Paints, Pigments, and Dyes

Chemistry's colors and coatings have long enhanced civilization.

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Chemistry is responsible for the real "world of color" through the creation of paints, dyes, and pigments to preserve, protect, and prettify everything from museum art to aircraft carriers. As detailed in the Kirk-Othmer *Encyclopedia of Chemical Technology*, paints are "any liquid, liquefiable, or mastic composition designed for application to a substrate in a thin layer which is converted to an opaque solid film after application." Pigments are "black, white, or colored inorganic substances produced and marketed as fine powders" used to create color or opacity in coatings such as paint, or as additives to inks, plastics, rubber, or paper. Dyes are generally soluble organic

compounds used as colorants, primarily in the textile industry. The commercial history of these coatings and colorants is one of the greatest success stories of the chemical industry.

All such protective coatings consist of several components—the binder (a resin, drying oil, or lattice), a volatile solvent used for dispersing (organic or water), and a colorizing or opacifying pigment or dye. Additional components can be used to vary the properties of the coating to improve ease of application, stability, colorfastness, longevity, and even resistance to biological attack. The industry is so vast and complex, it is almost impossible to summarize its history except in outline.

Paint Your Wagons

In the United States, the first ready-mixed paint was developed in 1867. This led, by the end of the 19th century, to an explosive increase in the paint industry. In 1892, one of the earliest major commercial successes was Muresco, introduced by the Benjamin Moore paint company (founded in 1883). Muresco was a dry paint mix to which water was added to make a spreadable coating. The company introduced the first lightfast oil-based flat wall paint, Sani-Flat, in 1907.

But perhaps the most powerful force driving the production of new protective coatings was the Western world's love affair with transportation. For example, Sherwin-Williams, one of the modern paint giants, was founded in 1866 by Henry Sherwin and Edward Williams to produce paints for carriages and buggies. But by the turn of the century, it was the needs of the fledgling motorcar industry that led to the greatest strides in coatings. The development of automobile paints, driven by the need for protection from the elements, created a new industry.

In the early days, you could have any color of car that you wanted—as long as it was black enamel. And its application process could take up to three days. But things changed with the accidental discovery of Visolac, a nitrocellulose lacquer finish developed by DuPont researchers in 1921. An improved version, named Duco, was developed, and it transformed the finishing process, allowing different colors to be applied on the assembly line with significantly less effort, cutting the number of coating steps by one-third.

In late 1923, the 1924 General Motors (GM) "True Blue" touring sedan was the first Duco-finished car, and many others quickly followed. Eager to compete, Ford commissioned the Glidden Co. to develop a different resin-based lacquer for its use in 1927. Everyone was eager to apply their technologies to the automobile. The Minnesota Mining and Manufacturing Co. (3M)—founded in 1902—introduced its first adhesives and coating products in 1931 and by 1935 was marketing the first automotive underseal coatings.

Similarly, in 1924, Rohm and Haas joined with the Karl Albert Co. to establish the Resin Products Co. for the purpose of producing synthetic resins for use as fast-drying varnishes. These resins were based on chemical modifications of Leo H. Baekeland's resins to make them soluble in a drying oil, and thus

Top: Paint cans, image by Tony Fernandez, 2004

Left : Rohm and Haas paint plant, *Chemical & Engineering News*

able to be used as coatings. Other types of resins followed—urea-formaldehyde resins (1929), vinyl copolymers (1939), and the very important melamine-formaldehyde and polyurethane resins (1939). In 1921, R. E. Kienle of the General Electric Co. developed the first successful alkyd coating by modifying alkyds (complex polyester binders formed by condensing polyhydric alcohols with polybasic acids) with drying oils. Alkyds provide one of the most extensively used (through modifications for a variety of applications) resin classes in the industry.

Above: Vinylite resins, Union Carbide and Carbon Corp. ad, 1950, *Chemical & Engineering News*

Colorful Consumption

As for colorants—in 1924, titanium dioxide (TiO_2) was introduced as a white pigment with exceptionally high hiding power. It was particularly valuable because coatings colored with TiO_2 weathered by slow erosion rather than cracking, as did the earlier lead and zinc whites. This improved its lasting power, appearance, and repainting qualities.

Although lead pigments were a staple, because of safety issues, industry consensus standards limited their use beginning in the 1950s. By 1978, the use of lead pigments in household paints was banned by the Consumer Product Safety Commission.

The colorfast pigment molybdate orange came into use in 1930 and phthalocyanine blue in 1937. Companies such as Ferro developed a wide variety of inorganic pigments suitable for coloring enamels, ceramics, and glass. World War II and the postwar era led to a boom in the paint and coatings industry. Although baked enamels had continued to be popular during the early 1930s, despite the new resinous lacquers, the incorporation of cross-linking resins after the war gave them a new life.

Silicone and styrenated and acrylated alkyd resins appeared in 1944. In 1947, Pittsburgh Plate Glass (now PPG Industries) opened an industrial coatings plant in Springdale, PA. Also in 1947, Dock Resins was founded by Philip Barbanel upon his return from service in the U.S. Navy (later the company would become part of Lubrizol), and epoxy resins became commercialized.

The demand for consumer goods from houses to farm implements and the rapidly expanding demand for automobiles dramatically intensified the need for new coatings—leading to an industrial boom. The explosive development of the canning industry with the introduction of aluminum cans stimulated companies such as Stoner-Mudge (now Valspar) to expand their range of operations throughout the 1950s. (The company had, notably, in 1935, produced a protective coating that made possible the first commercial beer can.)

In 1948, the revolution in water-based paints took off with Glidden's introduction of its Spread Satin brand of latex emulsions. Ease of application and cleanup led to rapid adoption of this type of paint by consumers and a slew of brands from companies such as Sherwin-Williams, National Lead, PPG Industries, and DuPont.

In 1953, following up on its development of the acrylic plastic, Plexiglass, Rohm and Hass introduced the first acrylic emulsions for use as paint binders. Acrylic binders would gradually become the dominant binders in the industry. Lightfast pale colors (such as yellows, reds, and violet) in automobile coatings arrived in the mid-1950s. These were made possible by the development of new "super enamels," introduced commercially in 1956, that were cross-linked with higher concentrations of melamine resins than before, allowing for efficient production of pastel tints.

Throughout the 1960s, acrylic lacquers and enamels adapted to the automobile industry became dominant, with GM leading the switch to all-acrylic enamels from its earlier nitrocellulose lacquers, followed rapidly by Ford, Chrysler, and American Motors.

Today, a wide variety of chemical companies produce the polymer emulsions and resins that form the backbone (binders) of the coating industries. These include Noveon (the former Performance Materials Division—founded in the 1870s—of the B.F. Goodrich Co.), Degussa, ADM, the Wacker Group, Crompton, and Akzo Nobel.

In 1987, BASF introduced an important innovation in the automotive coatings industry by marketing the first water-based basecoats for metallic finishes at the Opel factory in Bochum, Germany. This provided a significant environmental benefit compared with traditional solvent-based coatings, especially important as the controversy over the pollution effects of volatile organic compounds (VOCs) becomes more heated in the European Union. Currently, more than 80% of all new vehicles in Germany are produced with water-based basecoats, with GM, Volvo, BMW, Volkswagen, and DaimlerChrysler all having converted.

A Solid Investment

One of the most important innovations in protective coatings is the development of solvent-free powderized coatings, driven in part by costs, but

LINERS AND TUGBOATS AND BARGES, OH MY!

When things are foul in the maritime realm, it is a significant cause for worry. Antifouling coatings have been one of the most important—and difficult—fields of research on protective coatings, particularly because environmental considerations have called into question the use of highly toxic coatings adopted to prevent the growth of barnacles, algae, and bacteria. Until recently, tributyltin (TBT)-based paints, developed in the 1970s, were the antifouling standard. But throughout the 1980s and 1990s, the toxic TBT was blamed for significant damage to maritime ecosystems and was banned by the International Maritime Organization of the United Nations. (Fresh painting with TBT was banned in 2003, and all ships must have no TBT coatings by 2008.) Zinc- and copper-based biocides have been substituted, as have nonstick coating technologies. Akzo Nobel introduced the Interlux brand to provide long-lasting antifouling properties previously available only in TBT-based paints. The product won the 2003 National Marine Manufacturers Association Innovation Award and uses a patented self-polishing copolymer technology.

In another maritime-related paint story, early in the 20th century a Scottish-born sea captain, Robert Fergusson, noticed that raw fish oil spilled on rusty metal decks prevented corrosion from spreading. In 1921, the captain, after years of effort, perfected a fish-oil-based paint that stopped rust, dried overnight, and had no fishy aroma—Rust-Oleum (today part of RPM International).

mainly by demands for an environmentally friendly industry. The first patents on solid-powder (fluidized-bed) painting processes were given in Germany in the first half of the 1950s. Throughout the 1960s and early 1970s, propelled by both environmental regulations and the increasing cost of petrochemicals, a variety of powder coatings were developed, including epoxy, polyester, and acrylics. The U.S. appliance industry shifted from porcelain to powder throughout the 1970s, and by the latter part of the 20th century, companies such as PPG, Ferro, and others expanded rapidly into powder manufacturing. In 1995, automotive companies formed a consortium to evaluate powder systems in order to reduce VOC emissions.

Economically, the paint and coating industry has undergone similar consolidation in the past 20 years, as has occurred throughout the rest of the chemical industries. In 1998, for example, DuPont purchased Herberts GmbH, the coatings subsidiary of Hoechst AG, making DuPont Performance Coatings the world's largest supplier of automotive coatings and the third-largest coatings company overall.

Today, companies continue to research and produce coatings and coating additives that provide an ever-expanding array of protective and performance enhancements (see sidebar). Dover Chemical Co. produces additives that act as flame retardants and improve emulsification, adhesion, and water resistance. Angus Chemical Products produces an additive that enhances the electrospray application properties of coatings. OMG offers additives and drier compounds to improve paint drying. Lubrizol Paint and Coatings Additives offers a laundry list of properties to choose from through the use of additives, from abrasion resistance to metal-mark resistance to a "silky, soft feel"—a far cry from the paint job on that black enamel roadster at the dawn of the 20th century.

Center: Prufcoat ad, 1950, *Chemical & Engineering News*

Dye-ing to be Pretty

From the earliest mentions of dyestuffs in China in 2600 B.C. to the middle of the 19th century, dyes were derived from natural products, for example, from mollusks, flowers, and seeds. But in 1856, William Henry Perkin discovered the first synthetic "coal-tar" dye, which he called mauve (a basic dye now known as aniline), as part of his research into a cure for malaria. By 1868, the first synthetic substitute for a vegetable dye, alizarin (synthetic madder), was developed by Graebe and Liebermann in Germany. Throughout the rest of the 19th century, dyes proliferated in every color imaginable, creating the foundation for a significant industry. By 1900, the annual production of synthetic indigo was equal to the amount obtained from the entire 250,000-acre harvest of the natural indigo plant. The German companies BASF (formed in 1865) and Hoechst (formed in 1863) especially worked to capture this market in the early part of the century.

Continuing Perkin's quest for dye-based drugs, in 1909, Paul Ehrlich developed salvarsan, the first therapeutic drug against syphilis, from his research into the azo dyes.

In 1915, Neolan dye was developed, the first metallized chrome dye, one that required dyeing in a strong acid bath. Dyes of every hue proliferated: By the end of World War I, a company such as Hoechst could offer nearly 10,000 different products with a full spectrum of colors.

In 1922, the American Association of Textile Chemists and Colorists formed a subcommittee to study colorfastness in the wash of printed and dyed cottons and to develop standards for testing. In further medical developments, in the 1930s, a red azo dye gave rise to the first sulfa drug and launched the antibiotic era. In 1951, Geigy introduced Irgalin dyes, the first neutral premetallized dyes (which avoided the acid requirements of Neolan); the competing Cibalan dyes soon followed.

In 1956, ICI produced Procion, the first fiber-reactive dye (a dye that binds directly to the fabric fibers, remaining colorfast) developed from research on Cibalan Brilliant Yellow 3GL, first produced in 1953; in response, one year later, CIBA introduced the Cibacrons, reactive dyes to compete with the Procion brands.

Throughout the 20th century and beyond, research into every imaginable form and color of dye continued, from colorants for plastics to, especially, fiber-reactive dyes that work with the latest synthetic fiber textiles such as nylon, orlon, and polyesters. Today, dyes are far more than just pretty. They have also become indispensable tools for the biotechnology industry and biomedicine—from the colorimetric assays of enzyme interaction to the staining of cells to indicate composition and physiological function to the most sophisticated fluorescent dyes used in nucleic acid sequencing and the study of biological processes in vivo (see chapter, "Biotechnology and Genetic Engineering"). ◆