Generic Scenario: Formulation of Latex/Emulsion Coatings

Introduction

Latex coatings dominate the architectural coatings market in the United States because they are have good physical properties, are easy to apply, have minimal odor, are nonflammable, form a film at ambient temperatures, and clean up easily with water. In the industrial finishing market, use of latex coatings reduces in-plant volatile organic compound (VOC) emissions and therefore the power required for engineering controls on air emissions [9]. The market for latex coatings in industrial original equipment manufacturer (OEM) products, and in special-purpose coatings applications should increase in the coming years due to the development of better performing coatings with low or no VOC [10].

Most latex resins used in latex coatings formulations are prepared by emulsion polymerization as small, discrete particles of high-molecular-weight polymer or polymer precursor dispersed in water. Film formation is by coalescence (coming together of latex particles) at ambient temperature with the final film properties improving for days or weeks [8]. Although latex coatings sometimes are called "emulsion coatings," true emulsions are stable dispersions of one immiscible liquid in another [9,10]. Some true water-based emulsion coatings, such as emulsified epoxies, can be used alone or to crosslink acrylic latexes for tailoring coating performance properties [11,12].

Market

The current U.S. production of waterborne coatings has grown to approximately 24.5% of all coatings produced in the United States in 1991. Growth is expected to continue at a rate of 5 to 6% through 1999 [1,2,3,4]. Waterborne coatings (latex and water-reducible) are capable of decreasing VOC emissions, eventually approaching "zero" VOCs. The development of "zero-VOC" latex paints will require improved nonvolatile coalescing and wet edge agents that can reduce or eliminate VOCs while maintaining good performance. Developments of thickeners and better pigment dispersants have already improved flow and leveling, color uniformity, gloss, hiding, and resistance properties. Recent advances in latex coating technology include greater use of liquid additives, low-VOC or zero-VOC additives, microvoid pigments, mixed water-reducible and latex coating systems, automated production methods, and extensive reformulation to reduce the number of ingredients and interactions [5,6,7].

According to the U.S. Department of Commerce, U.S. paint sales totaled $12.3 billion for 1.1 billion gallons in 1992 [2] among three coatings groups: architectural coatings, industrial product (OEM) coatings, and special-purpose coatings. Latex paints hold approximately 70% of the North American architectural paint market and approximately 15% of the industrial finishing market [5]. For U.S. sales of about 450 million gallons in 1992. The latex architectural coatings market is estimated to grow to 85% by 1999 [5]. Latex coatings dominate the U.S. architectural coatings market because they are have good physical properties, are easy to apply, have minimal odor, are nonflammable, form a film at ambient temperatures, and clean up easily with water. In the industrial finishing market, latex coatings reduce in-plant VOC emissions and the power required for emission engineering controls [9]. The market for latex coatings in industrial OEM products and special-purpose coatings applications should increase in the coming years due to the development of better performing low-VOC or no-VOC coating [10].

Industry Background

The U.S. paint and coating formulation industry has at least 1,000 companies ranging in size from less than 10 employees to more than 1,000 [3]. Latex paints are manufactured in a batch process (typically 1,000 to 5,000 gallons per batch), although pigment dispersion may be semicontinuous. Use of statistical process control and computer-controlled production is increasing. Architectural paint formulators often produce two or three product lines of varying quality, comprising of two or three base paints each. One base paint is designed to be used alone or tinted to light colors. The second and third are formulated to maintain the correct tinting strength (volume of white pigment) for making medium or deep colors [10].

Latex paint production facilities are run much like food processing plants because microorganisms can attack latex paints in the can and in the final film. The water, the alkaline pH, and the thickeners as potential food sources all support bacterial growth. Good material handling and clean plants can minimize contamination by microorganisms. Pipes, pumps, tanks, and other equipment contacting latex coatings must be resistant to water corrosion. Stainless steel, glass-clad metal, or plastic components often are used. All aqueous raw materials including the latex must be protected from contamination. Equipment must be kept clean and free of lingering paint. Bactericides are needed to prevent spoilage that would change paint properties in the can. Fungicides are added to control mildew growth on the paint film after it is applied.

Composition of Latex Coatings

Latex coatings formulations often are complex, containing 15 to 25 ingredients of four types: (1) latex polymer, (2) pigments, (3) water, and (4) additives. Table 1 shows a typical formula for white latex paint.

Table 1. Typical Formula for White Latex Paint

Material	Pounds	Gallons
water	216.6	26.07
aqueous ammonia	2.1	0.28
antimicrobial	1.6	0.12
dispersing agent	12.3	1.24
ethylene glycol	52.4	5.66
diethylene glycol	20.4	2.57
wetting agent	1.0	0.12
defoamer	1.0	0.14
rutile TiO_2 pigment	256.7	7.45
water	97.4	11.73
dispersant	3.1	0.45
thickener	2.8	0.28
acrylic latex	400.3	45.74
defoamer	1.0	0.14
total	1069.0	102.00
manufacturing loss (2%)	1048.0	100.00

Volume solids (%)	29.3
– pigment vol.	7.3
– resin vol.	22.0
Wt/gal	10.48

Latex polymers generally are purchased by paint producers ready for formulation into coatings. In the United States, the main types of latex polymers are acrylic esters, vinyl esters, or a combination of the two to produce desired end properties. Relatively low-cost vinyl acetate latexes are used extensively for interior latex coatings. Acrylic latexes are used in exterior paints for good exterior durability. Styrenated acrylics produce higher gloss finishes. Vinylidene chloride comonomers are used increasingly in metal coatings to reduce water permeability of the final film. The choice of monomer affects pH and pH stability, mechanical properties of the final film, UV stability, color stability and retention, chemical resistance, odor, and water resistance. Commercial latex polymers include proprietary components such as surfactants to aid in emulsion polymerization and to stabilize the latex prior to coating formulation, as well as trace amounts of salts, monomers, and initiator fragments.

Pigments are insoluble particles used to provide color, hide substrates, modify application properties, improve final film properties, or reduce costs. Pigments, supplied to the formulator as dry powders, press cakes, or slurries, comprise four broad classes: white, inert extenders, color, and functional [8,10]. Titanium dioxide is the most important pigment in latex coating formulations. White pigments such as zinc oxide (still used as a fungicide), zinc sulfide, and lithopone are not used widely today. Inert extender pigments including calcium and magnesium carbonates, a wide range of clays, magnesium silicates, talcs, silicon dioxides, barium sulfate, and a few organic materials such as ground propylene or finely chopped synthetic fibers are added to adjust rheological properties of the liquid coating and to reduce cost. Color pigments provide color. Functional pigments modify some film property such as corrosion resistance [10].

Additives to control properties in the liquid state include surfactants (wetting agents, dispersants, defoamers), glycols for freeze-thaw stability, coalescing agents to improve film formation, fungicides and bactericides, pH control agents, thickeners, solution polymers to promote adhesion over chalky substrates, and sequestrants to control undesired ions in water. They often are sources of additional VOCs, detrimental to final film properties, and relatively high in cost. Secondary effects and interactions between them can complex.

Surfactants include anionic surfactants used primarily to wet and disperse pigments, nonionic surfactants to stabilize total dispersed systems, and defoamers (antifoam agents) used to prevent or control foam formation in paint during manufacture and application. Surfactants comprise only 0.2 to 3.0 % by weight of latex coatings but are indispensable to dispersion and system stability.

Process Description

Latex paint manufacture involves

- pigment dispersion
- mixture with latex polymer and additives
- tint and quality control
- dispensing as shown in Figure 1.

Pigment dispersion, one or more dry pigments are mixed with water, wetting agents, dispersing agents, and defoaming agents in the mix tank. The type of dispersing equipment used depends on the physical and chemical state of the pigment. Commonly used types of equipment include sand and bead mills, ball and pebble mills, attritors, vibration mills, stone and colloid mills, high-speed blade dispersers, and high-speed impingement mills [13,14,15].

Many operations now use titanium dioxide slurries and other inert pigments to reduce or eliminate pigment dispersion and reduce production time, labor costs, and waste. Handling, airborne dust, and raw material waste are controlled by pumping and metering slurries directly from on-site storage tanks into mixing tanks. Pigment addition and dispersion time can be reduced from 60 minutes to 10 minutes. The formulator mixes the pigment slurry or slurries with some water and defoamer.

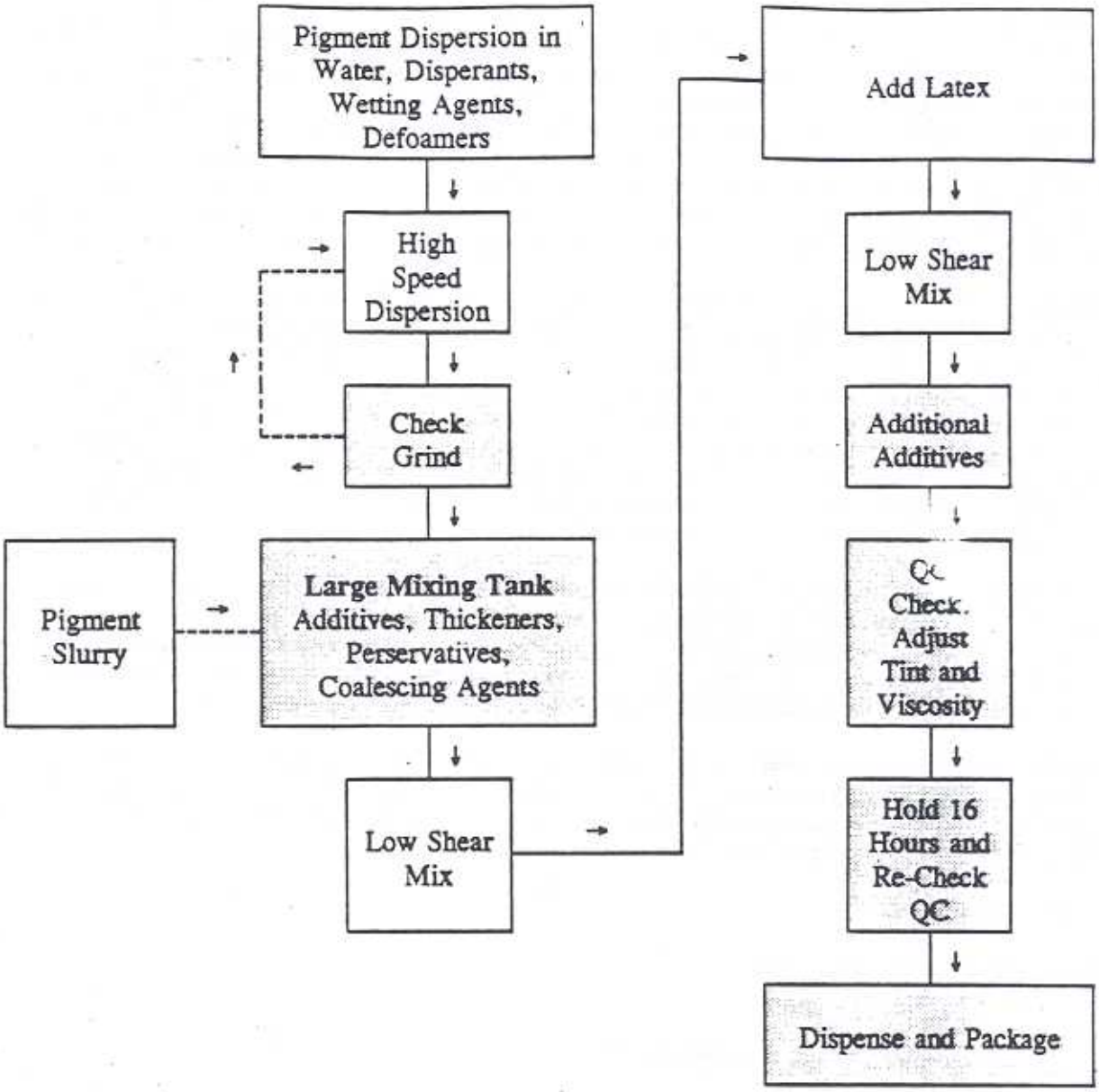

Figure 1. Flow diagram of latex formulation*

The dispersed pigments are diluted with water and other ingredients in large mixing tanks. Most additives are dispersed in the pigment/water before adding the latex polymer to avoid coagulating the latex or destabilizing it with high shear mixing. Thickeners, preservatives, and additional coalescing agents are added with low shear mixing after addition of the latex polymer. The batch is thoroughly mixed, checked for quality, adjusted for tint and viscosity, held for 12 to 16 hours for stabilization, and rechecked before being dispensed into containers for

*Gray areas indicate steps with potential worker exposure.

shipping. The finished coating can be discharged by gravity flow from the tank bottom to the dispensing equipment or by pumping. The finished coating is usually filtered as it is dispensed to remove any solid impurities that might interfere with application.

Waste Generation

The principal sources of waste in the formulation of latex coatings

- rinse liquid and sludge from equipment cleaning
- liquid paint from spills and off-spec paint
- raw materials not fully removed from bags and drums
- deposits on filters
- product returns.

Manufacturing loss per batch is estimated at 1 to 2% by weight of raw materials. Raw materials are expensive, so efforts are made to convert all materials purchased into product. Based on an annual production of 500,000 gallons of latex coating similar to the typical formulation above, a formulator could generate 53,000 to 100,000 pounds of waste solids per production year.

To minimize the volume of liquid waste, production schedules are arranged to formulate similar batches of paint one after another. Some plants minimized cleaning by dedicating dispersers and tanks to one paint type. Production equipment is flushed with water or water/ammonia mixture. A 1,000-gallon tank and pipes can be flushed with as little as 5 to 10 gallons of liquid. For a facility making 500 batches per year, 2,500 to 5,000 gallons of cleaning liquid could be generated. Some of this cleaning liquid can be recycled into subsequent batches of similar paint or used more than once for equipment cleaning. Nonhazardous rinsewater that cannot be reused or recycled is pumped into tanks for flocculation and settling. The heavy particles that settle out are disposed of as wet sludge or dried in drying beds to minimize weight. Sludge can be landfilled or incinerated. The relatively clear, nonhazardous liquid can be disposed of in public sewers. Rinsewater containing hazardous waste is sent to an approved, authorized hazardous waste facility for disposal. Off-spec paint and paint samples often are allowed to dry by evaporation and disposed of as sludge or solid waste. Solid waste including filters, rags, sampling containers, and cans are compacted for periodic incineration off site.

Polymers and pigments currently used in formulating latex coatings pose no special hazards to the workers and are nonflammable in storage. Normal good practices for handling all chemicals to avoid unnecessary exposure include avoiding breathing of vapors or spray mists and washing off with water any material that accidentally contacts the skin or eyes.. Proper addition to the dispersing and mixing tanks minimizes exposure.

Some additives may require special handling precautions to limit worker exposure. Liquid additive use has increased steadily to decrease handling, dust, and worker exposure by automated pumping and metering. Bactericides and fungicides are added to formulations in ready-to-use water-soluble packages. The latex coating industry is eliminating the use of heavy metals, especially in pigments and colorants. Aromatic mercury compounds used for years as preservatives, such as phenylmercuric acetate, are being replaced. The more toxic aliphatic organomercury compounds no longer are used [10]. To reduce solvent exposure, zero-VOC defoamers, coalescing agents, and pigment-dispersing aids are being tested.

Air Emissions: The volatile organics in latex paint come mainly from additives and carriers for additives: coalescing agents; freeze/thaw stabilizers; defoamers; surfactants; and carriers for colorants, biocides, etc. Glycols added to provide freeze/thaw stability and wet time are the primary contributors to VOCs in latex paint formulation. In-store tinting systems also often use glycols. Coalescing agents are the second major source of VOCs in latex paints. Lesser amounts of VOCs come from other additives and small fragments of volatile organic monomers present in the latex polymer. Efforts are made to limit or eliminate solvent loss during formulation by covering storage containers, mills, and mix tanks.

Due to the wide range of company size and facilities and the proprietary nature of the formulations and manufacturing process, it is difficult to describe a "typical" production process. To facilitate estimation of waste generation, environmental releases, and exposure-level calculations, the production of 500,000 gallon of latex coating per year in 1,000-gallon batches will be assumed.

Waste Generation, Environmental Releases, and Exposure-Level Calculations

PMN chemicals may be used as components in the latex polymer, pigment, surfactant, biocide, coalescing agent, stabilizer, defoamer, and carrier solvent used in formulating the latex/emulsion coating. For the environmental releases and worker exposure calculations conducted in this generic scenario, the PMN chemical is assumed to be introduced early in the formulation process, i.e., in the first mixing step were the pigment and additives are mixed with water in the mix tank. The PMN chemical used as the component is available as a liquid additive. This assumption appears reasonable in light of the current focus of manufacturers to reduce air emissions and worker exposure by eliminating powder-based additives. The calculations can be readily extended to address in PMN chemical added as a stabilizer, biocide, or other component at some other intermediate stage in the process.

Assumptions

%PMN:	weight percent of PMN chemical in the final latex coating (lb PMN/lb coating; assume additive at about 3%). If volume % of PMN is furnished, manufacturer will have to supply density for conversion to weight %. Weight figures should be used in calculations, because coating density varies.
W:	weight in pounds of one batch of 1,000 gallons of final latex coating; if formula weight not available, assume 10 to 12 lb/gal.
N:	number of batches made per day at the latex formulation facility
D:	number of days per year of operation of the latex formulation facility
B:	gallons per batch; assume 1,000 gal/batch for these calculations
S:	sites in United States, currently about 1,000 potential producers.

Environmental Releases (total lb/year at a single latex formulation facility)

Solid Wastes: Potential solid wastes from latex formulation operations include sludge from equipment cleaning and drying out of latex wastes, off-spec and quality control samples, unused raw materials, deposits from filters used to purify the finished latex prior to shipment, and miscellaneous cleaning and operating equipment. These wastes typically are compacted and incinerated. Waste solids are estimated to be 1 to 2% by weight of raw materials, corresponding roughly to a solid waste of about 33 to 68 lb per 1,000-gallon batch. Hence, the amount of PMN chemical released as solid waste can be estimated as follows:

%PMN/100 (lb PMN/lb coating) * (33-68) lb/1,000 gal * N * D * B = ? lb/year

Air Emissions: Air emissions of a PMN chemical component added in the mixture are likely to be small unless the chemical is volatile. Nonvolatile PMN chemicals added as a slurry or a liquid are not likely to result in significant air emissions. In the case of a volatile PMN, such as an organic carrier solvent for a biocide or colorant, emissions of VOCs will depend on the characteristics of the mixing process and the containers used to store the raw and finished materials. It is difficult to estimate the extent of volatilization that will occur for the generic PMN during the course of the latex formulation process. Approaches to determine the extent of volatilization include measurements in a prototype process, using data for analogous chemicals used currently in a latex formulation process, or using empirical relationships developed in the literature or by U.S. EPA [17].

Additives excluding surfactants and coalescing solvent account for less than 5% by weight of the latex coating. Individual additives usually are 0.01% to 3%. Assume PMN is 3% of the coating for air emission calculations if the actual percent is not known.

If PMN is volatile:

assume PMN is 100% volatile.

$$PMN \times W \times N = ?\ lb/site/day$$

If PMN is nonvolatile:

assume no air emissions.

Water: Liquid waste containing the PMN chemical could arise from rinsing liquids used in equipment cleaning, liquid latex from spills and quality control sampling, and latex that does not meet specifications. Each cleaning operation may produce about 5 to 10 gallons of liquid per 1,000-gallon batch tank. Cleaning solutions often are recycled back into subsequent batches of similar latex, or are used more than once for cleaning. Cleaning solutions that cannot be reused are put in flocculation/setting tanks for removal of solids by settling. The supernatant liquid is then disposed to water treatment plants. The amount of PMN chemical released in the water waste would depend on the concentration of PMN chemical remaining after flocculation and setting. To estimate potential water release before treatment or reuse, assume that all cleaning liquid is generated at 10 gallons per batch and released into water.

$$\frac{10\ gal\ cleaning\ fluid}{batch} \times N \times D = ?\ gallons\ per\ site\ per\ year$$

If cleaning fluid is 10% latex coating and PMN is 3% of latex coating, then PMN is 0.003% of cleaning fluid. If cleaning fluid is about 8.4 lb per gallon, the amount of PMN potentially used can be calculated.

Worker Exposure

Worker exposure to the PMN chemical may occur during (1) component loading and transfer operations, (2) addition of mix tanks, (3) final transfer of the latex formulation into cans or other containers, and (4) disposal and handling of the solid and liquid waste containing the PMN chemical. Accurate quantifications of the exposure is difficult with the limited information currently available. However, the potential routes of exposure to the PMN chemical are expected to be through dermal exposure and a limited degree of inhalation exposure depending on the nature of the PMN. Because of the holding time, many paint producers operate only on production shift per day. In a labor-intensive operation, one worker is required to produce one paint batch per day. Worker exposure estimates derived below are for 1 worker working an 8-hour shift, and for 1 day of latex formulation operations.

Inhalation Exposure:

General In-Plant Inhalation Exposure: The primary inhalation source will be in the form of liquid vapor from the formulated coating. Most of the components of latex coatings have very low vapor pressures and are considered nonvolatile. If the PMN is a volatile the vapor pressure (P) must be supplied by the manufacturer or estimated from known vapor pressures available in published literature to allow calculation of the concentration of respirable constituents in the air (CR). An inhalation rate of 1.25 m^3/hr will be assumed [1].

$$\text{Generic:}\ PMN \times CR \times IR \times H = \underline{??(mg/day)}$$

The production of latex coatings involves the transfer of liquids and solids to the mixing vessels. Inhalation of liquids will depend on the volatility of the liquid agent (assumed to be the PMN). The vapor pressure of the PMN can be used to calculate the concentration of the PMN in the air that might be expected during transfer

from a 55-gal drum to the mixing vessel [1]. This is a worst-case approximation, assuming open-system manual feeding. Transfer frequency is assumed to be one as a single contact is expected to result in exposure for the entire workday. Then, inhalation exposure during the transfer of liquid PMN material can be determined as:

$$CR(PMN) \times 1.25\ m^3/h \times 1 \text{ transfer per day} \times \text{hours per day} = \underline{??(mg/day)}$$

In some instances, the PMN materials may be a powder which will pose an inhalation threat when being added to the mixing vessel. In this instance the respirable dust should be considered to be comprised of 100% PMN. Total respirable dust exposure (15 mg/m^3) should be used. Therefore, inhalation exposure during the transfer of powder PMN material can be determined as:

$$15\ mg/m^3 \times 1.25\ m^3/h \times 1 \text{ transfer per day} \times 8 \text{ (hours exposure per transfer)} = \underline{??(mg/day)}$$

Dermal Exposure:

Dermal exposure will be limited to incidental exposure during transfer materials handling. This will include handling liquid and solid raw PMN materials used to formulate the coating, and exposure to the coating product containing the PMN during transfer of the product to containers for shipping. Exposures will be limited to contact with the materials during transfer operations. TR is assumed to be one as a single contact is expected to result in exposure for the entire day. Equations approximating exposure levels are based on data compiled on contact operations as given in Table 4-13 of CEB [16].

Liquids: $(1{,}300 - 3{,}900)\ mg/m^3 \times TR \times PMN/100 = \underline{??(mg/day)}$

Solids: $(6{,}500 - 18{,}200)\ mg/m^3 \times TR \times PMN/100 = \underline{??(mg/day)}$

Disposal Concerns

Drums or other shipping containers used to transport the PMN chemicals to the formulator are assumed to be recycled or cleaned to remove contamination, and appropriately landfilled or incinerated. All liquid and water wastes are assumed to be reused or air-dried and then disposed of as solid wastes. The manufacturer submitting the PMN must address any other potential mechanisms by which the PMN chemical may leave the latex formulator's facility.

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