

Handbook of
ORGANIC
COATINGS
A Comprehensive Guide for the Coatings Industry

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Preface

Too few books are available on coatings science which is a major consumer of synthetic polymers. Some of the available books emphasize practical applications and others emphasize polymer science theories.

We have not neglected either of these approaches in our self sufficient handbook but have placed most of our emphasis on readily understandable concepts which should be useful to practitioners in all phases of the coatings industry.

We have not used the metric system but have supplied a table in Appendix C for converting the english system to the metric system. For reasons of simplicity, we have avoided the use of structural formulas in the text but have identified most materials by simple chemical formulas and shown many structural formulas in Appendix B. We have also supplied a glossary, a list of pigments in Appendix A and a list of pertinent references at the end of each chapter.

It is our hope that the reader will find this handbook to be useful and that this and other contributions will help to continue to upgrade coating science and technology.

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CHAPTER 1

HISTORY OF PAINTS

1.1 Prehistoric Paintings

Painting was one of the first extra curricular activities undertaken by homo sapiens (wise men) nearly 100 thousand years ago. While many ancient civilizations used pigments for cosmetic purposes, the oldest painting arts known today are those on the walls of caves, or rock shelters at Lascaux, Gabillou, and Font de Gaume, France (1) and Altamira, Spain and the Obiri rock paintings in Australia (2). Carbon-14 dating techniques have indicated that wood in Altamira fire pits was 17 thousand years old. The rock paintings in Arnhem Land, Australia, are believed to be over 5 thousand years old but occasional retouching of this art work has prevented the precise dating of these aboriginal paintings.

The use of coatings extends further into the past than any other facet of polymer science. The 17,000 year old Cro-magnum cave paintings and most pre-17th century coatings were primarily decorative but paint was widely used as a preservative for wooden structures after lead paints became available in the 17th century.

The versatility of the early artisans was demonstrated by the use of sap from the lac tree, Rhus verncifera over 4,000 years ago. This vesicatory urush or lacquer was actually cured by exposure to the atmosphere.

The ancient artists also used aqueous dispersion of pigments and animal or plant glues or eggs as their coating materials. The Chinese in the Chou dynasty (1122-222 B.C.), de-emphasized the use of pigments and emphasized the use of resins in their lacquers which were used for decorating carriages and weapons. It is of interest to note that the term for solvent based coating composition was derived from the Hindu word lakh meaning 100 thousand, which was the number of lac insects (Laccifer lacca) whose secretions of alcoholic extractives was required to produce specific amounts of shell lac.

1.2 Early Egyptian Paintings

The Egyptians used a crude form of paint for decoration as early as 8000 B.C. Later, about 4000 B.C., they used slate palettes and rollers for smoothing the fresh paint (3). While the ancient artisan sought pigments to match the colors of the rainbow, they had to settle for black charcoal, yellow iron carbonate and white calcium carbonate (chalk). About 2000 B.C., the Egyptians expanded the available pigments to include red, green and blue by grinding baked potters' clay.

Egyptian blue was produced in about 3000 B.C. by the calcination of malachite, sodium carbonate and silica at 1525°F. The Egyptians also used gum arabic from the acacia tree as a binder for the paint pigments in 1000 B.C.

1.3 Roman and Greek Paintings

The Romans and Greeks were sufficiently impressed with the qualities of paint in 100 A.D. that they agreed with Pliny's statement "Neither the sea nor the wind nor the sun can destroy wood thus protected" by paint.

The early Roman builders used a mixture of pigments and wax to hide blemishes in marble columns and this led to the specification of maxwax i.e. sin cere which is also used in the english language.

1.4 The Genesis of Oleoresinous Paints

Linseed oil was available to the Egyptians but it was not used in paints until about 200 A.D. Linseed oil, which was widely used in paints in the 11th century, cured or crosslinked when exposed to oxygen in the air. The use of this oleoresinous coating has continued and was used to coat the horseless carriages of the early 1900's.

Pliny described the production of white lead ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) which was called flake white by medieval artists. This toxic pigment was produced in 400 B.C. by reacting air and lead sheets which were encased in vinegar. This primitive process was later replaced by the Dutch or stock process in which fermentation of tanners's bark provided the carbon dioxide and acetic acid was used in place of vinegar.

1.5 Medieval Varnishes

Alberti of Magdeburg used turpentine as a solvent or thinner in 1736. This led to the commercial production of varnish in England in 1820 and to the use of petroleum distillates as thinners in the US in 1880. The

Chinese used tung oil (china wood oil) as a vehicle or binder in the 17th century and this oil was exported to the US in the 19th century.

Because of their high degree of unsaturation, tung oil (Aleurites fordii), oiticica oil (Licaria rigida) and dehydrated castor oil (Ricinus communis) cure (dry) faster than less highly unsaturated oils, such as linseed (Linum usitatissimum) or fish oils. The varnish makers use the terms hard and soft to differentiate between fast and slower drying oils. The term spirit varnish is used to describe solutions of resin in volatile solvents, such as methanol, ethanol, hydrocarbons or ketones.

1.6 The Genesis of Driers

In contrast to lacquers, in which the deposited film remains soluble in the solvent, oleoresinous paints dry (crosslink) to an insoluble film when exposed to air. The rate of crosslinking via oxidative polymerization (curing) is accelerated by the presence of driers which act as catalysts for a characteristic free radical polymerization. Toxic lead salts which have been used for centuries, have been replaced recently, to some extent, by a mixture of cobalt and zirconium salts.

It is now believed that a hydroperoxide group is formed by the insertion of oxygen from the air on the allylic position of the unsaturated oil i.e., on the methylene group (CH_2) adjacent to the double bond of the nonconjugated unsaturated oil (6). This oxidative step is followed by isomerization in which the carbon-carbon double bond shifts to a conjugated position and the peroxide is transferred to different carbon atoms.

Varnish, which is a solution of a resin in a vegetable oil and a resin such as amber was used in 250 B.C. Thus, the term varnish was derived from the latin word vernix which means amber. Based on the ability of amber, when rubbed, to attract dust, W. Gilbert used the greek word for amber viz, electron and electric to describe this phenomena.

Since white lead was the preferred white pigments, Galen dispersed this colorant in linseed oil which was obtained from flax seed (Linum usitatissimum) and produced opaque coatings (paints). In about 60 B.C., Ludus, Vitruvius and Dioscorides described coatings and varnishes based on vegetable oils and punic wax (4). In about 200 A.D. Galen, about 400 A.D. Marcellus and in 540 A.D. Actius described the "drying" properties of oil from flax seeds and nuts. Eraclius described a more rapid drying mixture of linseed oil and litharge. That the basic lead pigments reacted with a trace of free oleic acid in the vegetable or nut oil to produce a drier was not recognized until 1840 when a "nondrying" paint was obtained when the white lead was replaced by zinc oxide (6).

The use of a crude paint stone mill in Boston, MA in 1692, was recorded for its historical value as the so called "black art" of paint manufacture which has progressed from the curing of tung oil to group transfer polymerization. The paint industry celebrated its 50th anniversary at the Paint Industry Show in 1985.

Oil soluble salts of heavy metals, such as lead were produced in 1885 and these resins and linoleates were used as driers in paints. More stable metallic naphthenates were introduced in Germany in 1925.

1.7 Early Application Techniques

Primitive artists used feathers, sticks or their hands to produce their murals from pigmented egg whites (distemper) on walls of caves. This art was upgraded in the premedieval years by artisans who produced frescos by applying the paint to freshly spread plaster while the plaster was still soft. The Egyptians also applied paint to sheets of papyrus (Cyperus papyrus) which were produced by slicing the pith of this tall sedge and pressing the wet strips to form sheets. Some early artists also applied mixtures of pigment and wax and fused these coatings with hot irons in a process called encaustic painting.

Some artists applied their paint to animal skins, cloth, wood and paper but most were employed as itinerant craftsman (schilderers), who decorated castles and cathedrals. The word schilderer continues to be used to describe a painter in the Netherlands. The painting of houses was restricted to the wealthy until the 18th century.

Recipes for paint were not revealed by medieval painters. However, the monk Theophilus published a recipe for varnish in the 11th century and Waten described varnish technology in a book which was published in England in 1777 and reprinted 14 times during the following 125 years. Isomerization is unnecessary when the oil contains conjugated carbon-carbon double bonds. The hydroperoxide then dissociates and the polymerization proceeds via a free radical type propagation.

Mechanization of the pigment mixing process was essential for the expansion of the art of painting from artistic painting to the painting of houses. The most famous of the crude paint mills is "ye olde paint stone" which was imported from England to Boston MA by Thomas Childs.

The expansion of the number of and improvements in these grinding tools lead to the introduction of ready mixed paints in 1867. The stone mills have been displaced, to a large extent, by roller mills and pebble mills.

While the binder continued to be an unsaturated vegetable oil until the mid 20th century and continues to be used to a smaller extent today, the

major advance in paint formulations during the past 250 years has been in the development of pigments and fillers (7). The pioneer white pigments viz, white lead, zinc oxide, zinc sulfide and lithopone (zinc sulfide/barium sulfate) were displaced, to a large extent, in the 1930's by titanium dioxide. This pigment is available as rutile and anatase crystalline forms but the former, which can be obtained by heating the anatase form at 1750°F is the most widely used pigment in the paint industry.

In addition to the known pigments, phthalocyanine green and blue, ferrocyanide blue (Prussian blue), lead chromate yellow, zinc chromate yellow, and chromium oxide green which were introduced in the 20th century, now provide a wide variety of pigments (8).

Paint brushes which replaced tufts of grass have been supplemented by automated mechanical brushes. Rollers, knives, rods, spray and fluidized bed are also being used in specific coatings applications (9)(10).

1.8 Natural Resins

Because of their ready availability, many naturally occurring resins were used in pioneer varnishes. These resins are classified as recent or fossil based on whether their source is a living tree or an ancient dead tree. These resins include manila, dammar, rosin (colophony), shellac (lac), mastic and sandarac (11).

While some of these natural resins continued to be used, they have been replaced to a large extent by synthetic polymers.

1.9 Cellulose Nitrate Lacquers

J. Pelouze produced cellulose nitrate (CN) which is erroneously called nitrocellulose in 1838 by the reaction of nitric acid and paper. H. Braconnet nitrated starch, which he called (xyloidine) in 1833 but starch nitrate has had limited use in coatings. Schönbein improved the nitration process in 1845 by using a mixture of nitric and sulfuric acids. J. Maynard and S. Bigelow dissolved CN in an equimolar mixture of ethyl ether and ethanol in 1848 and S. Archer used this collodion solution to cast photographic film in 1851.

While lacquers based on the exudate of Coccus lacca insects, which feed on the lac tree (shellac) and on the exudate of the sumac tree (Rhus vernicifera) were used in the 14th century, Wilson and Green patented CN lacquers in 1884. CN was not used, to any great extent, as a lacquer until the early years of the 20th century (12). The use of CN in a pigmented automobile enamel was hampered by the high viscosity of the CN solutions.

However, the viscosity was reduced significantly in 1922 by batch digestion and this degradation process was placed on a continuous basis

by use of the Milliken's digestion process in 1929 (13). Cellulose was nitrated on a continuous basis in 1956. CN, which has been blended with other polymers, such as glyptals and alkyds continues to be one of the major coating resins.

1.10 The Development of Polyesters

Many 19th century chemists produced polyesters by the reaction of dicarboxylic acids and diols. However, little progress was made until 1901 when W. Smith produced a resin which he called gly ptai by the condensation of glycerol and phthalic anhydride. GE chemists improved these glyptal resins and obtained several patents in 1914 (14).

GE chemists such as Arseni, Callahan, Dawson, Friedburg and Howell investigated glyptal systems in which other acids, such as oleic acid were present but none of these chemists modified glyptal with drying oil acids. Thus, R. Kienle was able to file a patent on such compositions, which he called al kyds in 1927. The basic alkyd patent, which was issued in 1933, was ruled to be invalid by the U.S. Patent Office (15).

Alkyds, which are the condensation products of glycerol, phthalic anhydride and unsaturated vegetable oils, have been blended with many other resins. One of the more widely used blends is produced by heating the alkyd with styrene and an initiator such as benzoyl peroxide. The original styrenated alkyds prepared by N. Bhow and H. Payne were essentially blends (16) but some graft copolymer is produced when appropriate copolymerization techniques are used (17). Alkyds continue to be one of the most widely used coating resins.

1.11 Development of Phenolic Resins

While most coatings technicians and technologists today are aware of the trifunctionality of phenol and its inherent tendency to produce crosslinked polymers, when condensed with formaldehyde, this was not always true. In 1872, A. Baeyer, who was one of the world's leading organic chemists, condensed phenol and acetaldehyde. Kleeberg repeated this type of condensation using formaldehyde and phenol in 1891 but both of these investigators and many other 19th century chemists discarded the infusible products and then directed their attention to classical organic compounds.

Arthur Smith patented phenolic resins in 1899 but these important polymers were not commercialized until Leo Baekeland showed how to control the condensation reaction to obtain useful polymers (18). The resole resins which were produced by the controlled alkaline condensation

of phenol and formaldehyde, could be applied as fusible coatings which became infusible when baked but the use of these coatings was limited.

In 1917, K. Albert obtained soluble varnish resins by modifying the phenol formaldehyde condensate with rosin (19). Aylsworth obtained oil soluble resins by using p-cresol in place of phenol in 1914 and resins based on the condensation of formaldehyde and p-phenylphenol were commercialized by Turkington in 1928 (20). These linear polymers and those obtained by the condensation of formaldehyde and p.tert.butylphenol and octylphenol are still in use as coatings today.

1.12 Development of Amino Resins

Einhorn, a contemporary of Baekeland, obtained resins by the condensation of formaldehyde and urea in 1908 (21). These water soluble amino resins were rediscovered, independently by Rossiter, Goldschmidt, Pollack and Ripper in the 1920's (22). While these urea-formaldehyde resins are widely used light colored molding resins, they have limited use as coatings. However, they are widely used as blends with flexible resins, such as alkyds and acrylics (23). Resins that are soluble in organic solvents were produced by Kadowaki who etherified the condensation products of formaldehyde and urea by butanol in 1934 (24).

The reaction of formaldehyde and melamine was reported by Hendrich and Kohler in 1936 (25) and much of the technical information on phenolic and urea resins was adopted by these and other investigators of melamine resins which are classified with urea and melamine formaldehyde coatings as amino resins. The alkylated melamine-formaldehyde coatings which have been commercially available since 1940 are more costly but are preferred over alkylated urea resins for coatings. Both urea and melamine condensates such as hexamethoxymelamine are used to crosslink other polymer coating systems such as acrylics and epoxies.

1.13 Development of Epoxy Resins

Epoxy or ethoxylene resins were patented by De Trey Freres in 1936 but initial marketing attempts were unsuccessful. These patents were licensed to Ciba AG which continues to market these resins under the trade name of Araldite. A condensation product of bisphenol A and epichlorohydrin was produced by Greenlee of Devoe and Reynolds in 1939. Union Carbide, Dow and Shell developed epoxy resins in the 1960's but Shell's Epon became the most widely used epoxy resin in the US (26). These resins which can be cured at ambient temperatures by polyamines are used widely as industrial maintenance coatings, heavy duty coatings, trade sales coatings and adhesives.

1.14 Developments in Polyvinyl Chloride and Polyvinylidene Fluoride

Polyvinyl chloride was available for many decades but was too insoluble to be used as a coatings resin. This deficiency was overcome by Reid (27) and Seymour (28) who patented soluble copolymers of vinyl chloride with vinyl acetate and vinylidene chloride in the 1930's. These coating resins were distributed by Union Carbide and Goodyear under the trade names of Vynlite and Pliovic.

In spite of the corrosive and heat resistant properties of polytetrafluoroethylene (Teflon), which was patented by R. Plunkett in 1938, it and the related polychlorotrifluoroethylene (Kel F) were too infusible or too insoluble to be used as coatings. However, polyvinylidene fluoride (Kynar) is soluble and is used in corrosion resistant coatings.

Kahlbaum produced polymethyl acrylate in 1880 (29) and Rohm spent several decades in the investigation of these resins which were produced by Rohm and Haas in Darmstadt in 1927 and in the US in 1931 (30). Thermosetting copolymers of methyl methacrylate and hydroxyethyl acrylate admixed with melamine-formaldehyde resin have replaced cellulose nitrate and alkyd automobile coatings to a large extent (31).

1.15 Development of Water-Borne Coatings

Since the major rubber companies were producing lattices of elastomeric copolymers of butadiene (75) - styrene (25) (SBR) based on a patent by Tschunkur and Bock (32), it was easy to reverse the ratios of the reactants and produce a nonelastic water-borne coating which Goodyear and Humble Oil sold under the trade names of Pliolite S-5 and Buton (33). These lattices and those of polyvinyl acetate continue to be used as water-borne coatings.

Vinyl acetate was produced by Miosnikoff in 1860 but was not available commercially until 1932 when Shawinigan Chemical built a plant with an annual capacity of 700 tons. This monomer was readily polymerized in aqueous emulsions but the polymer had limited use because of its low softening point. Nevertheless, when pigmented, these emulsions became the base for the most widely used water-borne coatings (34).

1.16 Development of Polyurethane

In the same manner that Carothers produced polyesters and polyamides by use of difunctional reactants in classical esterification and amidation reactions, O. Bayer produced polymers by using difunctional isocyanates and diols in the classical urethane reaction which was developed by Wurtz in 1868. Bayer, who was a researcher in the I.G. Farbenindustrie laboratories,

produced polyurethanes in 1937 and commercialized these abrasion resistant polymers in 1940.

Nevertheless, further progress was hampered by World War II and large scale production was delayed until the early 1950's when Monsanto and Bayer formed Mobay Chemical Corp. Because of the inherent toxicity of organic diisocyanates, such as tolylyl diisocyanate (TDI), Bayer used isocyanates blocked by phenyl groups which were cleaved when the coating reactants were heated (35). One component systems (urethane oils) based on the reaction of diisocyanates and unsaturated oils, two components systems and moisture cured coatings were also introduced and are still in use today (36).

1.17 Silicones

F.S. Kipping investigated siloxane (-Si-O-Si-) coatings in the early 1900's. However, since he mistakenly believed them to be ketones, he called them silicones and just prior to their commercialization by GE, Dow Corning and Union Carbide, he maintained that they had little, if any, commercial potential (37). Silicones are now widely used as heat and water resistant coatings in a wide variety of applications. Silicone coatings pigmented with powdered aluminum, can be used at temperatures as high as 1200°F (38).

1.18 Bitumens

Bitumens, such as asphalt, have been used as coatings and grouting materials for thousands of years but little was written about these natural products until 1841 when R. Boyce published his famous "Chemistra Scepticus". Coal tar pitch was patented by H. Becker and H. Serles in 1861. These asphalt type coatings and those from more sophisticated inexpensive resins, such as polymers of pinene and limonene (dipentene) continue to be used in traffic, marine, deck and aluminum pigmented coatings (39).

1.19 Cellulosics

Cellulose was nitrated by Braconnot in 1832 and this cellulose nitrate, which is erroneously called nitrocellulose was dissolved in a mixture of ethanol and ethyl ether by Maynard in 1846. This solution (collodion) which was patented by Wilson and Green in 1884 was the precursor of cellulosic lacquers which have been used on automobile bodies since 1923 (40). In spite of the advent of many new synthetic coating resins, the use of cellulose nitrate coatings continues both as classical coatings and as blends with other compatible resins such as ethylene-vinyl acetate copolymers, and polyurethanes. The latter are actually called "super lacquers".