Federation Series on Coatings Technology

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Federation Series on Coatings Technology

Unit One

INTRODUCTION TO COATINGS TECHNOLOGY

Federation of Societies for Paint Technology

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Introduction To Coatings Technology

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I. A CHEMICAL INDUSTRY

This booklet is the first of a series sponsored and published by the Federation of Societies for Paint Technology. The series is designed to serve as a text for courses in paint technology and also for independent study by individuals who wish to gain a better knowledge of the subject. Being introductory, this first booklet presents a perspective of the paint industry and of the position and problems of paint technology.

These days corporations and industries are concerned about the popular image that they evoke. Among all industries the paint industry probably is the one whose image falls farthest short of reality. Many people believe that paints are simple in composition and that they are made by just mixing several ingredients together. In truth, paint manufacture is an important segment of the broad chemical industry. Moreover, it is technically one of the most complex. It utilizes more kinds of raw materials than any other division of the industry and it employs a much larger number of separate materials. This point is most strikingly exemplified by the wide variety of resinous polymers that are used, which include chemical counterparts for most kinds of plastics, elastomers (rubbers), adhesives, and synthetic fibers. Plastics provide a good example. The better known types are pyroxylin (nitrocellulose), vinyl, polyethylene, phenolic (Formica® and Bakelite®), melamine (Melmac®), polystyrene (Styrone®), acrylic (Plexiglas® and Lucite®), polyester (boats and the like), and epoxy (Epon®). All of these types are used in paints, some of them in large quantity and in numerous variations. The first synthetic rubber was a polymer of neoprene and polymers of neoprene are the base for some specialty heavy-duty maintenance paints. Next came GRS or SB synthetic rubber, the type generally used in tire treads. It is a copolymer of styrene and butadiene, the same as the resin that has been widely used in "rubber base" latex paints. The main difference is that the paint resin contains a higher percentage of styrene. Among the important adhesives are casein, phenolic polymers, polyvinyl acetate, urea-formaldehyde polymers, epoxy polymers, and polyamides. All of these types are also used in paints. The same rule applies to synthetic fibers. In short, paints incorporate the almost complete spectrum of commercial organic polymers, a greater variety than any other kind of products.

Hundreds of Raw Materials Required

The complexity of paint technology is further indicated by the numerous types of raw materials required and the large total number. A plant that makes a broad line of trade sales, maintenance, and industrial paints requires 500 to 600 or more different raw materials and purchased intermediates. Most of these fall in the following classes: oils, metallic driers, resins, pigments, extenders (non-hiding pigments), plasticizers, solvents, dyes, bleaching agents, organic monomers for resins and additives of many kinds. Along with bewildering chemical terms like ortho-phthalic anhydride, pentaerythritol, and 2-hydroxyethyl methacrylate, a raw materials code list includes household words such as petroleum jelly (Vaseline), mineral oil, glycerine, talc, ammonia, urea, propyl alcohol (rubbing alcohol), water, and the base for permanent anti-freeze (ethylene glycol).

The need for so many raw materials springs mainly from the great diversity of finished products, each designed to best serve a specific purpose. Usually when people think of paint it is in relation to houses and other buildings. Many kinds of paint are required to take care of the various surfaces, conditions of service or exposure, and preferences as to appearance. Nevertheless, the standard lines of trade sales paints afford only a hint of the broad range of requirements that must be satisfied by more highly specialized paints. If the house siding is aluminum, the paint is factory-applied by roller, is baked hard in about one minute, and is expected to last about 15 years. Concrete swimming pools call for paints that are designed specifically for that purpose. Most of the things used in a house carry specialty paints: wallpaper, builder's hardware, furniture, TV, picture frames, fireplace equipment, fixtures, and appliances. Every motor on appliances is painted, both the housing, and the wires inside the motor. It would be in poor taste to mention that the miracle-working creations used on finger nails and eyebrows are paint. The exterior use of paint that creates most interest is on automobiles. The universal use of paint to protect bridges, storage tanks, and other steel structures is taken for granted. It is less widely known, however, that the useful life of underground pipe lines is being greatly lengthened by painting them inside as well as outside.

Paint or Coating?

To avoid confusion it seems advisable to interject an explanation of the use of the word paint, since it is commonly employed with various meanings. In the most narrow sense it applies only to pigmented products such as wall paint, exterior house paint, masonry paint, and traffic paint; other coatings being termed enamel, undercoater, primer (industrial), sealer, varnish, lacquer, filler, stain, etc. There is a movement in the paint industry to avoid the general word paint and to substitute organic surface coating, surface coating, or chemical coating. Aside from the inconvenient length of these terms they exclude some paints and include many materials that are not paint. This booklet will employ the word paint in its broad, established meaning to include all of the coatings mentioned above. When the discussion pertains to a single kind of paint, it will be designated by the customary word.

Trade Sales and Industrial

Two other terms that are used frequently should also be clarified: trade sales and industrial. The definitions that the U. S. Department of Commerce employs in its reports are as follows: "Trade sales products are stock-type commodities generally distributed through wholesale-retail channels. Industrial finishes are products specifically formulated to meet the conditions of application and use of the product to which applied and are generally applied as part of the manufacturing process." There is a group of products that is classified by some paint manufacturers as trade sales and by others as industrial. This group includes the paints that are sold to factories for use on buildings and equipment and that are sold directly to contractors for use on structures such as bridges and storage tanks. When given a separate classification, these products are termed industrial maintenance paints. Since they are usually stock-type, they come under the Department of Commerce definition of trade sales products and they will be so considered in this booklet.

II. SIZE AND GROWTH

In full stride with our growth in population and in national product, the paint industry is expanding rapidly. This growth is shown in Table 1 which is based on data of the U. S. Department of Commerce, Bureau of the Census.

The table makes clear that paint manufacture is now a two billion, eight hundred million dollar; eight hundred and seventy million gallon industry. The 1971 dollar volume was 55% trade sales and 45% industrial. In gallons the division was 49% trade sales and 51% industrial.

TABLE 1
Total Paint, Varnish and Lacquer Sales

Year	*Dollars*	*Gallons*
1909	110,000,000	
1919	300,000,000	
1929	501,000,000	
1939	443,000,000	
1949	1,106,949,000	
1959	1,727,400,000	
1960	1,763,600,000	663,100,000
1961	1,749,500,000	623,300,000
1962	1,832,800,000	643,400,000
1964	2,002,200,000	724,600,000
1965	2,169,300,000	775,400,000
1966	2,364,400,000	837,000,000
1967	2,348,200,000	781,500,000
1968	2,587,091,000	843,095,000
1969	2,776,768,000	880,474,000
1970	2,737,059,000	826,679,000
1971	2,830,781,000	874,439,000

To a greater extent than most industries paint manufacture is well distributed throughout the country, although the volume is definitely related to density of population. Paint factories differ enormously in size. The latest available data are for 1967. At that time there were 1,701 paint factories in the U. S. and the total employment was 66,100. Table 2 shows the relationship between the number of employees and the number of plants.

The figures in Table 2 offer abundant proof that in the paint business there is room for companies of all sizes, from very small to very large. It seems self-evident that the size of a company affects the degree of specialization of both the company and of the individual employee. Most of the smaller companies make only trade sales (including industrial maintenance) paints for distribution in a restricted area. Many companies of medium size and a few large companies make trade sales products only or industrial finishes only.

TABLE 2
Number of Employees and Establishments*

Average Number of Employees	*Number of Establishments*
1 - 4	468
5 - 9	242
10 - 19	311
20 - 49	350
50 - 99	171
100 - 249	113
250 - 499	36
500 - 999	8
1000 - 2499	2

* Source: U.S. Dept. of Commerce, Bureau of the Census, Census of Manufacturers, 1967.

Most large and very large companies are active in both areas. A few manufacturers of industrial paints concentrate in a rather narrow field, e.g., automobile paints, while others make a broad line of industrial finishes. Industrial paints demand so much specializaton in formulation and in technical service that no single company undertakes to serve all industries.

Composition of Paint

Another digression to explain a few terms that follow. One way of expressing the composition of a paint is by dividing the total between pigment and vehicle, as percentages by weight. In this case the pigment includes both hiding and extender pigments and also any mineral matter used for flatting or other purposes. The vehicle is the complete liquid portion of the paint. Normally it consists partly of non-volatile matter and partly of volatile. In specifications the non-volatile portion of the vehicle is shown as vehicle non-volatile but paint chemists more often use vehicle solids, binder, or film former. The volatile part of the vehicle is the solvent and usually it is designated by that name. The sum of the pigments and binder is the total non-volatile or total solids. The most common mistake in terminology is the use of vehicle when referring to the binder or film former only.

III. SIXTY YEARS OF TECHNICAL PROGRESS

In step with its enormous growth in size, the paint industry is keeping fully abreast of the general advancement in science and technology. Sixty years ago the number of chemists in paint factories was limited and their sphere of activity was restricted. Technology was largely empirical, by trial and error. White lead in oil was still standard for exterior house paint, although ready-mixed paint containing white lead and zinc oxide was making headway. Titanium dioxide pigments were still around the corner. Bright red pigments allowed a choice only between para toner, toluidine toner and, possibly, lithol toner. In blue pigments there were iron blue and ultramarine blue. Bright yellow pigment meant chrome yellow. The one green pigment was chrome green, a mixture of iron blue and chrome yellow. Phthalocyanine blue and green, with their much better color fastness and alkali resistance, were in the distant future. First quality white enamels were pigmented with zinc oxide and the binder was heat bodied linseed oil. For better hiding and non-yellowing, the pigment in mill whites was mainly lithopone and a portion of the bodied oil was soybean. The practical varnish maker still held sway and resented any intrusion by upstart chemists. The principal varnish oils were linseed and tung but perilla was also used. Predominant among the varnish resins were the hard fossil gums, Congo and kauri. New wonder varnishes that dried faster and would not turn white in water were made by combining tung oil and ester gum, which was made by heat reacting rosin and glycerol.

Then chemists in the paint industry and allied industries made things begin to happen and they are still happening at an ever increasing tempo. A method of greatly reducing the viscosity of nitrocellulose was discovered and lacquer started climbing to the important position that it holds today. The extensive use of nitrocellulose required a companion product, a good nitrocellulose solvent of medium evaporation rate, slower than ethyl acetate. This was provided by the fortunate and timely development of an economical process of making butyl acetate. Today there are numerous active solvents of both ester and ketone types. Next the Germans developed phenol modified rosin esters. In combination with tung oil, they produced so-called four-hour varnishes and enamels. Several years later Bakelite Corp. introduced oil soluble 100 percent phenolic resins. Solubility was achieved by changing the phenolic component to a substituted phenol. These 100 percent phenolics gave varnishes a further boost in speed of drying, water resistance, flexibility, and exterior durability.

Alkyd Resins

Next came a development of far reaching import: oil modified alkyd resin, which, when dissolved, may be properly called a varnish. Alkyds in various modifications and in blends with other resins have proved the most widely used, versatile binder. Excepting water paints and oil house paints, alkyds are used for at least part of the binder in the majority of trade sales, maintenance, and industrial coatings. For some years alkyd resins, used alone, were the standard binders for industrial baking enamels. Then amino resins (urea-formaldehyde and melamine-formaldehyde) came along. They possessed in high degree the very properties in which alkyds were deficient: fast baking, hardness, color retention, and resistance to various agents. Blends of the two types of resin became the common binder for industrial baking enamels.

Other new and valuable resins followed in rapid succession: thermoplastic acrylics, vinyl chloride-acetate copolymers, silicones, epoxies, polyamines, unsaturated polyesters, thermosetting acrylics, and polyurethanes. The epoxies proved especially useful and have shown steady growth to a position of considerable importance. When cooked with the fatty acids of drying oils, they form epoxy esters that make excellent air drying varnishes. Baking metal primers were significantly upgraded by mixtures of urea-formaldehyde resin with epoxy resin and, later, with epoxy esters. Mixtures of the lower molecular weight epoxies with amines, such as diethylene triamine, and with resinous polyamides air dry to films that exhibit high resistance to water, solvents, and chemicals. These mixtures also offer one of the routes to coatings having substantially 100 percent solids.

The earlier assumption that acrylic resins are inherently thermoplastic was rudely jolted by the advent of thermosetting acrylics. Over a period of several years these resins have gained first place in quality baked finishes for appliances and other interior products having similar requirements. They are used in combination with resins of the melamine-formaldehyde, epoxy and, occasionally, alkyd types. Another resin entry is polyurethane type, which comes in five modifications as to the process of conversion. Since polyurethanes offer certain combinations of desirable properties that heretofore were elusive, they hold considerable promise. One of their most conspicuous successes has been in heavy duty floor finishes.

Water Emulsion Resins

Starting about 24 years ago with flat wall paint, water emulsion resins probably have passed solution binders in the volume of trade sales paint in which they are used. They dominate in flat wall paints and masonry paints, are challenging solution paints for exterior wood surfaces, and hold promise for interior enamels. During the early stage of this development the resins were copolymers of styrene and butadiene. These have been largely superseded by copolymers of vinyl acetate with dibutyl maleate and acrylic monomers. Acrylic polymers hold first place for exterior house paints, but there is substantial use of vinyl acetate copolymers and of highly polymerized linseed oil.

For the sake of brevity this sketch of resin or binder developments omits numerous types, some of which are used in appreciable volume. Each type of resin is made in a few to many grades and grades may differ widely in properties. In many formulas, especially for industrial paints, the resin types are seldom used singly but in combinations. Most baking industrial coatings contain two or three types of resin. Surprisingly, the older resins seldom disappear, because they remain the best or most economical solution for a few problems. Even the first synthetic, rosin ester, continues to be used in most paint factories. The implication of these facts is clear: a competent formulator needs a working knowledge of the properties of the whole range of resins. When planning a problem of formulation, usually the first decision that must be made is which resin types to include in the program.

White Pigments

The development in paint resins has been matched by the improvement in the other classes of ingredients. White pigments furnish a striking example. Prior to 1920, the available white pigments were basic carbonate white lead, basic sulphate white lead, zinc oxide, leaded zinc oxide, and lithopone, the latter relatively new. The lead pigments and zinc oxide, being quite reactive with acidic vehicles, seriously restricted the choice of binders. The lithopone (28 percent zinc sulphide and 72 percent barium sulphate) then produced was more or less susceptible to turning gray when exposed to sunlight and moisture. Later this shortcoming was overcome. Possessing highest hiding and lowest reactivity, lithopone served a highly useful interim purpose. However, it steadily declined in volume after the introduction of titanium oxide whites, with their superiority in hiding, exterior durability, chemical inertness, and economy.

Titanium dioxide pigment became widely commercially available around 1925. The first pigment was a composite of 30 percent anatase titanium dioxide and 70 percent barium sulphate. It was rapidly adopted for both interior and exterior paints. For exterior paints it was used in combination with white lead and zinc oxide. Its use resulted in better hiding and also in the greater chalking and fading that are characteristic of anatase titanium dioxide. About 1932, pure titanium dioxide became a commercial product and it gradually replaced the barium sulphate extended pigment. In addition to providing much greater hiding, the pure pigment allowed a choice of extenders. The next significant advancement was a composite pigment containing 30 percent of calcium sulphate. It had better pigment properties than the barium sulphate composite and it was widely adopted for interior paints.

Next a truly major gain was made by the production of titanium dioxide having the rutile crystal structure. The rutile pig