulty of this stage depends greatly on the individual pigments because some pigment aggregates are easily separated, while others are not. The equipment used during processing must be selected to account for this difference. Equipment differences are mostly related to how much shear the disperser imparts into the solution. If the pigment's aggregates are easily separated, a low shear dispersing device can be easily used, if the aggregates require more shear to separate them, different equipment must be used, if the pigment is small or of low density, it is usually more difficult to disperse than if it is large and or high density. The shear forces will act more favorably on a larger, higher density cluster of pigment particles than on a small, low density cluster.

4.1. High Speed Dispersers. High-speed disk dispersers provide relatively good shear dispersion with low capital investment and low operating costs. These dispersers consist of a disk mounted to a shaft that rotates at a high speed to disperse pigments relatively easily. High-speed disk dispersers are used in vertical cylindrical tanks. The dimensions of the tank and the disk must be carefully chosen so as to maximize the efficiency of this disperser. High-speed disk dispersers can be used for premixing, dispersion, and letdown without having to switch tanks. In general, these blades are used at a fairly low speed for premixing, then the pigments are added and the speed is increased to separate the aggregates. The speed is then dropped again before adding the let-down components, such as a latex resin. Because the shear stress imparted is relatively low, high-speed disk dispersers cannot be used with aggregated pigments that are hard to separate. However, when they can be used, the added benefit of then being easily cleaned when switching from one batch to another or one color to another is obtained (5).

4.2. Ball or Pebble Mills. Ball mills, or pebble mills, can be used to impart a higher degree of shear. These consist of a horizontally mounted cylinder that is approximately half filled with steel balls in a ball mill or ceramic balls or cylinders in a pebble mill. The cylinder of the steel ball mill is usually made of steel, and that of the pebble mill is made of porcelain. Pebble mills originally used large round pebbles, which is where it got its name. The term ball mill is often used to describe the general type of processing. These mills are effective because there is a thin layer of the mix between the balls that is subjected to high shear when the balls interact. The cylinder is turned at such a rate as to ensure that the balls slide down the slope of the other balls, but slow enough to ensure that they do not fall and impact the other balls. This not only ensures that the balls are not destroyed entirely in the process, but also because this imparts high shear. Even at optimal conditions, the balls will undergo wear. This can sometimes be problematic, because the steel particles from wear can impart a grey hue to the ingredients being mixed. This is not always a problem, since some primers are already grey. When there is a problem, the pebble mill

can be used to avoid this issue to an extent since the ceramic particles are usually white or colorless in the coating. Another important point to note is that the pigment particle size will be changed by this technique. The longer the mill is run, the smaller and usually the broader the pigment particle size distribution becomes. Never ball mill titanium dioxide since it is surface coated to make it uv stable. Ball milling titanium dioxide will damage this coating, and when exposed to uv, will result in yellowing and degradation of the resin. Ball mills do not require premixing, and most pigments can be dispersed with them, but they often require that let down is done in a separate container. The capital costs of ball mills can be high, but the operating cost is quite low, and the ball mills can often be run without anyone in attendance. The size of the ball mill determines the batch size that it can be used for, so they are not very flexible in this regard. Ball mills also can be quite difficult to clean so they tend to lend themselves toward being used for making the same formulation repetitively, and if used for a variety of tinted paints, care must be taken that they are cleaned well and that they are used for the lighter tints before the darker tints to reduce the risk of cross-contamination (5).

4.3. Media or Sand Mills. When media mills were first invented, they usually contained, and many still contain, sand. For this reason they were called sand mills. Now, media mills can contain anything from small ceramic balls, a bead mill, small steel balls, or a shot mill of approximately 1 mm diameter. These mills can be vertical or horizontal. In the vertical version, a high-speed rotor is in the center of the shaft which is partially filled with media. The mill base is premixed and is fed in through a tube in the bottom of the mill. This mill base is exposed to high shear as it flows up the mill because the media particles are rapidly moving and the aggregates are passed between many particles as it goes up the mill and passes through the screen filter at the top. The aggregates can be subjected to more shear by reducing the flow rate or by passing them through the mill repeatedly or by passing them through a series of media mills. Horizontal mills are basically the same system that is set up horizontally instead of vertically. Both the operating costs and capital investment are fairly high for media mills and batch sizes are flexible. Let down, however, must be done separately, and cleaning is difficult resulting in most media mills being committed to a specific color range to minimize problems. Also, while media mills are effective at separating aggregates, the aggregates must be small when compared to the size of the media particles (5).

4.4. Roller Mills. Roller mills were once widely used for dispersion, but their use today has declined. These mills generally fall into two categories: three-roll and two-roll mills. Three-roll mills break up aggregates by passing the mill base through a series of three rollers. The mill base is exposed to the air during this processing, instead of being contained in a closed container, which results in solvent loss if the solvent's vapor pressure is too high. Also, the capital investment and operating costs are quite high for three-roll mills, skilled operators are a definite requirement, and both premixing and let down must be done separately. However, the shear rate is high and this allows the separation of difficult aggregates. In addition, batch size is versatile and the equipment is cleaned easily. Two-roll mills are similar, but have a much higher shear rate and can be used for even the most challenging aggregates. This mill can be extremely

beneficial for use with expensive pigments. As with the three-roll systems, the capital and operating costs are quite high, but the two-roll mills also require further processing if the dispersion needs to be in liquid form for addition to a formulation. These are mainly used with companies that make these specialty dispersions (5).

4.5. Rotor-stator Mills. The high-speed impingement mill is a rotor-stator mill such as the Kady mill. This mill consists of two concentric rings. The mix enters the inner ring, the rotor, and is spun outward through the slots as it rotates. The outer ring has a series of notches in it, and is called the stator. The stator is relatively close to the rotor and does not spin. When the aggregates are spun out of the rotor, they will primarily hit the walls of the stator and the other aggregate particles, resulting in the aggregates breaking apart. No premixing is required, it can be done within the mill. First, the solution, without pigment, is added to the tank before the mill is turned on. The rotor is then started, and the pigment is added to the mixture in the tank. This addition must be carefully done so that the speed of addition corresponds to the amount that can be easily added to the flowing mixture smoothly. Experienced operators are necessary to make this system run smoothly (6).

4.6. Pumping and Transfers. Paint can be shear unstable. Pumps, in general, impart shear. The most effective pumping system used is a diaphragm pump. This air driven system is low in shear and easily maintained. Most paint must be passed through a filter to remove large contaminants that may have entered the paint. A simple in-line bag filter is usually used. Once filtered, the paint then flows to the filling unit where volumetric syringe pumps are used to fill the containers. Due to the large error in filling by volume, weights are taken on filled containers to ensure that each gallon contains at least one gallon of paint.

4.7. In-store Tinting. Paint, once produced, will usually require tinting. After all, it would be cost prohibitive for each store to maintain an inventory of every common color. Typically, stores maintain three bases that are tinted to the desired color. They are usually called a white, a medium base, and a deep base. The white may be used as-is for a white paint or tinted to produce a very light pastel. The medium base contains less titanium dioxide and requires tinting. It is designed for deeper colors and mid-tones. The deep base contains little or no titanium dioxide and is designed for deep fully pigmented colors such as reds, greens, or navy blue. If the customer wished to have a paint match a color, they simply have the store use a spectrophotometer to record the reflectance spectra of the desired color. The computer-based color matching program, which is based upon Beer's and Lambert's laws and the Kubelka-Munk equation, is then used to find a mixture of colorants that will produce the desired paint color. The store personnel then add the calculated amounts of each pigment to tint the paint. Producing the correct database used to do the formulation is difficult to achieve and much care must be exercised.

5. Coating Types and End Uses

Paint can generally be categorized into three groups: flat, semi-gloss or high-gloss. The degree of gloss is controlled in large part by the percentage of free

binder, which is determined by the pigment–volume concentration (PVC). PVC is the percentage volume of pigment in the total volume of the solids in the dried coating film. When paints are formulated above a certain point known as the critical PVC, or CPVC, the dried film will not contain enough binder to fill all of the space between pigment particles, and the paint will become porous. Paints formulated above the CPVC also tend to weather faster outside, in addition to losing some of their abrasion resistance and flexibility (7). Typically, high-gloss paints will have a low PVC of around 15–25% (3). High-gloss paints tend to have better abrasion and stain resistance than flat paints, but they amplify irregularities in the substrate. A high ratio of pigment to volume results in a flatter paint than one with a low PVC.

The gloss of a paint may also be controlled by flattening aids which migrate to the air interface and reduce the specular gloss. These are often used in higher performance coatings where the high extender pigment loading may reduce the performance of the coating. For flat coatings, the size of the extender pigment can be used to flatten the coating. As the size of the extender increases, the probability of the pigment sticking out above the resin increases. When this occurs, the coating gloss decreases. Since larger extender pigments are less costly, this can be a cost effective way to lower the gloss.

5.1. Interior Coatings. The PVC level for interior coatings depends on their intended use. Coatings for ceilings should breathe and obscure small defects, which are properties of high-PVC. The design of today's structures aims to allow moisture to traverse vertically to the attic and escape through the roof vents. Since the walls are lined with plastic, moisture cannot escape through the walls. If the ceiling is painted with a moisture-barrier coating such as a good wall paint, the moisture is trapped in the house and mold and mildew will form, resulting in a sick house. High PVC paints are more porous than low PVC paints, so they interfere less with the acoustic properties of substrates such as plaster and acoustical tile (7). Also, high PVC paints are flat, and therefore obscure slight defects in the substrate. Textured ceiling coating, which is appropriate for concrete, stucco and wallboard ceilings, is another type of coating.

The PVC of wall coatings depends on the desired appearance, although high-PVC, flat coatings can suffer from durability issues. The chosen coating should be preceded by the appropriate preparation of the substrate. Plaster surfaces should be allowed to cure before coating, otherwise the level of alkalinity and moisture may interfere with adhesion. Drywall must have the sanding dust removed and then be treated with a latex-type primer before painting. Alkyd or oil-type primers tend to affect drywall and plaster surface adversely due to their alkalinity, so they should not be used in this instance (7). After the primer dries, the wall can be recoated with a flat, semi-gloss or high-gloss topcoat.

5.2. Exterior Wood Coatings. Wood coatings fall into three categories: paint, stain and varnish. Paint is an opaque coating system that requires priming, filling and finishing a wood surface. These needs can be met by a traditional three-product system, which includes a primer, an undercoat, and a topcoat. One-product systems are also available that perform all three functions. The function of a primer is to seal the grain and provide a smooth surface for the

paint to bond to. Primers serve as a barrier against stains and moisture, as well as an aid bonding between the substrate and coating.

Wood primers usually contain preservatives such as fungicides. These primers tend to be formulated to achieve maximum penetration into the substrate at the expense of a contribution to film building (3). The undercoat helps cover sharp edges and adds opacity to the system. Topcoats are often high-gloss finishes that are formulated to be highly durable, but also flexible enough to withstand the fluctuating dimensions of the substrate. There are two major difficulties associated with painting wood. Because paint has a low degree of moisture permeability, water can become trapped and cause decay underneath the coating. Also, expansion and contraction of the wood due to moisture changes as well as temperature leads to cracking, flaking, and peeling (7). Many coatings today are more elastic and can track the movement of the wood without cracking.

The most common alternative to paint is a stain. A stain is a penetrating compound that contains a preservative and is semi-transparent. Stains should contain a type of fungicide to inhibit fungi growth on the surface of the substrate. The volume of solids in a stain has a high impact on its performance. A low-solids stain does little to prevent moisture movement through the substrate, which can lead to splitting and warping. By increasing the volume of solids to create a high-solids stain with a thicker film, a higher degree of moisture resistance is achieved. However, the thicker film can result in the same type of cracking as occurs with paint. Raising the level of solids also decreases the degree of penetration into the substrate. These stains perform best when applied to wood that has been pretreated with a low-solids coating.

Varnish is a solvent-borne, transparent, glossy coat. It wears better than stain on high traffic areas such as doors. A problem with varnish is its susceptibility to photodegradation and yellowing. This can be combated by the addition of a uv absorber.

Wood is readily degraded by uv. Ultraviolet light degrades the lignin that binds the cellulose bundles together. When the lignin is destroyed, the wood will become black and the cellulose bundles will begin to unravel. This also makes the wood more susceptible to water attack (8). Wood coatings must therefore block uv from reaching it. The use of titanium dioxide pigments will effectively block uv, however for clear coats, uv absorbers or nano-scale titanium dioxide, <10 nm, will help. Titanium dioxide particles of less than 10 nm do not scatter visible light, but still absorb it.

In addition to varnishes, today clear water-borne wood finishes are also available. These are often based upon a dual resin approach. It may contain a urethane dispersion and an acrylic latex resin. Grain raising is a problem when clear coating new wood. These coatings are finding an increased market due to the VOC restrictions.

5.3. Masonry Coatings. Paint used to coat exterior masonry is typically formulated with a PVC similar to an interior flat paint at 30–45% (3). Primers intended for use with masonry often contain alkali-resistant components to combat the alkalinity of dried masonry. These alkali-resistant primers can also be used to improve the adhesion of paint on plaster substrates (3). Concrete must be freed from oil and dirt before the application of a coating in order to ensure maximum adhesion. Concrete walls can be treated with a latex-type primer,

and then recoated with a flat, semi-gloss, or high-gloss topcoat. New concrete floors need both cleaning and acid-etching to allow for maximum coating durability. After the concrete is etched and all traces of the acid have been removed, the floors are treated with sealers to increase moisture resistance and decrease the rate of wear. These sealers should have low viscosity to allow for penetration into the substrate. If the floor is to be painted directly, the first coat can be thinned in order to allow the coating to penetrate the concrete and provide a better bond between the substrate and the paint. Alkyd coatings should not generally be used on concrete since it is highly alkaline and will hydrolyze the resin forming calcium soaps which are mold-release agents under the coating and the resultant loss of adhesion will cause massive delamination (7).

6. Analysis and Testing

6.1. General Properties Testing. A grind gauge is a test method, ASTM D1210, used to determine the fineness of grind of the pigment dispersion. A grind gauge consists of a metal block with a groove. A small sample of paint from the pigment dispersion grind is placed on the top part of the groove, the deepest part, and is pulled down the plate with a metal scraper. The gauge is then inspected visually for where the pigment particles are visible. If the pigment is properly dispersed, this will correspond to the manufacturer's reported pigment size. Several scales can be used, including the popular Hegman scale.

There are many different ways to measure viscosity. The three main methods measure by rotational, efflux, and comparison methods. Comparison methods are by far the most simplistic method. An example of this method is using bubble comparison tubes, Gardner tubes. Each standardized tube contains a liquid of known viscosity and a bubble. The sample is placed in a similar tube and is inverted and compared to the known tubes. The viscosity is assigned as the number of the tube whose bubble moves at the same speed as that of the sample. Two of the more prominent efflux methods, Ford cup and Zahn cup, involve a metal cup with an orifice in the bottom that is filled with paint while the hole is covered. When the fluid is released, the time until the stream breaks is recorded and is used to determine viscosity. Rotational viscosity is often a preferred method for determining viscosity. The two most common rotational viscometers are the cone and plate and Stormer viscometers. The Stormer viscometer, ASTM D562, consists of a shaft with a paddle on the end which is submerged in a paint sample. The paddle moves at a set speed and records the force required to rotate the paddle blade. The viscosity measurement is often reported in Krebs units (KU). The cone and plate viscometer, ASTM D4287, is much more complex and involves a series of cones and a plate and varies speed or shear rates to better analyze the effects of high shear on the coating. This method will produce a useful curve which will help determine the thixotropy of a coating.

The percent of solid material in a paint is an important characteristic because it helps determine the thickness of the dry film and thus impacts the hide of the paint. Percent solids can be determined several ways, such as ASTM D4758 and ASTM D2369. One method involves a set mass of paint being dispersed in a set volume of appropriate solvent. The sample is then placed

in an oven for a set length of time and then cooled in a desiccator. After cooling, the weight is determined and the percent solids is calculated based on the difference and the amount of paint in the original sample.

A coating's density is often reported in pounds per gallon as its weight per gallon. To determine weight per gallon, a density cup is used. This cup consists of a small metal cylinder with a lid. The inside of the lid is conical with the point of the cone having a small hole in the center. The cup is filled and the lid is put in place. Ideally, a small amount of the cup contents should come up out of the hole in the lid. This shows that the cup is entirely full and that there are no air bubbles inside. The cup is then wiped clean. The cup is calibrated by determining the difference in weight between the empty cup and the cup filled with water. This difference should be 8.33 pounds per gallon. A coating is tested in much the same manner: the cup is filled, and the weight difference is determined resulting in the weight per gallon of the coating.

The length of time required for a given paint to dry is an important factor as it affects how long the coating must dry before another coat can be applied as well as how long a coating must dry before contact. This property is particularly important in coatings for flooring and other such applications. One method for determining dry time utilizes a mechanical dry time machine, ASTM D5895, which drags a stylus through the wet paint that has been applied to a glass strip. The machine can be set to one of several speeds depending on the coating being tested. These speeds include 6 hours, 12 hours, and 24 hours. After the coating has dried and the stylus has finished dragging through the coating, the coating is examined to determine the distance from the start point to each of the four phases of drying. This can be determined because each phase of drying results in a different type of mark on the coating, from a line of exposed glass to just a slight mar on the surface, to no marks whatsoever. The speed of the stylus can be measured and can be used to convert the distance measurements to times. A second method, ASTM D1640, involves a more subjective approach to determining dry time. In this method, the coating is applied to a glass plate and is continually checked during drying to determine the five phases of drying. In the first phase, the coating is touched with a clean finger at intervals and is touched to a piece of clean glass. When no more paint is transferred, the coating is dry to the touch. In the second phase, cotton fibers are dropped on the coating and when they no longer stick to the coating after blowing across it, the coating is dry to dust-free. The third phase uses a tack-tester to determine tack-free time, the fourth involves pressure of the thumb on the surface to determine dry-hard, and the fifth phase uses thumb pressure in a twisting motion to determine dry-through time.

Package stability, ASTM D1849, examines how well a paint recovers from a period of time at a high temperature which can be related to how well a paint can sustain the high temperatures associated with shipping, storage in a garage, etc. In this test, the paint is kept at a high temperature for thirty days and then is returned to room temperature and evaluated for gellation and other modes of failure as well as changes in weight, gloss, color, and other properties.

Freeze-thaw resistance testing, ASTM D2243, examines how well a paint deals with changes in temperature in the range from room temperature to sub-zero temperatures. In this test, the paint is cycled for eight days with each day

consisting of 17 hours at a freezing temperature and 7 hours at room temperature. The paint is drawn-down at specific intervals, such as after the first, third, fifth and eighth cycle and is evaluated for changes in gloss and color. The paints are examined after each cycle, even the ones not requiring draw-downs, for failure such as gellation.

The color and hiding ability of a paint are often extremely important. Color can be analyzed using a variety of methods. Spectrophotometers, or color computers, are often employed as a method of providing numerical data with which to identify a sample's color within three dimensional color space. Several sets of three dimensional axes can be used, such as $L^*a^*b^*$ and XYZ. The axes in the color space relate how light or dark and how red, green, blue or yellow the sample is. Spectrophotometers can also be used in comparisons between samples to analyze shifts in color as a result of different batches or after staining. Spectrophotometric methods provide reproducible data that is can be more accurate than visual comparisons. The hiding ability of a paint can be determined from a simple contrast ratio. A paint is applied to a black and white chart, allowed to dry, and then a spectrophotometer is used to collect data of the color of the paint over the black and over the white. Then, if the $L^*a^*b^*$ axes are used, the L^* over black is divided by the L^* over white to give the contrast ratio, an indication of the hiding ability of a paint. A contrast ratio of greater than 99.5% is typical of a good one-coat hide paint.

A gloss meter can be used to determine the gloss of a dry coating sample. The angle of incidence that a gloss meter can analyze depends on the gloss meter, with the most common angles being 20, 60, and 85 degrees.

6.2. Performance Testing. The ability of a paint to resist wet abrasion is often measured as its scrub resistance, ASTM 2486. To determine this characteristic, a standard brush with abrasive media is pulled back and forth across a film of uniform thickness by a mechanical scrub machine. The number of cycles until wear-through is then recorded as an indication of the paint's wet abrasion resistance.

A coating's ability to resist dry abrasion can also be an important characteristic especially for floor coatings. This characteristic is often tested using a circular or linear abrasion tester, ASTM D4060. A circular abrasion tester rotates the sample like a record underneath abrasive disks, while a linear abrasion tester runs an abrasive back and forth along a straight line across the sample. To test abrasion resistance, the samples are coated, cured and weighed. Then, the samples are run for a specified number of cycles and are re-weighed. The weight difference is used as an indication of abrasion resistance. A variety of abrasives and weights can be used to best evaluate the abrasion resistance of the paint.

It is preferable for a paint to be able to withstand marring that would result from objects rubbing across the paint causing a change in gloss. A paint's mar resistance, ASTM D6037, can be evaluated in a similar manner to that used in the abrasion testing mentioned above. Instead of measuring weight, the sample's gloss is evaluated before and after a specified number of cycles, and the change in gloss is used to evaluate the mar resistance of the paint.

A coating's resistance to staining or stain bleed-through is another important characteristic. One method to evaluate stain resistance is to cast and cure a film of the paint and apply a series of stains to the dry paint, ASTM D4828. The

stains are allowed to dry and then are washed with a standard sponge, loaded with a nonabrasive media, either by hand or with a mechanical scrub machine. The stained areas are then evaluated for changes in color and gloss. Stain bleed-through can be analyzed in several methods. One method evaluates tannin bleed-through, ASTM D6686. This property is important because some paints are applied over woods. In this method, the paint is applied over wood, and after a period of time, often at elevated temperatures, the color is evaluated to determine how much the wood's tannin bleed affects the color of the coating. Because some paints are applied over existing stains, the ability of a paint to resist bleed-through staining is important. To examine this property, stains are applied to a substrate, such as drywall, and allowed to dry. The paint is then applied over the stains. After drying, color measurements are taken and compared to a standard applied to the same substrate to determine how much of the stain bled-through the paint.

Blocking resistance, ASTM D4946, is measured by casting and curing a film on a chart which is then cut into six squares. The squares are then paired and placed face-to-face under weights in an oven for an hour. The squares are then cooled to room temperature and are peeled apart and the degree of sealing is evaluated. This test is important since when the door and jam are both painted and allowed to dry, if the coatings have poor block resistance the door will stick shut when closed. A typical door has approximately 100 in² of surface area which can be in contact. If as little as 10 lbs/in² adhesion occurs, the door will take as much as 1,000 lbs of force to open it.

When a brush is used to apply a paint, the brush often leaves brush strokes behind if the paint exhibits poor flow and leveling. A paint that exhibits good flow and leveling characteristics easily reduces the appearance of brush strokes by allowing the paint to flow so that the surface levels itself. The New York Paint Club leveling bar is often used to evaluate flow and leveling, ASTM D4062. It evaluates a set of parallel lines of paint of different thicknesses and their ability to flow together. All tests of this type are dependent upon application. Textured paints should have little flow while high gloss finishes must have good flow.

Sag is the continued flow of a coating after it has leveled. An anti-sag bar is used to draw-down a sample of the paint on a chart in ASTM D4400. An anti-sag bar consists of a series of stripes that increase in thickness. The paint is drawn-down and the chart is turned so the stripe with the highest film thickness is across the bottom after the coating is applied. As the film dries, paints with poor sag resistance will sag from one line to the next. Those with higher sag resistance will not sag as much. The dried coating is evaluated by determining the highest film thickness which resisted sagging.

Most architectural paints are exposed to some degree of ultraviolet radiation, even if they are interior coatings, although exterior coatings obviously are subjected to much more exposure. An accelerated weathering chamber is often used to analyze the effects of ultraviolet radiation and/or condensation exposure. This test, ASTM D4587, is often called a uv weatherometer test. This chamber consists of ultraviolet light bulbs and a heater to induce condensation. Most of these units can be used for solely ultraviolet radiation, solely condensation, or a combination of the two exposures as a cycle, making them quite versatile for different types of accelerated exposure testing. Two other uv

accelerated weathering test cabinets have been used are carbon arc and xenon arc weatherometers and conform to ASTM D822/D5031 and ASTM D3424/D4303, respectively. In addition to the accelerated uv testing, paint manufacturers usually do exterior exposure studies in Florida, Arizona, and often New Jersey. Each of these environments offer a unique set of advantages. Arizona is dry and high in uv, Florida has both uv and rain, while New Jersey offers uv, freeze/thaw, rain as well as low pH rain, ie, acid rain. Typically, paints are exposed for many years with periodic evaluations.

Another type of accelerated testing unit is a salt-fog unit, ASTM G85, which consists of an enclosed chamber which can be used to expose samples to different types of condensation such as constant fogging, assorted salt fogs, fog-dry cycling, etc. The reservoir tank can be filled with any salt solution desired, and several standard salt solutions are recommended in ASTM or other protocols. Some coatings are subjected to cohesion testing, which cycles the samples between uv's ultraviolet, with 4 hours uv cycles and 4 hour cycles of condensation without uv alternating for 7 days and salt fog, for 1 hour and dry cycling for a 1 hour period with repeat cycling for 7 days with the 14-day cycle being repeated as many times as needed.

The surface tension of a paint can be an indication of the foam stability of a paint, or how easily foam is dispersed in the paint. Surface tension can be analyzed in several different ways. In the ring method, ASTM D1331, a ring of very fine wire of known diameter and thickness, often platinum iridium wire, is dipped into a temperature equilibrated sample of the paint. The wire is then withdrawn at a constant speed recording the force and distance traveled while pulling the ring out of the paint until it breaks completely free. These values can then be used to calculate the surface tension.

It is also desirable for a paint to exhibit good adhesion properties. The ability of a paint to adhere to a substrate, such as wood or drywall, can be tested by several means. The most common methods are tape, ASTM D3359, and puck adhesion tests. In tape adhesion testing, the paint is applied to the substrate and allowed to dry. Then a series of cuts are made in the film and pressure sensitive tape is applied over the cuts and removed, and the degree of paint removed is analyzed, with perfect adhesion resulting in no removal. The cuts can be made as a series of lines at specific intervals, made by using a guide, or by two cuts making an X on the film. The tape is removed rapidly and as close to itself as possible to eliminate complications resulting from the angle of the tape pulling. There are several methods of testing adhesion with pucks instead of tape. The substrate is once again coated and allowed to dry, but once dry, metal pucks are attached to the surface with an adhesive, and a cut off ring is used to ensure that the puck is only adhered on the bottom and not on the sides of the puck. After drying, the pucks are removed. The pucks can be removed by a torque wrench which provides values for the maximum force required to remove the puck by twisting the pucks off. The pucks can also be removed by a pull-off adhesion tester which pulls the puck straight off the substrate, and provides the maximum force required to remove the pucks straight off the substrate. It is important to note that the substrate of the pull-off adhesion must be thick enough to not bend while the pucks are being removed, which would reduce the validity of the acquired data. These methods can be used to test the paint's

adhesion directly to a substrate, to an undercoat, such as a primer, or as the undercoat with a top coat applied over the coating. All of these provide different information about the adhesion of a paint.

Sometimes when a coating is applied over wood, such as door or window trim, the grain of the wood can be raised through the paint resulting in a textured surface. This grain raising is evaluated by tactile and visual inspection of a paint after it has been applied to a wood substrate and allowed to dry. Water-borne coatings are more prone to this problem than solvent borne.

7. Economic Aspects

In 2003, the United States coatings industry shipped 1.46×10^9 gallons of paint and allied products, valued at $\$18.1 \times 10^9$. Shipments of architectural coatings amounted to 773×10^{10} gallons, with a value of $\$8.1 \times 10^9$. Architectural coatings account for 52.9% of the quantity of coating shipments, and 44.8% of the shipments' total value. The cost to the manufacturer averages \$10.49 per gallon of architectural paint, and \$12.37 per gallon of all coatings. Table 3 is a summary of total quantity and value of shipments of architectural coatings in the U.S. (9).

The total cost of materials consumed by the U.S. paint and coatings manufacturing industry in 2002 amounted to $\$9.36 \times 10^9$, as opposed to $\$8.92 \times 10^9$ in 1997. In 2002 the U.S. paint and coatings manufacturing industry was comprised of 1,139 companies and employed 46,086 people. Of these companies, 170 made shipments of architectural paint valued at over \$100,000, and only 166 companies specialized in architectural coatings. In 1997, the industry had 1,205 companies and employed 52,772 people (10).

8. Health and Safety Factors and Environmental Concerns

Coatings impact all of the major health, safety, and environmental areas. The safety issue relates to the flammability of the coating. The health issue covers the toxicity of the components in a paint which may be ingested, inhaled or absorbed through the skin. The environmental areas include heavy metal contamination such as lead, VOC emissions which may form smog, ozone depleting substances, ODS, which many help destroy the ozone layer as well as waste and spill issues which may contaminate ground water.

Today, the major issues of paint revolve around safety and the environment. Coatings for architectural application are generally formulated to minimize health issues and make the coating as environmentally safe as possible since the consumer is not as technically aware of these issues. Many federal, state, and regional rules have been established to regulate the amount of VOCs a given type of paint can have. A 2.5 lb/gal-VOC paint may be acceptable for Kansas, but not for Southern California. Therefore the VOC content of paints are carefully monitored to meet these regulations. In addition to VOC, the hazardous air pollutants, HAPs, under the Federal Clean Air Act are an important consideration. Coatings manufacturers are required to minimize the content of these components in the paint which are potentially hazardous air pollutants.

New low and zero-VOC technologies are being developed by coatings, resin, and raw materials manufacturers to ensure regulatory compliance without a dramatic cost increase and also without sacrificing coating performance (11,12). Several solvents are considered to be exempt. Currently these include acetone, methyl acetate, water and 4-chlorotrifluoromethyltoluene.

The lead-based paint remediation in homes, offices, and any structure built prior to 1978 is still a significant issue. Federal law now requires all homes built prior to 1978 to be checked for lead prior to sale. Lead poisoning, primarily in children, has been linked to ingestion of paint dust and/or chips containing lead. Paint manufacturers began to phase out lead even prior to 1950. However some lead was used up to 1978. Lead paint removal is costly and when disturbed will create more dust which will only increase problems. Most efforts have been targeted at over-coating the lead paint to secure it and prevent any dusting. Loose chips are removed and rigorously cleaned before allowing children into the areas. Encapsulation of the lead in this manner will reduce exposure of the occupants to lead.

Crystalline silica also poses a potential health risk. Crystalline silica dust can cause lung problems if inhaled. If a coating contains crystalline silica above the government set level, it must have a warning statement on the label. Many end users have specifications which preclude the use of these paints.

Much of the research effort in the paint industry today is targeting environmental issues. Manufacturers are continuously developing new technologies to reduce the environmental impact of paint and maintain or improve the performance of the coating while keeping the cost down.

BIBLIOGRAPHY

"Paint" in *ECT* 1st ed., Vol. 9, pp. 770–803, by H. E. Hillman, Eagle Paint & Varnish Corp., W. G. Vannoy, E. I. du Pont de Nemours & Co., Inc., and R. Carlisle and L. K. Doraiswamy, R. L. Carlisle Chemical & Manufacturing Co., Inc.; in *ECT* 2nd ed., Vol. 14, pp. 426–485, by D. Cannell, The Sherwin-Williams Co.; in *ECT* 3rd ed., Vol. 16, pp. 742–761, by G. G. Schurr, The Sherwin-Williams Co.; "Paint (Architectural)" in *ECT* 4th ed., Vol. 17, pp. 1049–1069, by A. A. Leman, Rohm and Haas Co.; "Paint, Architectural" in *ECT* (online), posting date: December 4, 2000, by A. A. Leman, Rohm and Haas Co.

CITED PUBLICATIONS

1. A. F. M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Inc., Boca Raton, Fla., 1983.
2. J. V. Koleske, R. Springate, and D. Brezinski, "2005 Additives Guide", *PCI Paint & Coatings Industry* **21**, 5 (May 2005).
3. R. Lambourne, ed., *Paint and Surface Coatings: Theory and Practice*, Halsted Press, New York, 1987.
4. *Rheology Handbook: A Practical Guide to Rheological Additives*, Rheox, Inc., Hightstown, N.J., 1991.

5. Z. W. Wicks Jr., F. N. Jones, and S. P. Pappas, *Organic Coatings Science and Technology*, 2nd ed., Wiley-Interscience, New York, 1999.
6. T. C. Patton, *Paint Flow and Pigment Dispersion*, John Wiley & Sons, Inc., New York, 1964.
7. G. E. Weismantel, ed., *Paint Handbook*, McGraw-Hill Book Co., New York, 1981.
8. T. Daniel and co-workers, *JCT Coatings Tech.* **1**, 9 (Sept. 2004).
9. *Paint and Allied Products: 2003*, Current Industrial Reports, MA325F(03)-1, U.S. Census Bureau, Washington, D.C., 2004.
10. *Paint and Coating Manufacturing: 2002*, 2002 Economic Census Manufacturing Industry Series, EC02-31i-325510(RV), U.S. Census Bureau, Washington D.C., 2005.
11. K. Pianoforte, *Coatings World*, **10**, 5 (May 2005).
12. C. Challener, *JCT Coatings Tech.* **2**, 12 (Jan. 2005).

GENERAL REFERENCES

References 5 and 7 are also general references.

M. Ash and I. Ash, *Handbook of Paint and Coating Raw Materials*, Volume 1: Trade Name Products, Gower Publishing Limited, Vermont, 1996.

Annual Book of ASTM Standards, Section 6: Paints, Related Coatings, and Aromatics, ASTM International, Pennsylvania.

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Table 1. A Semi-Gloss Alkyd White Paint Formulation

Material	Lb	Gal
alkyd resin high solids	243.18	29.16
Rule 66 Mineral Spirits	36.70	5.70
bentonite rheology modifier	3.67	0.43
dispersant	12.47	1.55
titanium dioxide	220.00	6.61
silica 10 micron	400.00	17.75
high speed disperse to Hegman 6 grind		
alkyd resin high solids	156.00	19.02
cobalt drier 6%	3.05	0.37
manganese drier 6%	3.07	0.37
zirconia drier 6%	3.02	0.37
calcium drier 6%	3.81	0.47
antiskinning aid	3.67	0.48
Rule 66 mineral spirits	128.44	20.07
<i>Total</i>	<i>1217.08</i>	<i>102.35</i>
Typical performance data for semi-gloss alkyd white formulation are as follows		
non-volatile	83.14%	
VOC	245 g/L	
	2.05 lb/gal	
PVC	37%	
pigment to binder ratio	1.72:1	
Stormer viscosity	91 KU	
ICI	5.1 Poise	
gloss	5–20°, 20–60°, 42–85°	

Table 2. An Interior High Quality Flat Latex Paint Formulation

Material	Lb	Gal
water	200.0	24.01
glycol	30.2	3.63
cellulose thickener	1.5	1.30
nonionic surfactant	2.0	0.22
mineral oil defoamer	2.0	0.25
in can biocide	2.3	0.25
amine pH modifier	2.0	0.25
titanium dioxide	200.00	5.45
calcium carbonate	100.00	5.45
clay	100.00	5.35
high speed disperse Hegman 4 grind		
defoamer	2.0	0.25
vinyl acetate latex resin	450	50.85
coalescent aid	15.8	1.99
associative thickener	7.5	0.75
<i>Total</i>	<i>1115.3</i>	<i>100.00</i>
Typical performance data for an interior high quality flat latex paint formulation are as follows		
non-volatile by volume	40.3%	
VOC	1.39 lb/gal	
PVC	40.3%	
Stormer viscosity	101 KU	
gloss	4–20°, 8–60°, 10–85°	

Table 3. **Estimated Total Quantity and Value of Paint and Allied Products Shipments**

Year	Quantity, $\times 10^6$ gal	Value, \$	Value/Quantity
2003	772.8	8,104.5	10.49
2002	709.8	7,610.1	10.72
2001	667.0	7,038.3	10.55
2000	650.6	6,461.4	9.93
1999	660.2	6,617.9	10.02
1998	631.6	6,115.2	9.68