PAINT DRIERS

Driers are materials that promote or accelerate the curing or hardening of film formers that contain oxidizable or drying oil components. Air drying is the formation of a solid film at ambient temperature by oxidation processes from an applied liquid coating. Such coatings are convertible coatings in that the film, after drying, does not re-dissolve in the original carrier solvent. The air-drying process can be described as autoxidation, as it takes place automatically after the coating has been spread. Autoxidation is a chemical process that is greatly affected by temperature and the presence of catalysts. Humidity also affects autoxidation of conventional paints and the presence of light is helpful.

The autoxidation of unsaturated drying and semi-drying oils does not proceed rapidly enough to be commercially acceptable: for instance linseed oil with conjugated unsaturation requires over 24 hours to become non-tacky. The so-called ‘non-yellowing’ drying oils with non-conjugated unsaturation autoxidize at even slower rates. The conversion of these oils into higher molecular weight polymers (alkyds) with greater propensity to oxidize still does not give commercially acceptable drying times unless autoxidation catalysts or added.

Driers are a long established yet rather specialized group of additives. Because of their specific effects on oxidizing film formers, driers do not normally form part of formulations in which film formation is by other mechanisms. Thus lacquers and latex paints that dry by evaporation of solvent or water, and epoxies, urethanes, and baking enamels that form films by chemical reaction do not contain drier additives as oxidation catalysts. The chemical compounds forming the majority of driers are metallo-organics (metal carboxylates) formed from a metal base and an organic acid. An older term is ‘heavy metal soap.’ Many other organic compounds have been assessed for ‘drying’ capabilities but only one compound, 1:10 phenanthroline has achieved commercial acceptance and its use is synergistic to metallo-organics. Metallo-organics may be classified by their activity into primary and secondary types.

Primary driers (or active driers) are compounds of cobalt and manganese, which have the highest catalytic activity and most pronounced accelerating effect on film formation. Primary driers are known as ‘surface’ or ‘skin’ driers since in oxidizable vehicles, cobalt or manganese, when used alone, will cause the surface of the film to rapidly set to a near solid while the underlying film does not reach this advanced state of oxidisation. This uneven hardening will, in thick films, cause the defect known as ‘wrinkling’.

Secondary driers (or auxiliary driers) are compounds of lead, calcium, zinc or zirconium. While they possess a much lower level of catalytic activity, these metals, when used in combination with cobalt and/or manganese, give films that do not surface-dry as rapidly and thus harden through more uniformly. Such films are said to ‘through harden’ and secondary driers are known as ‘through driers’. Lead compounds are the major drier of this type. For a more detailed description of the processes of oxidation film formation see chapter 8.
29.1 HISTORY

A study of the history of driers parallels that of the paint industry. The eminence of the Dutch school of painters has been ascribed, by circumstantial association, to their technological contribution to Renaissance materials of portraiture; the \textit{in situ} formation of manganese linoleate from fatty acids in aged drying oils and reactive manganese components in natural earth colours (umbers and ochres) gave previously unattainable speed to their painting. The practice of cooking natural earth oxides (umbers and ochres) with linseed oil to form ‘boiled oil’ was well established in the late seventeenth century and was the precursor of the whole oleo-resinous varnish making industry. The nineteenth century use of basic-carbonate white lead in house paints gave \textit{in situ} formation of lead linoleate soaps with reasonable paint drying times, although unacceptably slow by present standards.

Increasing substitution of zinc oxide for white lead for improved opacity in the late nineteenth century brought recognition of the function of white lead in the drying process. Continued development of zinc oxide based house paints with reasonable drying times was possible only with the introduction of ‘oil-soluble driers’ or ‘terebinies’ in about 1885. These ‘oil-soluble driers’ were lead and manganese soaps of linseed fatty acids and/or resin, that is, linoleates or resinates or mixtures thereof. The terebinies had the major disadvantage of poor stability on ageing since the organic linoleate or resinate radical itself is prone to autoxidation, becoming insoluble and precipitating from solution. This resulted in variable drying properties owing to loss of drier concentration and activity. This defect was a major contribution to the poor reputation of the early factory-prepared paints when compared to the fresh paint prepared on site by the tradesman master painter of those times. Thus it was possible for master painters to persist with linoleate/resinate terebinies until the late 1940s when factory-prepared paints with good stability gained the master painters’ grudging acceptance.

While lead and manganese were used perhaps without full recognition from early times, cobalt was introduced about 1910. Oddly, it did not meet with ready acceptance, mainly because its very powerful surface drying properties, in combination with the linseed oil vehicles then used, gave paints that were prone to wrinkling in thicker films. Indeed, it was not until the development of phenolic oleo-resinous varnishes from 1925 onwards (and the later development of alkyd resins with improved through-drying performance) that any substantial quantities of cobalt driers were used.

The recognition of the deficiencies of linoleate based terebinies resulted in 1925 in the development of oil and solvent soluble, non-autoxidizing (and hence stable) naphthenate driers in Germany. The commercialization of naphthenates was most successfully carried out in the U.S.A. by Leon Roon and the Nuodex Company. The availability of stable, standardized and consistent driers closely paralleled the development of alkyd resin enamels from the early 1930s onwards. These alkyd enamels compounded with naphthenate driers allowed, for the first time, production of stable, fast drying, durable, coloured enamels.

The 1950s saw the introduction of metallo-organics based on synthetic acids of high purity and the introduction of zirconium and rare-earth driers. Recent developments have been aimed towards products of higher concentration and driers suitable for use in water-soluble drying-oil-containing polymers.

29.2 TYPES OF DRIERS AND MANUFACTURING METHODS

Metallo-organics, rated in terms of decreasing volume usage in Australia, are compounds of:

(a) lead,  
(b) calcium,  
(c) cobalt,  
(d) manganese,  
(e) zirconium,  
(f) zinc, iron,  
(g) rare earth, aluminium.