OCCUPATIONAL EXPOSURES IN PAINT MANUFACTURE AND PAINTING

1. Historical Perspectives and Description of Painting Trades

1.1 Description of paint products

The term *organic coating* encompasses conventional paints, varnishes, enamels, lacquers, water–emulsion and solution finishes, nonaqueous dispersions (organosols), plastisols and powder coatings. The following definitions have been used commonly, although they have not always been strictly applied.

Paint is a suspension of finely divided pigment particles in a liquid composed of a binder (resin) and a volatile solvent, sometimes with additives to impart special characteristics. The volatile solvent evaporates from the drying film after application, while the binder holds the pigment in the dry film, causing it to adhere to the substrate. Some high quality, hard gloss paints are referred to as *enamels* (Piper, 1965; Schurr, 1981).

Lacquer is defined as a coating that dries primarily by evaporation rather than by oxidation or polymerization. Because the solvents used in lacquers are relatively volatile and no chemical change is required for formation of the film, lacquers dry very rapidly (Piper, 1965; Hamilton & Early, 1972).

Varnish is defined as a homogeneous, transparent or translucent liquid that is converted to a solid, transparent film after being applied as a thin layer (Schurr, 1981).

The basic components of paints may have a widely varying chemical composition, depending on the colour, durability and other properties required from the paint.

(*a*) *Pigments*

Pigments can be classified as (i) inorganic, (ii) organic and (iii) earth pigments, such as ochre. They can also be classified into whites, colours, metallic flake pigments and powders. They are generally added in considerable proportion by weight (20–60%) and are used in paints to provide colour, opacity and sheen and also affect the viscosity, flow, toughness, durability and other physical properties of the coating. The physical properties of pigments, such as particle shape and size, vary; the diameter of the particles is generally < 3 μm. The particles in dry pigment powders (0.5–10 μm) are partially in the range of respirable dust (Krivanek, 1982).

(i) *Inorganic pigments*

Inorganic pigments are an integral part of numerous decorative, protective and functional coating systems, such as automobile finishes, marine paints, industrial coatings, traffic paints, maintenance paints, and exterior and interior oil, alkyd and latex house paints. Inorganic pigments belong to numerous chemical classes, primarily including elements, oxides, carbonates, chromates, phosphates, sulfides and silicates (Schiek, 1982).

Many forms of lead have been used for more than 200 years in pigments; these include carbonate (white lead), oxides (litharge, red lead), sulfate, oxychloride (Turner's yellow), acetate, borate and chromates (IARC, 1980a,b; Schiek, 1982).

Zinc chromate, little known before 1914, was widely employed during the Second World War to inhibit rust on all sorts of equipment (Brunner, 1978). Other chromium pigments that have been used in paint for many years include lead chromates, barium chromate and chromium oxide (IARC, 1980b). Other inorganic pigments include cadmium sulfide, cadmium sulfoselenide and antimony trioxide (see monograph, p. 291). Various grades of naturally occurring ferric oxide provide yellow, red and brown pigments (Schiek, 1982).

White pigments constitute over 90% of all pigments used (Krivanek, 1982). Until the nineteenth century, white lead in linseed oil was used primarily, and prior to 1920 the available white pigments were basic carbonate white lead, basic sulfate white lead, zinc oxide, leaded zinc oxide and lithopone (Martens, 1964; Federation of Societies for Paint Technology, 1973). Increasing awareness of the toxic hazards of white lead stimulated the development of other pigments, which became available to paint manufacturers in the early part of the twentieth century (Brunner, 1978).

The most common pigment employed in paint is the white pigment titanium dioxide (see monograph, p. 307), produced in two different crystal forms - rutile and anatase. Although it was introduced shortly after 1918, it was not used widely because of its high cost. The first titanium dioxide pigment was a composite of 30% titanium dioxide (anatase crystal structure) and 70% barium sulfate. A major gain was made by the production of titanium dioxide with the rutile crystal structure, which has almost 25% greater opacity than the anatase form. Because of the chemical inertness of titanium dioxide, its extreme whiteness, excellent covering power and lack of toxicity, compared to white lead, it soon dominated in the manufacture of white paint and, by 1945, represented 80% of white pigment on the market. Concomitantly, the use of white lead in paints fell during 1900–45 from nearly 100% to less than 10%. The share of lithopone, a coprecipitate of 28–30% zinc sulfide and 70–72% barium sulfate (Schiek, 1982), introduced before the First World War, rose to 60% by about 1928 but fell to 15% by 1945 (Brunner, 1978). Calcium carbonate and aluminium silicate have also been used as white pigments.

The most common metallic dusts and powders used in paint are aluminium powder, zinc dust (Schiek, 1982) and bronze powders, which consist of metals in a finely divided state; e.g., gold bronzes are alloys of copper with varying proportions of zinc or aluminium.

Materials used as extender pigments include barium sulfate (barytes), calcium carbonate (ground limestone and chalk), silica (diatomaceous and amorphous; see IARC, 1987a,b), clays (hydrated aluminium silicate), talc (hydrated magnesium silicate; see IARC, 1978c,d) and mica (hydrated potassium aluminium silicate). These minerals are often added to paint to reduce cost, improve physical characteristics and increase resistance to wear; their effects are largely governed by the average particle size (Martens, 1964).

(ii) *Organic pigments*

Hundreds of organic pigments, comprising a broad spectrum of structural classes, are used in the paint industry. Organic pigments may be classified as azo or nonazo pigments.

Azo pigments are formed by successive diazotization of a primary amine and coupling. Monoazo and diazo pigments contain, respectively, one and more than one chromophore (-N = N-) group and are subdivided into two types, the pigment dyes and the precipitated azo dyes. The most important and established uses for pigment products include the coloration of surface-coating compositions for interior, exterior, trade and automotive applications, including oil and water emulsion paints and lacquers (Fytelson, 1982).

Prior to the discovery of Perkins' mauve in 1856, colour was obtained from natural sources, i.e., woad, madder, indigo, cochineal and log wood. The development of synthetic colouring materials continued with the discovery of fuchsin in 1858 and of other triphenylmethane dyes, such as alkali blue, methyl violet and malachite green. Lakes of these dyes were used as the first synthetic organic pigments. The largest single advance in pigment technology after the First World War was the discovery in the 1930s of phthalocyanine blue (Monastral blue) and, later, its halogenated derivatives (Monastral greens) which were widely used in automotive finishes (Brunner, 1978; Fytelson, 1982). Other main categories of nonazo organic dyes and pigments used in paints and related products include quinacridones, thioindigos, perinones, perylenes and anthraquinone (Fytelson, 1982).

(iii) *Earth pigments*

Iron oxides are the most widely used of the coloured pigments derived from natural sources. Natural iron oxides are processed from several different ores, including haematite (see IARC, 1972, 1987e), limonite, siderite and magnetite, and provide a range of reds, yellows, purples, browns and blacks (Schiek, 1982).

(*b*) *Binders (resins)*

The vehicle portion of paints contains components collectively termed 'binders', which hold the pigment in the dry film and cause it to adhere to the surface to be painted. Almost all binders in modern paint films are composed of polymer materials, such as resins, and drying oils, whose main functions are to provide film hardness, gloss, surface adhesion and resistance of the film to acids, alkalis and other agents (Krivanek, 1982). A large variety of both natural and synthetic resins has been employed in paints. Natural resins have been used in paints for centuries, while synthetic resins have been commercially available since the early 1900s.

(i) *Natural resins and oils*

From early times, various natural resins have been used to reinforce linseed oil and other drying oils, since paints based only on pigment and oil yield only very soft films. Shellac (Brunner, 1978) and insect exudations are natural oleoresins that have been used in paints for centuries. Oleoresins from tree saps (shellac) are a mixture of single- and fused-ring compounds with various oxygenated groups possessing a wide range of molecular weights, solubilities and chemical and physical properties.

Kauri, a fossil resin, was used widely but had been replaced by the beginning of the twentieth century by Congo copal, which is a much harder resin but which requires prolonged heat treatment, known as 'gum running'. The term 'copal' is a generic name covering a number of fossilized and recent resins found in many tropical and subtropical parts of the world, which include all the harder resins used for oil varnishes (Brunner, 1978).

Another useful natural resin is rosin (colophony), which is obtained as a residue after distilling pine oleoresin for the production of turpentine. Rosin consists of about 85% rosin acids and 15% neutral substances and can be classified into two main types – gum rosin and wood rosin. Rosin has been used in paints (principally alkyd resins) for many years. They are often upgraded to yield higher quality resins by chemical reactions, including liming (calcium rosinate), esterification of rosin with glycerol, and reactions with trimethylolpropane, phthalic anhydride, maleic anhydride, adipic acid and sebacic acid (Krivanek, 1982).

Vegetable and fish oils have long been used as binders in traditional paints and varnishes. White linseed oil has been the most important oil in standard exterior paints, despite its moderately slow drying rate. It is infrequently employed in interior paints because of yellowing. Other important oils include castor oil, tall oil, soya bean oil, coconut oil, cottonseed oil, tung oil and various fish oils (Brunner, 1978; Lowell, 1984).

Although raw oils are useful as paint binders, it has been advantageous to use them in conjunction with refined oils and oils treated with heat to increase viscosity (heat-bodied oils) which isomerize the oil and improve the drying rate of the films. Oleoresinous varnishes are made by cooking oils with natural or synthetic resin, resulting in more rapid drying and a harder film (Lanson, 1978).

(ii) *Synthetic resins*

A wide variety of synthetic resins has been commercially available since the early 1900s. Those that have been most frequently employed in paints, varnishes and lacquers include cellulosic, phenolic, alkyd, vinyl, acrylic and methacrylic, and polyurethane resins, chlorinated rubber derivatives, styrene-butadiene and silicone oils (Martens, 1964; Krivanek, 1982).

Mixtures of different synthetic resins are often incorporated into a paint to furnish certain properties not provided by a single resin. While the amount of resin in paint varies, values of 20-35 wt% are common (Krivanek, 1982). The choice of a resin(s) for a particular application depends on factors such as appearance, ease of application, cost and resistance to chemicals, heat and wear.

Some resins (polyurethanes, epoxys; see IARC, 1976a) are blended immediately before use with cross-linking agents between the individual polymer chains, resulting in a hard, serviceable film.

Alkyd, acrylic, polyurethane and polyester resins have broad areas of use in paints, including paints for houses, automobiles, furniture and appliances, as well as in the protection of metal surfaces, e.g., in chemical plants and oil refineries.

Phenolic resins: The first synthetic resins used in paints were phenolic resins, which were introduced in the 1920s and are made from formaldehyde (see IARC, 1982a, 1987f) and phenol (see monograph, p. 263) or substituted phenols in the presence of alkaline or acid catalysts. Depending on the type and proportion of reactants, and on the reaction conditions, the resins may be heat-reactive or not. The first product of the reaction is methylol phenol, which reacts further. With an excess of formaldehyde under alkaline conditions, methylol groups react slowly with phenol, are retained in the reaction product and can act as reactive sites in varnish preparations or for cross-linking in finished products (Lowell, 1984).

The early phenolic resins developed between 1905 and 1910 were based on unsubstituted phenols, e.g., cresols, *para*-phenylphenol and *para-tert*-butylphenol, which are oil-soluble, and constituted a new type of varnish with superior hardness and resistance to water, solvents, chemicals and heat. Heat-sensitive phenolic resins that are insoluble in oil may be dissolved in solvents and employed as the sole vehicle for metal coatings (Lowell, 1984).

Alkyd resins: The advent of alkyd resins is considered to be a major breakthrough in modern paint technology. Alkyds are oil-modified polyester resins produced by the condensation reaction of polyhydric alcohols, polybasic acids and monobasic fatty acids, e.g., linseed or soya fatty acids (Lowell, 1984). The specific definition, which has gained wide acceptance, is that alkyds are polyesters modified with monobasic fatty acids (Lanson, 1978). The alkyds used initially were principally products of the chemical reaction of phthalic anhydride and glycerol with certain vegetable oils or their corresponding fatty acids (Brunner, 1978).

In recent years, the terms 'non-oil' and 'oil-free' alkyd have been used to describe polyesters formed by the reaction of polybasic acids with polyhydric alcohols in excess of stoichiometric amounts. These products are best described as saturated polyesters containing unreacted -OH or -COOH groups (Lanson, 1978).

Monobasic acids modify the properties of alkyd resins by controlling functionality, and thus polymer growth, as well as by the nature of their inherent physical and chemical properties. The majority of monobasic acids used in alkyd resins are derived from natural glyceride oils and are in varying degrees of unsaturation. The most common fatty acids present in these oils include lauric, palmitic, stearic, oleic, linoleic, linolenic, eleostearic, ricinoleic and licanic acids. Alkyd resins with relatively high fatty acid contents are called 'long-oil' alkyds; when the oil percentage is relatively low, they are known as 'short-oil' alkyds (Lanson, 1978).

Although glycerol and pentaerythritol are the major polyhydric alcohol components of alkyd resins, a number of other polyols are employed to a lesser degree, including sorbitol, trimethylolethanol, trimethylol propane, dipentaerythritol, tripentaerythritol, neopentylglycol and diethylene glycol. The principal polybasic acid for alkyd resins is phthalic acid, which is prepared and used as the anhydride. Isophthalic anhydride is also employed to yield somewhat faster drying and tougher, more flexible films than the analogous *ortho*-phthalic resins.

Long-oil alkyds are soluble in mineral spirits and are widely employed in architectural brushing enamels, exterior trim paints and wall paints, and their flexibility and durability have made them useful for top-side marine paints, metal maintenance paints and as a clear varnish. Medium-oil alkyds are the most versatile of the alkyd class, and their superior air drying, flexibility and durability allow for their use in maintenance paints, metal primers and a variety of general-purpose enamels. Short-oil alkyds are either drying or nondrying, require a strong aromatic solvent, such as toluene or xylene (see monographs, p. 79 and p. 125), and have been employed principally as industrial baking finishes.

Many polymeric materials and reactive functional materials can be used to produce suitably designed alkyds and to impart improved and/or special film-forming properties, including nitrocellulose, polyisocyanates, urea-formaldehyde resins, silicones, melamine-formaldehyde resins, reactive monomers, phenolic resins, cellulose acetobutyrate, chlorinated rubber, phenolic varnishes, vinyl resins, polyamides, chlorinated paraffin, natural resins, epoxy resins and monobasic aromatic acids (Lanson, 1978).

Short-oil alkyd resins with a phthalic anhydride content of 38–45% contain a higher proportion of hydroxyl groups, which provide reactive sites for alkylated urea-formaldehyde and melamine-formaldehyde resins. These alkyds are generally based on tall-oil fatty acids, soya bean oil or fatty acids. Amino-alkyd resins are widely used in industrial baking enamels (Lanson, 1978).

The compatibility of alkyd resins with nitrocellulose extends up to 55% nitrocellulose content, and nitrocellulose lacquers are produced in large quantities. Alkyds modified with short-chain acids, such as those from coconut oil and castor oil, are widely used in high-grade furniture lacquers (Lanson, 1978).

The general effect of the alkyd modified resins has been to upgrade the gloss, adhesion and durability of nitrocellulose lacquers. Alkyd resins have been used in protective coatings for over 40 years, and they still rank as the most important synthetic coating resin, constituting about 35% of all resins used in organic coatings (Lanson, 1978). The largest market for alkyds in product finishes includes machines and equipment and wood and metal furniture and fixtures (Connolly *et al.*, 1986).

Vinyl resins: Vinyl polymers and copolymers were among the first synthetic polymers and are widely employed in trade paints. Although synthesis of polyvinyl chloride (see IARC, 1979a) was first reported in 1872 and that of polyvinyl acetate (see IARC, 1979b) in 1913, neither was developed commercially until the mid-1920s (Powell, 1972).

Vinyl monomers can be induced to polymerize readily by the addition of initiators, such as peroxides and azo compounds, which decompose at reactor temperature to generate free radicals. Polymerization processes involve radical formation, initiation, propagation, including chain transfer, and termination (Powell, 1972). The principal vinyl resins of importance in the paint industry are polyvinyl chloride, polyvinyl acetate and polyvinyl butyrate, which are available in a range of different compositions for specific uses and in grades that can be handled as true solutions in organic solvents, as high-solid dispersions ('organosols' or 'plastisols'), as dry powders or as water-borne latexes. Polyvinyl acetate is extensively used in emulsion paints, providing exceptional flexibility, toughness and water and chemical resistance. Vinyl chloride copolymer coatings are used in coil coatings and in industrial and marine coatings (Lowell, 1984; Connolly *et al.*, 1986).

Water emulsions of high molecular-weight polyvinyl acetate have been widely used in interior house paints. Copolymers of vinyl acetate with acrylic monomers are also employed in exterior emulsion house paints. Latexes of vinyl chloride polymers and copolymers have been commercially important for a number of years, e.g., as copolymers in exterior house paints, which often include a vinyl chloride-acrylic ester copolymer modified with a specially designed alkyd resin. Polyvinyl acetate and vinyl acetate copolymers are used in latex-based interior and exterior paints (Powell, 1972).

The principal modifying monomers that have been used with vinyl acetate include dibutyl maleate and fumarate, butyl-, 2-ethylhexyl- and isodecyl acrylates and higher vinyl esters (Powell, 1972). Copolymers of the acrylates and vinyl acetate are commonly called vinyl acrylics and generally contain 15% acrylic monomer by weight (Connolly *et al.*, 1986).

Acrylic and methacrylic ester resins: Acrylic resins have been divided into four specific types: water-based, solvent-based thermoplastic (lacquer types), solvent-based thermosetting and powder coating resins (Connolly *et al.*, 1986).

Commercial acrylic and methacrylic polymers are made from a variety of acrylic and methacrylic monomers (see IARC, 1979c). The major monomers used are the methyl, ethyl, butyl and 2-ethylhexyl esters of acrylic and methacrylic acids, which readily undergo polymerization in the presence of free-radical initiators, such as peroxides, to yield high molecular-weight polymers (Allyn, 1971; Lowell, 1984; Connolly *et al.*, 1986).

Monomeric acrylic esters are produced commercially by several processes based on ethylene cyanohydrin, acetylene, β-propiolactone (see IARC, 1974a) and ethylene oxide (see IARC, 1985a, 1987g). The acetone-cyanohydrin process is the major method for the production of monomeric methacrylate esters (Allyn, 1971).

Several types of functionality can be incorporated into acrylic and methacrylic monomers. These are principally the amide, carboxyl, hydroxyl and epoxy types and are used to confer cross-linking capabilities and thermosetting properties on the resulting polymers (Allyn, 1971). Other monomers are used in conjunction with the acrylic monomers to achieve different properties, including vinyl acetate (see IARC, 1986a), styrene (see IARC, 1979d), vinyl toluene, acrylonitrile (see IARC, 1979a, 1987h) and methylacrylamide (Allyn, 1971).

Acrylic and methacrylic polymers are used in the formulation of clear and pigmented lacquers. Dispersions in water and in organic solvents provide latex and organosol coatings, respectively. Polymethacrylates are harder and less flexible than the corresponding acrylates (Lowell, 1984).

Although thermoplastic acrylic emulsions have been commercially available since 1925, they were not widely used in coatings until 1953 when new grades specifically designed for paints were introduced (Allyn, 1971). In the late 1950s, lacquers of greatly improved durability, based on polymethylmethacrylate or thermosetting acrylic enamels were adopted by the automobile industry (Lowell, 1984). By the 1960s, the use of acrylic emulsion polymers had been firmly established in exterior coatings for wood surfaces, a field long dominated by oil paints (Allyn, 1971).

Epoxy resins: Epoxy resins were first derived from bisphenol A and epichlorohydrin (see IARC, 1976b, 1987i) and introduced into the paint industry in the late 1940s. Two major types of epoxy resin exist - glycidyl ether epoxy resins (see monograph, p. 237) and epoxidized olefins - the former of which is the most important. Epoxy resins based on bisphenol A and epichlorohydrin are the most prominent of the glycidyl ether category and are produced by a condensation reaction in which bisphenol A and epichlorohydrin are reacted in the presence of alkali (Allen, 1972). The resultant diglycidyl ether resin has a functionality of two reactive epoxy groups per molecule. Epoxy resins can be polymerized through their reactive epoxy group using amines or polyamides (Allen, 1972; Lowell, 1984).

Epoxy resins of a second major type, epoxidized olefins, are based on epoxidation of the carbon–carbon double bond. Coating compositions derived from epoxidized olefin have better weathering characteristics than analogous systems based on bisphenol A diglycidyl ether resins (Allen, 1972).

In order to proceed from the relatively low molecular weight of the coating composition, as applied, to the high molecular-weight polymer necessary for optimal film properties, a 'curing' or polymerization must take place, which can involve either the epoxide or free hydroxy groups in the resin, or a combination of the two. Some of the principal reactions that have been used include chemical cross-linking *via* the amine–epoxide reaction, an anhydride–epoxide reaction, reaction with methylol groups, e.g., between the secondary hydroxyl groups of the higher molecular-weight resins and the methylol groups of phenol-formaldehyde and urea-formaldehyde resins, cross-linking *via* the isocyanate–hydroxyl reaction and esterification reactions between solid-grade epoxy resins and carboxyl-containing compounds, particularly drying-oil fatty acids (Allen, 1972).

Solid-grade glycidyl ether resins are readily soluble in polar solvents, such as ketones, esters and ether-alcohols, as well as in chlorinated hydrocarbon solvents (Allen, 1972).

Glycidyl ether resins of high molecular weight (number average[1], about 7000; weight average[2], about 200 000) are unique among epoxy coatings in that they form coatings by solvent evaporation alone (Allen, 1972). Because of their toughness, adhesion and corrosion resistance, epoxy resins are used in many applications, including industrial maintenance, automobile primers and coatings for appliances and steel pipes. Epoxys combined with phenolic resins and thermosetting acrylic resins yield high bake finishes with hardness, flexibility and resistance to chemicals and solvents (Lowell, 1984).

Polyurethane resins: Although polyurethanes were synthesized in 1937, the utility of weather-resistant polyurethane coatings became manifest only in the 1960s. Polyurethanes are obtained from the reaction of polyhydric alcohols and isocyanates. Nonreactive polymers can be prepared by terminating the polymer chains with monofunctional isocyanates or alcohols. Cross-linked polymers are formed from polyfunctional isocyanates or alcohols (Lowell, 1984). Isocyanates that have been employed include toluene diisocyanate (see IARC, 1986b) and hexamethylenediisocyanate.

Because of the wide range of physical properties obtained through variations in formulating polyurethane coatings, they are used in industrial and maintenance coatings, as well as in coatings for wood, concrete and flexible structures (Lowell, 1984). Polyurethane coatings are being used increasingly for automobiles and aircraft. Urethane ester-type resins (also

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[1] Molecular weight value from number of molecules each multiplied by molecular weight and total divided by number of molecules

[2] Molecular weight value from sum of number of grams of material with a particular molecular weight each multiplied by its molecular weight and total divided by total number of grams

called urethane alkyds or uralkyds) are used primarily in architectural coatings. Two-component systems are used as high-performance coatings for maintenance and product finishes (Connolly *et al.*, 1986).

Silicone resins: Silicones are characterized by a siloxane backbone, e.g., -Si-O-Si-O-, with organic groups which determine the properties of the final polymer attached to the silicon atoms. The monomeric precursors of silicone polymers are mono-, di- and trisubstituted halosilanes (usualy chlorosilanes). Monosubstituted silanols condense to highly cross-linked polymers, which are chiefly used in coatings. The degree of cross-linking and consequent physical properties are controlled by adjusting the ratio of mono- and disubstituted chlorosilanes. Alkyd resins with terminal hydroxyl groups can be condensed with silicones to produce hybrid polymers (Lowell, 1984).

Silicone resins are used to waterproof masonry and are blended with alkyds to formulate industrial maintenance coatings for storage tanks and other metal structures (Lowell, 1984).

Cellulose derivatives: Cellulose nitrate, commonly misnamed nitrocellulose, is the oldest cellulose derivative, first prepared in 1838 from cotton linters using a nitrating mixture of nitric and sulfuric acids (Jones, 1938; Sears, 1974). Before the early 1920s, only very high molecular-weight cellulose nitrate was available, which had limited utility in lacquers. The development of stable cellulose nitrate with lower viscosity after the First World War resulted in fast-drying lacquer coatings which were used extensively in automobile and furniture production. In the USA, three types of commercially available cellulose nitrates are distinguished by their nitrogen content and solubility. Each of these types is available in a variety of viscosity grades, which are a measure of the polymer chain length (Hamilton & Early, 1972; Brewer & Bogan, 1984).

Cellulose nitrate lacquers have also been formulated to contain resins, plasticizers, solvents and thinners. The resins that were employed initially with cellulose nitrate lacquers include shellac, sandarc, mastic and ester gums, which were added in amounts of about two-thirds of the weight of cellulose nitrate. Plasticizers are usually added at about 10% of the weight of cellulose nitrate. Camphor, which was first used in the USA in the mid-1800s, was replaced by castor oil; by the late 1920s, plasticizers such as triphenyl phosphate, tricresyl phosphate, dibutyl phthalate and butyl tartrate were being used increasingly. The principal solvents used initially with cellulose nitrate included ethyl, butyl and amyl acetates, acetone, 'diacetone alcohol', industrial spirit, ethanol and mixtures of alcohol with benzene or toluene and of alcohol with esters (Heaton, 1928; Hamilton & Early, 1972).

Another cellulose derivative, ethyl cellulose, is made by treating cellulose from wood pulp or cotton with a solution of sodium hydroxide to obtain primarily what is commonly referred to as 'alkali' or 'soda' cellulose. Further treatment with ethyl chloride under heat and pressure yields ethyl cellulose, which can be made in different viscosities. It is widely used in clear, dyed or pigmented lacquers for flexible substrates. Although less often used in paints, it has been formulated with silicone coatings to prevent pigment settling and sagging (Singer, 1957; Hamilton & Early, 1972).

Cellulose acetate is a linear high polymer that is obtained by first pretreating cellulose with a reduced amount of acetic acid to cause a certain amount of swelling, and then reacting it with acetic anhydride in the presence of sulfuric acid. Cellulose acetate lacquers are stable to light and heat and have good resistance to oils, greases and weak acids (Singer, 1957).

Methylcellulose, carboxymethyl cellulose and hydroxyethyl cellulose are water-soluble polymers that are used as thickeners in latex-based coatings. Cellulose acetate-butyrate is used as a resin modifier in automobile lacquers based on polymethylmethacrylate.

(*c*) *Solvents* (see also the monographs on solvents, pp. 43 *et seq.*)

Solvents are widely used to keep paints in liquid form so that they can be applied easily. Until the late nineteenth century, turpentine and alcohol were the only solvents of any importance. Since the early 1900s, the number of solvents has increased considerably to encompass initially a broad range of petroleum and coal-tar distillates, alcohols, esters, ketones, glycols and halogenated hydrocarbons and, more recently, synthesized glycol ethers and esters. A large variety of mixtures of these classes is also employed.

Solvents in the turpentine category are derived mainly from the resinous exudations of various species of pine and other conifers and consist essentially of mixtures of various terpenes such as α- and β-pinene (Heaton, 1928).

A petroleum distillate, known as 'white spirits' (see the monograph on some petroleum solvents, p. 43), which consists mainly of aliphatic, alicyclic and aromatic hydrocarbons, was introduced as a solvent in the paint industry in 1885. For many years it was regarded as a cheap adulterant for turpentine but, as its use developed, it attained recognition as a different solvent. In addition to white spirits, several other paint solvents are prepared from petroleum and coal-tars (see IARC, 1985b, 1987j). Coal-tar distillates were the original source of commercial quantities of solvents such as benzol (a mixture containing mainly benzene, with smaller amounts of toluene, light hydrocarbons and carbon disulfide), benzene (see IARC, 1982b, 1987k), toluene, xylene and solvent naphtha (Heaton, 1928).

(*d*) *Additives*

Additives are defined as those chemicals that perform a special function or impart a special property to paint. They are present at low concentrations, generally 0.2–10%, and include driers, thickeners, anti-skinning agents, plasticizers, biocides, surfactants and dispersing agents, antifoam agents and catalysts (Krivanek, 1982).

(i) *Surfactants*

Surfactants, which are classified into anionic, cationic, amphoteric and nonionic categories, are used as pigment dispersants in both nonaqueous and aqueous systems. Dispersants employed in nonaqueous systems include lecithin, zinc naphthenate, calcium naphthenate, copper oleate and oleic acid. Ionizable dispersants that are usually employed in aqueous coatings include tripotassium polyphosphate, tetrapotassium pyrophosphate, sodium salts of arylalkyl-sulfonic acids and sodium salts of carboxylic acids (Lowell, 1984).

In addition to pigment dispersion, surfactants are used in paints as emulsifying agents, protective colloids, wetting agents, thickeners and antifoaming agents. A number of water-soluble resins and gums have been used as protective colloids or thickeners in emulsion paints. Water-soluble hydrophilic colloids include agents such as gum arabic, gum tragacanth, starch, sodium alginate, methyl cellulose, hydroxyethyl cellulose, polyvinyl alcohol, ammonium caseinate and sodium polyacrylate. The acrylate salts, casein and cellulosics, have been widely used in acrylic paints, while the major thickeners for styrene-butadiene paints have been alkali-soluble proteins (soya bean proteins). Methyl cellulose and hydroxyethyl cellulose are common thickeners for polyvinyl acetate paints (Martens, 1964).

Noncellulosic thickeners used in latex paints include maleic anhydride copolymers, mineral fillers, such as colloidal attapulgite (see IARC, 1987l,m) and treated magnesium montmorillonite clays, natural products (e.g., alginic acid, casein and soya bean protein), polyacrylamides, polyacrylic acid salts and acid-containing cross-linked acrylic emulsion copolymers (Connolly *et al.*, 1986).

A recent partial list of surfactants employed in water-borne paints includes aluminium stearate, cellulose ethers, polydimethyl siloxanes, polyethylene, alkali metal phosphates and sodium dioctyl sulfosuccinate (Hansen *et al*, 1987).

A variety of other surface-active agents are added to paints to control flow, levelling, sagging, settling and viscosity, including hydrogenated castor oils, lecithin, metallic soaps (e.g., linoleates, palmitates and stearates), treated montmorillonite clays, peptized oil gels, polyolesters, silicas and soap solutions (Connolly *et al.*, 1986).

(ii) *Driers*

Driers (siccatives) that have been used in water-borne paints containing unsaturated polymers (e.g., alkyds) to accelerate curing are principally metal salts (lead, calcium, cobalt, manganese, zirconium, barium, zinc and cerium-lanthanum) of naphthenic acid, tall oil acid, 2-ethylhexanolic acid and neodecanoic acid, generally at levels ranging from 0.3 to 0.8% (w/w; Hansen *et al.*, 1987). Cobalt-based driers are the most commonly used commercially and are active catalysts in both air drying and heat cure systems. Manganese is another major active drier. Other metal driers serve as auxiliary driers and are usually used in combination with cobalt and manganese. Lead (see IARC, 1980a, 1987n) driers were at one time the major auxiliary driers; however, legislation limiting the amount of lead that can be used in surface coatings has resulted in a sharply reduced use. The most suitable replacements for lead appear to be zirconium, calcium and cobalt-zirconium compounds (Connolly *et al.*, 1986). In addition, 1,10-phenanthroline has been employed at levels of 0.02% (w/w; Hansen *et al.*, 1987).

(iii) *Plasticizers*

The early use of plasticizers is illustrated by the incorporation of castor oil and glycerine into alcoholic spirit varnishes and of camphor into spirit varnishes and lacquers, as well as into cellulose ester enamels and lacquers in the late nineteenth and early twentieth centuries (Heaton, 1928). In 1912, triphenyl phosphate began to replace camphor for the plasticization of cellulose nitrate; later, tricresyl phosphate was used. The use of plasticizers was generally expanded by the mid 1920s with the introduction of di(2-ethylhexyl)phthalate (see IARC, 1982c) and dibutylphthalate in the mid-1930s (Sears, 1974).

Plasticizers that are generally added in quantities of up to about 2% include dibutyl-, diethyl-, diethylhexyl- and dioctylphthalates and, to a lesser extent, the low molecular-weight esters of adipic and sebacic acid, tributyl phosphate and castor oil. Polyester resins, including maleic residues, sulfonamides, triorthocresyl phosphate and chlorinated diphenyls, have been used occasionally (Piper, 1965; Krivanek, 1982).

(iv) *Biocides (fungicides, preservatives and 'mildewcides')*

Biocides are generally added to paint at low concentrations – less than 1% – for preservation in the tin. Each biocide formulation can contain several agents.

The function of a preservative is to retard the enzymatic degradation of cellulosic and other thickeners in latex paints in the tin. The function of a mildewcide is to retard the growth of fungi on applied exterior latex and solvent-based paints. These compounds are often the same, but are used in different quantities. Much less preservative is needed to preserve a latex paint than the amount of mildewcide required to retard mildew growth on an exterior paint (Connolly *et al.*, 1986).

Phenylmercury compounds (e.g., acetate, propionate, benzoate, dodecyl succinate and oleate) were previously used extensively as mildewcides. Although mercuric compounds are no longer employed in solvent-based paints in the USA because of legislative restrictions, they are still permitted in water-based paints. Biocides that have been employed include tributyltin oxide, chlorothalonil (see IARC, 1983a), 1,2-benzisothiazolin-3-one, carbendazim, benzyl alcohol mono(poly) hemiformal, 1-(3-chloroallyl)-tetra-aza-adamantane hydrochloride, 5-chloro-2-methyl-4-isothiazolin-3-one, dodecyl dimethylammonium chloride, 5,8,11,13,16,19-hexaoxatricosane, 3-iodopropynyl butyl carbamate, 2-methyl-4-isothiazoline-3-one, formaldehyde, sodium nitrite and sodium benzoate (Connolly *et al.*, 1986; Hansen *et al.*, 1987).

(v) *Antiskinning agents*

Antiskinning agents are added to paints to retard the formation of skin on the surface of the liquid coating, in either closed or open tins, without retarding the drying of the product. The principal antiskinning agents are oximes or phenol derivatives; the major oxime used is methyl ethyl ketoxime. Smaller quantities of butyraldoxime and cyclohexanone oxime are used. The phenol derivatives used are mainly methoxyphenol, *ortho*-aminophenol and polyhydroxyphenol. Minor quantities of cresols, guaiacol, hydroquinone (see IARC, 1977a), isobutoxysafrol and lignocol have also been used as antiskinning agents (Connolly *et al.*, 1986).

(vi) *Miscellaneous additives*

Other additives are employed in paints, including polymerization initiators such as benzoyl peroxide (see IARC, 1985c) and azobisbutyronitrile; antioxidants such as hydroquinones, phenols and oximes; ultraviolet light absorbers, luminescent and fluorescent materials and heat stabilizers (Connolly *et al.*, 1986).

1.2 History of the manufacture of paints and related products

(*a*) *History of paint manufacture*

The history of paints and other related products has been reviewed (Heaton, 1928; Jones, 1938; Singer, 1957; Martens, 1964).

Paint has existed from the earliest times – literally from the beginning of history. Water-based paint was used for pictorial and decorative purposes in caves in France and Spain as early as 30 000–15 000 BC. The earliest efforts of cavemen were expressed by daubing coloured mud on the walls of their caves. The addition of crushed berries, blood, milk, eggs, dandelion or milkweed sap and other natural materials, such as chalk, earth colours, charcoal and ashes, to early paints improved both adhesion and utility.

The earliest pigments were natural ores. By 6000 BC, calcined (fired) mixtures of inorganic components and organic pigments were employed in China. By 1500 BC, the Egyptians were using dyes such as indigo and madder to prepare blue and red pigments, and by 1000 BC they had developed a varnish from gum arabic that contributed to the permanence of their art. Although paint and varnish have existed since earliest times, it was not until the 1700s that commercial manufacture of paints began in Europe and the USA. The early manufacturers of paint ground their pigments on a stone table with a round stone.

Whitewash, which is essentially water-slaked lime, was used during the early history of many countries. Various materials, such as Portland cement, were added to improve the material and it gradually evolved into the present-day cement paints. Skimmed milk and, later, casein were added to improve adhesion and durability. The addition of pigments, whiting and clay and, finally, the replacement of lime traced the evolution from whitewash to casein paint. Drying oils were later added to casein paints to improve water resistance. Casein paints were continually improved and, by the 1930s, they contained highly refractive index pigments similar to those used in oil paints.

In the late 1800s, grinding and mixing machines were developed to enable manufacturers to produce large volumes of paint. However, it was not until the twentieth century, during the period from the mid-1920s to prior to the Second World War, when improvements in paint technology began to parallel more closely advances in chemistry, that paint became sophisticated with regard to the process of manufacture, its use and the methods of its application. The development of highly efficient paint-making equipment and an expanding scope of areas of utility, e.g., automobile, marine and architectural areas, contributed to these advances. Paint technology advanced most rapidly in countries where industrialization developed fastest, i.e., in western Europe and the USA, the greatest advances occurring after the Second World War (Brunner, 1978).

For centuries, it was common practice for painters to prepare their own products from pigments and oils (principally linseed oil). Little 'ready-mixed' paint was available until just before the beginning of the twentieth century, when a large number of factories were established, principally in Europe and the USA (Brunner, 1978).

Mixing was originally conducted in an apparatus known as a 'pug mill', the general construction of which was a cylinder fitted with a vertical shaft carrying arms. Until the introduction of machinery, grinding was generally accomplished by rubbing down the mixed paint with a large 'muller' of glass or granite on a slab of similar material. Cone mills were later employed which were made in various sizes - small ones for hand use and larger sizes for factory use. Grinding machinery was introduced into paint manufacture in Europe around the late 1870s and developed enormously in design and efficiency during the twentieth century. Two- and, later, three-roller grinding mills were first introduced which greatly enhanced the speed and efficiency of grinding. Multiple-roll mills, e.g., four and five as well as combinations of edge-runner, horizontal mixers and roller mills, were all used in the 1920s for paint production and were employed until the advent of more modern plant methods. The conversion of paste paints to the liquid or 'ready-mixed' condition required a step called 'thinning' or the addition of a thinning vehicle. Vertical mixers were used for this purpose (Heaton, 1928).

(*b*) *History of lacquer manufacture*

The use of lacquer dates from about 500 BC when the Chinese and Japanese used the sap of the tree, *Rhus vernicefera*, to prepare lacquer for the ornamentation of woods and metals (Singer, 1957).

In the early manufacturing processes of the late eighteenth and early nineteenth centuries, the most frequent method of mixing the components of lacquers was by use of a slowly revolving churn that contained baffles. In older works, these were merely wooden barrels, but later they were specially designed and made of aluminium, since other metals are likely to affect the colour of clear lacquers due to the acidity of the solvents or resins used. At larger installations, a method that involved lifting up a container by means of a special lifting carriage to a battery of paddle stirrers was also used. After completion of dissolution, the container was covered and lifted by crane to its storage bench as standardized lacquers or stock solutions for further mixing (Heaton, 1928; Jones, 1938).

(*c*) *History of varnish manufacture*

The use of oil varnishes and resins was already well understood at the time of Theophilus the monk, who wrote about them in the eleventh century. The preparation of a drying oil by treating linseed oil with lime and litharge was described at an even earlier date by Eraclius in the ninth century (Barry, 1939). The travels of Marco Polo and the discovery of the New World brought a great variety of exotic gums and resins to Europe.

Towards the end of the eighteenth century, paints and varnishes were based on natural resins, e.g., copal and amber, and vegetable oils, e.g., linseed, walnut, hempseed and poppy seed oils. By the nineteenth century, fossil and semi-fossil gums replaced amber, which was by then scarce and expensive. These principal substitutes included gum arabic, gum elastic, copal, mastic and shellac (Singer, 1957). Early in the twentieth century, the first practical phenol-formaldehyde resins were developed. Research over the following two decades provided the basis for greatly improved varnishes.

Varnishes can be divided into three main types - oil, spirit or alcohol and water - of which the oil varnishes are the most important, such that the term 'varnish' generally implies oil varnish. The manufacture of oil varnishes involves the following operations: (i) 'gum running' or melting the resin; (ii) boiling the oil and mixing with the melted 'gum'; (iii) boiling the varnish; (iv) introducting driers; (v) thinning the varnish; and (vi) maturing the varnish (Heaton, 1928).

1.3 Construction painting and paint products used

Paints that are used on architectural structures (indoor and outdoor surfaces) are comprised of primers or undercoats for walls and woodwork and mat, semigloss or gloss finishing coats. The primers and finishing coats differ primarily in pigment/vehicle balance and in additives and vehicle type. Primers (usually called 'primers/sealers') are used to seal the variable porosity of the substrate (e.g., wood) and to adhere to the substrate and to subsequent coats of paints. For most architectural uses, an alkyd-based primer/sealer is used (Schurr, 1981).

(*a*) *Exterior house paints*

Casein paints, which have been used since the mid-1800s, were continually improved so that, by the 1930s, they contained high-refractive index pigments. Later, a drying oil was added to casein to produce an emulsion paint (Martens, 1964). Traditionally, linseed oil and oleoresinous vehicles have accounted for the bulk of architectural (house) paints. Several other oils have been used, but to a much lesser degree than linseed oil, and often in conjunction with linseed oil. The more important have been tung oil, perilla oil, soya bean oil, fish oils, safflower oil and dehydrated castor oil. Modern oil-based house paints generally contain combinations of untreated drying oil (unbodied oil) and drying oil treated (polymerized) so that its viscosity is increased (bodied oil) (Schurr, 1974).

A wide variety of thinners and solvents has been employed traditionally - principally turpentine, white spirits, benzene and solvent naphtha. Turpentine was the accepted thinner until the 1930s, at which time white spirits were introduced for reasons of cost and odour (Schurr, 1974).

The classic house paint consisted of ~80% basic lead carbonate - white lead - and 11% raw or boiled linseed oil which contained a small amount of drier in the form of metallic soaps. The paint was thinned with additional oil for application. Gradually, other primer pigments and inert fillers were introduced into the basic lead-in-oil formula. These included zinc oxide, leaded zinc oxide, lithopone and, finally, titanium dioxide (see monograph, p. 307). The use of lead pigments has been increasingly curtailed because of legislation (Schurr, 1974, 1981).

In the late 1930s and 1940s, alkyd paints were gradually introduced, particularly in the dark colours, with a marked improvement in properties such as colour and gloss retention. In the 1960s, white alkyd house paints without lead pigments were marketed by a few paint companies; they usually contained phenylmercury oleate and other arylmercury derivatives as fungicides. By the 1970s, alkyd house paints were replacing oil house paints, the faster drying time of the alkyds being obtained with cobalt and calcium soaps.

Around 1957, the first exterior water-based house paints were introduced. Most of these were based on acrylic-type latexes, and the paint had excellent colour retention on exterior exposure. Since that time, water-soluble and emulsified linseed oil house paints have been marketed which combine the advantage of an oil paint and a water-type paint in one product (Martens, 1964). Because of ease of application, cleaning ability with soap and water and good service, latex paints comprise most of the exterior paint market. Among the more common latexes are the acrylics, polyvinylacetate-dibutylmaleate copolymers, ethylene copolymers and acrylate copolymers (Schurr, 1974). Table 1 lists the ingredients of typical white house paints with oil and latex binders (Fisher, 1987).

Table 1. Examples of formulations of white house paints from the 1980s[a]

Type of paint and ingredients	Weight (%)
Oil-based	
Titanium dioxide (anatase) Titanium dioxide (rutile)	12.7
Zinc oxide (acicular)	19.8
Water-ground mica	6.2
Magnesium silicate	23.2
Refined linseed oil	23.4
Bodied linseed oil	7.8
Lead and manganese soap solution	1.3
Mineral spirits	5.7
Acrylic latex	
Titanium dioxide (rutile)	20.2
Titanium dioxide (anatase)	0.8
Water-ground mica	2.5
Magnesium silicate	8.4
Calcium carbonate	6.9
Acrylic latex	41.9
Water	7.0
Cellulosic thickener	8.0
Nonionic emulsifier	0.9
Alkyl-aryl surfactant	0.2
Commercial defoamer	0.2
Ethylene glycol	2.1
Ammonium hydroxide	0.2
Organic mercurial fungicide	0.2
Pine oil	0.6

[a] From Fisher (1987)

The main categories of organic pigments used in interior and exterior construction or architectural paints include phthalocyanine and monoazo dyes (Volk & Abriss, 1976).

(*b*) *Interior paints*

Until the early 1930s, the vehicles employed in interior paints were based on oils treated to increase viscosity (bodied oils) and heat-treated oils, usually combined with rosin, ester gum or other natural gums. Most solvent-type paints for interior use contain some oil and dry by oxidation. Oils that have been used in interior compositions include bleached linseed oil, dehydrated castor oil, soya bean oil, tung oil and oiticica oil. The principal pigments used for interior white paints are titanium dioxide, zinc oxide and various carbonate and siliceous extenders which are used to control pigment volume and gloss. From about 1927, with the development of alkyd resins, a variety of architectural enamels for interior and exterior use was based on these resins. However, the bulk of enamels produced for interior use contained oil treated to increase viscosity (bodied oil) and/or varnish as the binder until after 1945 (Volk & Abriss, 1976).

Early water-based interior paints were alkyd-resin emulsions stabilized with large amounts of casein and other stabilizers. The alkyds used were generally long-oil vehicles and the paints generally had poor emulsion stability. Three types of latex polymers are used most commonly in the manufacture of latex paints: styrene-butadiene types, polyvinyl acetate types and acrylics. Copolymer blends of styrene and acrylate have also been employed, combining the most durable features of each monomer into a single polymer (Volk & Abriss, 1976).

After the Second World War, the excess capacity for manufacturing styrene-butadiene rubber (see IARC, 1979d) was adapted to make styrene-butadiene latexes that could be used in paint. These water-based latexes appeared in the USA around 1948 in interior wall finishes (Martens, 1964; Schurr, 1981). Although polyvinyl acetate latexes have been in existence since the late 1930s, they were used as adhesives rather than in paints until after the Second World War (Volk & Abriss, 1976).

The general categories of extender pigments that are used in latex paints include clays, calcium carbonates, silicates, diatomaceous earths, silicas, barytes and talcs (see IARC, 1987a,b,c,d). Along with latex, surfactants, pigments and several other additives are usually incorporated into the formulation to obtain a stable and satisfactory product, including thickeners, defoaming agents, freeze-thaw stabilizers, coalescents and pH adjusters. Although natural thickeners, such as casein, were formerly used, their use has decreased appreciably in recent years. The thickeners employed most commonly are cellulosics - principally hydroxyethyl cellulose and methyl cellulose - polyacrylates, polyacrylamide, polyvinyl alcohols and many others. Ethylene and propylene glycols serve as freeze-thaw stabilizers. Coalescents are additives designed to optimize the coalescence of latex particles (Volk & Abriss, 1976) and include hexylene glycol, butyl cellosolve and butyl carbitol.

(c) *Masonry paints*

Casein-based paints applied to masonry and plaster surfaces were used in early construction work. These paints usually contained about 10% casein with some lime to insolubilize the casein after application (Martens, 1964). Latex-based primers/sealers are now often used for masonry surfaces. The latex vehicle is generally more resistant to alkali and permits evaporation of water from masonry surfaces without disruption of the film. Both alkyd and latex vehicles adequately seal porous surfaces (Schurr, 1981). Also, oil paints and styrene-butadiene copolymer, polyvinyl acetate emulsion, resin-emulsion and chlorinated rubber paints have all been used extensively on masonry surfaces.

Concrete floor coatings must possess good water resistance and adhesion over damp surfaces. Powdery concrete is first covered with a solvent primer. A satisfactory floor paint can be formulated using a styrene-butadiene latex fortified with an epoxy ester (Martens, 1964). Two examples of concrete floor enamels are presented in Table 2. Acrylic emulsion paints are widely used outdoors on concrete, stucco and cinder block because of their durability, adhesion and flexibility (Allyn, 1971).

Table 2. Examples of formulations of grey concrete floor enamels from the 1950s[a]

Type of paint and ingredients	Weight (%)[b]
Polystyrene-butadiene-based	
Titanium dioxide (rutile)	17.6
Lampblack	0.5
Organic ester	0.2
Polystyrene-butadiene copolymer resin	27.0
Raw linseed oil	1.9
40% Chlorinated paraffins	4.7
High-flash naphtha	25.0
White spirits	24.4
Chlorinated rubber-based	
Titanium dioxide (rutile)	17.2
Lampblack	0.5
Organic ester	0.3
Chlorinated rubber	13.8
40% Chlorinated paraffins	3.2
Thermolysed tung oil	3.5
Alkyd resin	7.8
Soya lecithin	0.4
Dipentene	7.5
High-flash naphtha	14.1
Aromatic high-solvency petroleum solvent	24.6
White spirits	6.4
Antiskinning agent	0.1

[a] From Singer (1957)
[b] Calculated by the Working Group

Although cement paints are used on all types of masonry, they tend to be brittle and to 'powder off'. Cement paint typically contains white Portland cement, gypsum, calcium chloride and hydrated lime added to water. Fortified cements have been prepared using latexes such as styrene-butadiene, polyvinyl acetate and acrylic esters added to Portland cement in amounts ranging from 10 to 40% latex on a solid basis (Martens, 1964).

(*d*) *Waterproofing paints*

These paints are applied on the outside of unpainted concrete, brick, stucco, etc., and have been formulated in a variety of ways to include components such as wax, aluminium stearate and silicone resins. The earliest, simplest waterproofing formulations were of the wax type and consisted of paraffin wax, raw chinawood oil and white spirits. Stearate formulations consisted of aluminium stearate in white spirits, with occasional addition of paraffin wax. A significant advance in the manufacture of waterproofing paints in the mid-1950s involved the use of silicone resins. A typical formulation of silicone waterproofing contains silicone resin and xylene. Another commonly used product contains special silicones, such as sodium methyl siliconate, in aqueous solution (Singer, 1957).

1.4 Surface coating in the wood industry and products used

Shellac and other gums or resins, such as elemi, sandarac, manila and benzoin, dissolved in alcohol or spirits of wine were introduced by the French in the seventeenth century and have been used for a long time in Europe for finishing wood grain and for their quick-drying properties. By the beginning of the eighteenth century, use of varnishes on furniture increased rapidly, particularly in France and England, although the manufacture of varnishes was still incidental to the work of painters, decorators and gilders. By the mid- and late eighteenth century, varnishing of furniture was well established in Europe (Jones, 1938; Barry, 1939).

Four properties are considered to be essential in furniture varnish: quick, hard, tough drying (3–4 h); good sanding and polishing properties; good resistance to water, acids, alkalis, etc.; and good heat resistance (Singer, 1957). Table 3 gives the formulation of a best-grade furniture varnish used in the 1950s.

Table 3. Formulation of a furniture coating from the 1950s[a]

Type of product and ingredients	Weight (%)[b]
Phenolic resin-based furniture varnish	
para-Phenyl phenol, pure phenolic resin	16.5
Modified phenolic resin, hard-oil type	11.0
China wood oil	17.3
Dehydrated castor oil	4.4
Xylene	16.5
White spirits	35.8
Cobalt naphthenate	0.3
Lead naphthenate	0.7
Antiskinning agent	0.3

[a] From Singer (1957)

[b] Calculated by the Working Group

Four categories of wood stains were employed in the late nineteenth and early twentieth centuries: (i) water stains which consisted of water-soluble dyes or colouring agents (e.g., potassium permanganate, potassium bichromate, pigments such as Venetian Brown, Bismark Brown); (ii) oil stains (e.g., brownish resins, bitumens, asphalts or pitches in white spirits, or petroleum tinted with oil-soluble dyes); (iii) naphtha stains, which consisted of naphtha-soluble dyes dissolved in coal-tar naphtha and containing a little resin such as coumarone or ester gum as a binder; (iv) and spirit varnish stains which consisted of methylated spirit-soluble dyes with a little alcohol-soluble gum and usually contained manila as a binder (Jones, 1938).

The range of organic dyes that are found in wood stains (see IARC, 1981) include rosaniline [magenta; see IARC, 1974b], nitrosine, indigo, amaranths, carmoisine (see IARC, 1975), croceine, rhodamine (see IARC, 1978a) and several CI solvent and acid dyes (Krivanek, 1982).

Finishing operations for wood include staining, wash coating, filling (if necessary), sealing, sanding, application of one or two lustre coats and polishing. Two types of oil stains - soluble and suspended pigment type - impart the desired colour to wood. Wood stains are dissolved in a vehicle that enables the stain to soak into the wood rather than stick to its surface as a film. After the staining operation, a clear, thin coat of lacquer is often applied before application of a filler, which is called a 'wash coat'; it stiffens the protruding fine wood fibres and can be removed by light sanding. In some procedures, filler is used to fill the depressions before the sealer and finish coats are applied. These finishes are cured by solvent evaporation; finish coats usually contain cellulose nitrate (Lowell, 1984). Some typical sanding sealer formulations that have been used contain cellulose nitrate in ethanol, zinc stearate paste, maleic resin solution, castor oil, butyl and ethyl acetates, toluene and petroleum lacquer diluent (Singer, 1957).

Oil stains based on linseed oil and tung oil have been used in the finishing of furniture, since they protect against staining without leaving an apparent film on the surface. Varnishes based on urethane oils rather than oil resins are being used increasingly (Wicks, 1984).

Formulations of paint utilized for furniture are principally dependent on the end-use. Nursery furniture, for example, requires extremely hard, tough coatings containing non-toxic pigments. A wide variety of coatings has been used on furniture, including low-bake finishes based on urea-formaldehyde resins, polyurethane paints based on diphenylmethane diisocyanate and hexamethylene diisocyanate, and lacquers composed of ethyl cellulose or cellulose acetate butyrate combined with acrylic resins (Singer, 1957; Lowell, 1984).

1.5 Painting in the metal industry and paint products used

(*a*) *Metal primers, finish coats and corrosion inhibition paints*

Since iron and steel rust in time when in contact with moisture and oxygen, many products made with these metals are coated with rustproof primers and finish coats (Schurr, 1974).

Primers are vehicle-rich coatings intended for application as foundation and adhesion-promoting coats. Metal primers are used to form a firm adhesive bond with the surface and also serve as an impermeable barrier between the environment and metal surface. When active rust prevention is essential, rust-inhibitive pigments that retard oxidation chemically are used.

Although there are many formulae for structural steel primers, red lead (Pb_3O_4; see IARC, 1980a) in a linseed oil vehicle has been used for a long time. Other formulations of red lead include combinations with alkyd resins and with red iron pigment. A typical red lead–iron oxide primer formulation is shown in Table 4. Zinc chromate (zinc yellow; a double salt of zinc and potassium and chromic acid) was introduced during the Second World War and is still used extensively. It is usually formulated as the basic pigment with an alkyd resin or linseed oil. Less zinc chromate is required to give the same protection as red lead, and zinc chromate is often combined with red iron oxide (Singer, 1957).

Because of restrictions on the use of lead and chromates, the pigments favoured in industrial maintenance coatings are now mainly zinc metal, zinc oxide, molybdates and phosphates (Schurr, 1981).

Finish coats cover the metal primer and seal it. Some metal products are covered by enamels which contain alkyd resins and dry by oxidation. The most durable coatings available are generally used on machinery and other industrial equipment and are based on epoxy or polyurethane resins which are cured by chemical reaction. Typical formulations are shown in Table 4.

(*b*) *Marine paints*

Paints for surfaces that are continuously immersed in seawater must be formulated with antifouling properties to resist the growth of marine fauna. Diverse species of hard and soft fauna which require a permanent anchorage in order to mature and reproduce form colonies on hulls.

The Phoenicians used copper on the hulls of their ships more than 3000 years ago. During the early nineteenth century, compounds (generally oxides) of copper, tin, lead, mercury and arsenic (see IARC, 1980c, 1987o) were the biocides used in antifouling paints, since these agents are effective against the broad range of organisms encountered in the marine environment. Biocides based on lead, mercury and arsenic are now prohibited from use in many countries (Brunner, 1978; Brady *et al.*, 1987).

Antifouling coatings based on derivatives of triphenyl or tributyl tin have been introduced during the past 15–20 years. In some coatings, an organotin compound, such as the acetate, chloride, fluoride or oxide, is simply mixed into the formulation. These coatings are known as 'free-association' coatings and are characterized by a leach rate of organotin which is quite high when the coating is new but rapidly diminishes until it is insufficient to prevent fouling. A more useful formulation is obtained when the organotin in 'copolymer' coatings is covalently bound to the resin of the coating and is released when the bond hydrolyses in seawater. Since organotin compounds do not prevent accumulation of algae on hulls, some commercial organotin coatings contain a small amount of cuprous oxide to control algae and grasses (Brady *et al.*, 1987).

Table 4. Examples of formulations of metal paints

Type of paint and ingredients	Weight (%)
Red lead–iron oxide primer (from 1950s)[a]	
Stearated processed clay antisetting agent	0.3
Red lead (97%)	28.2
Red iron oxide (85% Fe_2O_3 min)	7.0
Magnesium silicate	14.1
Mica, white, water-ground	3.5
Alkyd	27.9
White spirits	18.3
Cobalt naphthenate (6%)	0.1
Lead naphthenate (24%)	0.4
Antiskinning agent	0.1
White epoxy powder paint (from 1980s)[b]	
Epoxy resin (1400 D)	60
Dicyanamide curing agent	4
2-Methylimidazole (accelerator)	1
Calcium carbonate (extender)	15
Titanium dioxide (pigment)	15
Acrylic polymer flow additive	1
Water-based white epoxy enamel (from 1970s)[c]	
Epoxy resin emulsion (50% solids)	28.3
Polyamide resin curing agent (65% nonvolatiles)	20.0
Titanium dioxide	22.2
Hydroxyethyl cellulose	0.1
Water	29.4
White polyurethane enamel (from 1980s)[d]	
Hydroxyl-functional resin (solids)	21.0
Dibutyl tin dilaurate (catalyst)	<0.1
Titanium dioxide (pigment)	19.0
Aromatic hydrocarbons	6.0
Propylene glycol monomethyl ether acetate	29.0
Polyisocyanate resin (solids)	8.0
Butyl acetate	1.0
Ethyl acetate	17.0

[a] From Singer (1957); weight calculated by the Working Group
[b] From Peltonen (1986); two-component product
[c] From Allen (1972); two-component product
[d] From Dupont (1988); two-component product

Most commercial antifouling paints contain a vinyl binder, although products with other binders are also available. Rosin or some other leaching agent is generally added to cuprous oxide formulations to permit its controlled release into seawater, where it is lethal to fouling larva forms. More recent developments in antifouling methods have involved use of a sheet material of black neoprene rubber impregnated with tributyl tin (Drisko, 1985). An antifouling coating used extensively by the the US Navy consists of cuprous oxide dispersed in a mixture of natural rosin and a vinyl chloride–vinyl acetate copolymer (Brady *et al.*, 1987).

More recent strategies have focused on nontoxic alternatives to antifouling paints. These include the use of fluoropolyurethane foulant–release coatings. One such formulation consisted of Desmodur-N-75 (an aliphatic polyisocyanate), polytetrafluoroethylene (38% by volume; see IARC, 1979c), titanium dioxide (see monograph, p. 307) and solvent (Brady *et al.*, 1987).

(*c*) *Automobile coatings*

The development of low-viscosity cellulose nitrate lacquers in the early 1920s revolutionized the painting of automobiles. Although these lacquers did not flow well and required an expensive buffing operation to obtain an acceptable gloss, their fast-drying characteristics permitted production line assembly and painting of automobiles for the first time (Lowell, 1984).

Cellulose nitrate lacquers were followed by the introduction of alkyd enamels to the automobile industry in the early 1930s. These compositions were usually modified with small amounts of amino resins to provide harder, more thoroughly cross-linked films. These were followed by the adoption of thermosetting acrylic enamels in which alkyds were replaced by acrylic copolymers containing hydroxyl groups which could still react with melamine modifiers (Lowell, 1984).

In the late 1950s, lacquers of greatly improved durability and gloss, based on polymethylmethylacrylate or thermosetting acrylic enamels, were adopted by the automobile industry (Lowell, 1984).

Today, many new polymers, including maleic resins, amino resins (urea–formaldehyde and melamine–formaldehyde polymers), silicones, epoxides, polyesters and polyurethanes form the basis of highly diverse coating systems. In addition, nonaqueous dispersion lacquers and acrylic enamels have been developed. Steel used in automobiles is pretreated with a conversion coating (phosphating or bonderizing) to improve corrosion resistance and adhesion. In the traditional procedure, which is still employed to some extent, the solvent-borne primer was sprayed onto the automobile body shell followed by a surfacer which could be sanded. The primer and surfacer were often combined into a single adhesive formulation which could be sanded. The vehicles of primer–surfacers were combinations of oxidizing alkyd, epoxy and amino–formaldehyde resins, alkyd- and rosin-modified phenolic resins and others. Applications of the colour coats followed applications of the primer–surfacer combinations (Lowell, 1984).

Solvent-borne primers have been almost completely replaced by water-borne electrodeposited primers. The original anodic type has been largely replaced by the cathodic type which is superior in corrosion protection. The binders for cathodic deposition are typically acid salts of amino-treated epoxy. The formulations contain polyepoxides or blocked polyisocyanates which cross-link the coating when it is baked. Prior to application of the top coat, a coat of solvent or water-borne epoxyester primer-surfacer is applied (Lowell, 1984).

Very solid top coats are being used increasingly, thus eliminating lacquer-type formulations. Versions of conventional thermosetting acrylic enamels that can be applied in about 40–50% volume solids are now available (Lowell, 1984).

A broad range of organic pigments is employed in automotive finishes. These include Hansa yellows (prepared from chloro- and nitroanilines and acetoanilides), diarylide yellow, nickel azo yellow (nickel (see IARC, 1976c, 1987p) chelate of diazotized 4-chloroaniline and 2,4-dihydroxy quinoline), lithol reds (precipitated azo pigments comprised of a family of the sodium, barium, calcium and strontium salts of the coupling product from diazotized 2-naphthylamine-1-sulfonic acid and 2-naphthol), yellow BON-maroon (manganese salt of the coupling product of diazotized 4-chloroanthranilic acid with 3-hydroxy-2-naphthoic acid), and naphthol reds and maroons (monoazo pigments such as the copper precipitation product from the coupling of diazotized 4-nitroanthranilic acid with Naphthanil RC). Other classes of nonazo organic pigments that have been employed in automotive finishes include quinacridones, thioindigos, perinones (diimides of naphthalene-1,4,5,8-tetracarboxylic acid), perylenes (diimides of perylene-3,4,9,10-tetracarboxylic acid) and anthraquinones (Fytelson, 1982).

Table 5 gives a typical formulation of a lacquer for automobile finishing.

Table 5. Formulation of an automobile paint from the 1970s[a]

Type of paint and ingredients	Weight (%)
Blue metallic lacquer	
Acrylic resin	41.8
Methyl methacrylate (93%)	
Butyl acrylate (7%), comprising 40% nonvolatiles in toluene	
Cellulose acetate butyrate	4.4
Plasticizer	8.2
Aluminium pigment (65%)	1.8
Phthalocyanine blue pigment dispersion	1.4
Acetone	10.5
Methyl ethyl ketone	10.0
Xylene	4.0
Ethylene glycol monoethyl ether acetate	13.0
Mixed methyl esters of adipic and glutaric acid	4.9

[a] From Williams (1977)

(*d*) *Aluminium paints*

Aluminium paints sold today in ready-mixed form are used as protective coatings on iron and steel, aluminium, magnesium and other metals, providing high resistance to moisture penetration and heat and a high reflectance for ultraviolet radiation. These paints contain aluminium pigment in finely divided form and are formulated in two types - non-leafing and leafing. The former consists of aluminium ground to a powder that is dispersed in vehicles to give a metallic-grey finish. 'Leafing' is a phenomenon in which finely divided aluminium flakes rise to the surface and form a continuous metallic finish consisting of intermeshing aluminium flakes (Singer, 1957).

(*e*) *Coil coatings*

One of the most rapidly growing areas of industrial coating is coil coating. The coil stock consists of enormous rolls of thin-gauge steel or aluminium, which are coated at steel mills, aluminium mills or by specially equipped contractors. The coils are unwound, coated on high-speed roller coaters, heat cured and rewound. Binder compositions include alkyd-amino-formaldehyde combinations, vinyl chloride-vinyl acetate copolymers (see IARC, 1979a,b) and thermosetting acrylics, often modified with small amounts of epoxy, which produce coatings that are flexible, durable and adhesive. In the coil coating industry, solvent vapours are often collected and disposed of by incineration (Lowell, 1984).

1.6 Other painting trades and paint products

(*a*) *Traffic paints*

The major requirements for traffic (road) paints are fast and hard drying. The paints that are generally used contain a high pigment volume, fast-drying vehicles, such as resin combinations with low oil content or oil-free synthetic resins, and low-boiling solvents (e.g., petroleum fractions with distillation ranges of 100-150°C). Solutions of plasticized chlorinated rubber made of styrene-butadiene copolymers (containing an aromatic hydrocarbon solvent to maintain solubility) have been used. Glass spheres are added to formulations of reflecting paints (Lowell, 1984).

Conventional alkyd formulations (including both straight alkyd and alkyd/chlorinated rubber types) still account for most of the traffic paints used in the USA. However, there has been a significant increase in the use of more durable pavement marking materials, such as two-component polyester and epoxy systems and one-component hot extruded thermoplastic types (Connolly *et al.*, 1986).

Although traffic paints can be made in any colour, the most widely used are white (titanium oxide) and yellow (chrome yellow; Connolly *et al.*, 1986).

(*b*) *Fire-retardant paints*

Fire-retardant or intumescent paints, when applied to wood or other combustable surfaces, retard the spread of fire by foaming at elevated (but less than charring) temperatures. A number of intumescent formulae employed in the mid 1950s contained a chemical combination of polyol (e.g., pentaerythritol), a mono- or diammonium phosphate and an amide (e.g., dicyandiamide; Martens, 1964; Lowell, 1984). Certain pigments such as antimony oxide and borates are also added to enhance the fire-resistant properties of such paints. Other intumescent paint formulae have included polyvinyl acetate and acrylic latexes (Martens, 1964).

(*c*) *Aerosol colours*

A large variety of paints have been packaged in aerosol tins for touching up and painting small areas, hobby aircrafts and other such objects. The principal types of paint used are of alkyd composition, are thinned out to a low viscosity (generally with ketones and aromatic hydrocarbons) to allow atomization, and contain a gaseous propellant which is liquid under pressure (e.g., propane, butane and isobutane or dichloromethane, which has replaced dichlorofluoromethane in many countries). Other aerosol paint compositions include acrylic and cellulosic lacquers and epoxyester systems (Cannell, 1967; Lowell, 1984; Connolly *et al.*, 1986).

(*d*) *Paint and varnish strippers*

Before the advent of chemically-resistant synthetic paint vehicles, simple organic solvents, mixtures of solvents or solutions of caustic alkalis could be used to soften and strip most paints and various films (Downing, 1967).

Dichloromethane (see IARC, 1986c, 1987q) is the most widely used paint stripper base of the organic group. Other chlorinated hydrocarbons that have been used with dichloromethane are, in order of decreasing effectiveness, 1,2-dichloroethane (see IARC, 1979f), propylene dichloride, dichloroethyl ether and *ortho*-dichlorobenzene (see IARC, 1982d, 1987r). Other solvents that can soften paint films are, in (approximate) decreasing order of effectiveness, ketones (e.g., methyl ethyl ketone), esters, aromatic hydrocarbons (toluene (see monograph, p. 79) and naphthas), alcohols and aliphatic hydrocarbons (Downing, 1967).

Phenols and chloroacetic acids have been used in certain, specific situations, such as for stripping epoxy coatings. In addition, many less common solvents have been used, some primarily for specific applications, including 2-nitropropane (see IARC, 1982e), dimethylformamide (see monograph, p. 171), dimethyl sulfoxide, tetrahydrofuran and 1,1,2-trimethoxyethane (Downing, 1967).

The main inorganic compounds that have been used as paint strippers are alkalis, principally in the form of a boiling solution of sodium hydroxide and, to a lesser degree, potassium hydroxide and lime or soda ash (anhydrous sodium carbonate). Additives such as sequestering agents (e.g., gluconic acid and alkali metal gluconates), surfactants (e.g., sodium resinate, fatty acid soaps, sodium lignin sulfonate, alkylarenesulfonates and petroleum sulfonates), water-soluble activators (e.g., phenolic compounds and their sodium salts - cresol, chlorocresol, sodium pentachlorophenate) and solvents (e.g., monoethers of ethylene glycol and diethylene glycol) are often used to increase the stripping rates of inorganic paint removers. Paint removers that are used on steel, aluminium and other nonferrous alloys often contain corrosion inhibitors such as phosphates and chromates (Downing, 1967).

Molten and fused alkali baths are also employed to salvage ferrous metal parts with defective finishes. At temperatures up to 500 °C, even heavy films of epoxy and silicone coatings can be removed rapidly (Downing, 1967).