WHAT IS PAINT?

Paint, surface coating, lacquer and varnish are terms which have become somewhat synonymous and confused.

International Standard ISO 4618-1 gives the following definitions:

**Paint**: a pigmented *coating material* in liquid or in paste or powder form which when applied to a substrate forms an opaque film having protective, decorative or specific technical properties.

**Varnish**: a *coating material* which when applied to a *substrate* forms a solid transparent *film* having protective, decorative or specific technical properties.

Historical Development

Coating materials have been used for thousands of years as can be seen in the photograph below. This shows some of the detail from cave paintings found in Lascaux, France which have been dated at 15,000 BC. The paints used were based on animal fats, coloured earth and charcoal.
The first materials to resemble modern coatings were the lacquers developed by the Chinese around 2,000 BC. These lacquers had smooth glossy surfaces and it is probably fair to say that the Chinese invented coatings technology. The Chinese lacquers were based on the milky sap of the Chinese lacquer tree (rhus vernicifera).

The next important historical reference is from around 1,000 AD; the monk Rodgerus Von Helmershausen records the use of combinations of vegetable oils and tree resins (vegetable products remained the most important raw materials for coatings manufacture until the beginning of the 20th century).

Initially, coatings were used primarily for decoration; however, since the middle of the 19th Century, the protective capabilities of paint have become more important. The need for protection, however, highlighted the shortcomings of the traditional vegetable based coatings and this led to the development of synthetic (man-made) resins such as cellulose nitrate, phenolic resins and alkyd resins early in the 20th century.

It is really only since the 1940s that we have seen fast progress in coating technology, and only since the 1960s that significant improvements have been made.

**Paint Composition**

Coatings are a combination of numerous ingredients, all of which fulfil a specific purpose:

- **Pigment**
- **Binder**
- **Solvent**

**Film formers:** are either macro-molecular products (eg chlorinated rubber) or low molecular mass products which react to form macromolecular structures (eg epoxy/amine).

The molecular mass has a critical bearing on the final paint as it influences mechanical and application properties inversely – the right blend is crucial for optimum overall performance. Most film formers are known as resins.

**Resins:** the essence of a resin is that it can be made to form a continuous adherent film when applied to a substrate.

**Plasticiser:** are organic liquids of oily consistency and low volatility. They are used to modify the film characteristics of the film former/resin being used, for example by improving flow and increasing flexibility.

**Binder:** Film former/resin/plasticiser combinations are often referred to as the binder of the system.

**Pigments:** are responsible for colour, hiding power and, in special cases, for specific properties (eg passivation or fouling control). Pigments are finely ground, crystalline solids dispersed in the paint. Metals, inorganic, organic and organometallic compounds are all used as pigments.
Extenders: are naturally occurring or synthetic materials which have little hiding power or effect on colour. Extenders are used to impart specific properties to the paint (e.g., gloss control, abrasion resistance or reinforcement). Typical extenders are barytes, talc, mica, and dolomite.

Solvents: are volatile fluids used to assist in dissolving solid resins and to aid the application of paint. Solvent evaporates from the coating during drying and essentially plays no part in the final coating performance.

Additives: a wide range of materials are used in paint at low levels to improve the properties of the finished product.

Film Formation (Drying)

During the film formation process, the paint is transformed from a liquid (usually) to a coherent, tightly adherent film on the surface of the item being coated.

There are essentially two drying mechanisms used in marine coatings:

(i) Physical drying – referring to non-convertible coatings.
(ii) Chemical drying – referring to convertible coatings.

Non-Convertible Coatings

Such coatings dry by simple solvent evaporation. No chemical reaction takes place. Binders are usually long chain polymers, which can interlock to form continuous films without chemical reaction. To facilitate film formation, it is necessary to dissolve the polymers in appropriate solvents due to the inherently high viscosities of the polymers in use. This means that any usable paint will typically have a very low solids content.

The current legislative position with regard to the use of volatile organic compounds is having a major impact on the use of low solids (high solvent) coatings.

Physically drying paints can be redissolved in appropriate solvents as no chemical changes take place. This has advantages and disadvantages, the most important advantage being effectively an indefinite overcoating period with good intercoat adhesion. Solvents, in a freshly applied coat, will penetrate into the underlying paint film and, on drying, the layers will have become interlocked.

Another key feature of such systems is the ability to dry at a wide range of temperatures, the only variation being a change in drying time due to a change in the solvent evaporation rate. Over a wide application temperature range, physically drying systems will ultimately yield a film of the same properties.

There are two principal disadvantages associated with non-convertible coatings, the most important being the low solids levels of the paint produced. The use of high molecular weight polymers as film formers with their inherently high viscosities results in the need to develop low solids coatings in order to achieve products which can be applied efficiently to substrates. This in turn leads to low film build, resulting in the need to apply several coats to achieve the film thickness necessary for the level of protection required. This can add extra time and cost to coatings projects.
A further disadvantage of non-convertible systems is that the polymers used typically have low Tg\(^1\) values. This leads to the paint film being susceptible to softening by heat – known as thermoplasticity. This precludes their use on certain vessel areas and in certain climatic conditions.

**Convertible Coatings**

Such coatings dry by chemical reaction, i.e. they are converted from their original state into a new state. Once they are fully cured they cannot be redissolved in the original carrier solvent, unlike non-convertible coatings.

The film forming substances are usually relatively low molecular weight materials which react together to form large cross linked molecules.

In the marine coatings industry three main reactive mechanisms are commonly used:-

- reaction with atmospheric oxygen
  - Oxidative Drying

- reaction with chemicals (curing agents)
  - Chemically Curing

- reaction with water
  - Moisture Curing

**Oxidative Drying**

Early paints were based on natural oils, such as linseed oil. These are generally long chain aliphatic systems containing reactive CH\(_2\) groups between C=C double bonds, eg: CH\(_2\)-CH=CH-CH\(_2\)-CH=CH-CH\(_2\).

The reactive CH\(_2\) reacts with oxygen free radicals in the atmosphere enabling crosslinked systems to be built. Reactivity is dependent upon the number of double bonds in the oil molecule.

Oil molecules are fairly small, so drying to produce a dense film can take a long time. To reduce the drying time it is possible to modify the original oil to create larger basic molecules. The most common forms of modification are the alkyd resins. These are based on natural oils but can be modified to give a range of materials with very specific properties. Full dry/cure of these systems requires penetration of oxygen right through the film, hence applied film thickness tends to be low to prevent surface drying (skinning) only.

**Chemically Curing**

Chemically curing materials require the mixing of two components for film formation to occur. Individually neither component is capable of producing an acceptable paint film.

Once mixed, the two components react chemically. This process is irreversible.

Two pack materials have a finite usable lifetime during which application is practical. This can vary from seconds to days. This is termed the “pot life” of the product. There are a huge variety of possibilities for two pack systems, resulting in a range of products with broad or specific properties, e.g. light resistance, abrasion resistance, chemical resistance, corrosion resistance etc.

\(^1\) Glass transition temperature.
The most common two pack systems in the marine business are currently epoxies and polyurethanes.

**Moisture Curing**

These are coating systems which cure by absorbing atmospheric moisture.

The main use of moisture cure in the marine business is with zinc silicate paints. The binder is typically an alkyl silicate which reacts with moisture to form a hard cross linked matrix. If blended with metallic zinc (a sacrificial pigment) systems can be developed which are extremely effective in preventing corrosion.