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# A REVIEW OF CURRENT AND FUTURE CHALLENGES IN PAINTS AND COATINGS CHEMISTRY

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## Abstract

Paints and coatings are very important to everyday life. However, their formulation is becoming more and more complex due to legislative demands, driven by environmental and health concerns, to reduce or eliminate completely volatile organic compounds (VOCs) and any solvents considered hazardous air pollutants (HAPs). Liquid coatings formulation must simultaneously meet VOC limitations and HAP restrictions by shifting to high solids, low-solvent coatings as well as water-borne coatings. Non-aqueous formulations that meet existing and pending VOC and HAP regulations and offer the performance customers expect/require are still being produced. Switching to environmentally-friendly coatings involves more than simply replacing organic solvents with VOC-free ingredients such as water. Efficient formulation demands that basic rules governing the rheological behaviour are well-defined. This paper highlights the formulation and some of the current and future challenges in the paints and coatings industry with emphasis on the chemical aspects.

Keywords: Coatings, Environmentally-friendly, Paints, Rheology, volatile organic compounds, water-borne coatings

## 1. Introduction

Paints and coatings are very complex and versatile materials, offering more challenges to the formulators than most other products. The paints and coatings industry has changed over the years and continues to change. The basic composition of the paints and coatings, their methods of composition as well as environmental factors are driving innovation in the industry [1]. The legislative demands, driven by environmental and health concerns, is to reduce or eliminate completely volatile organic compounds (VOCs) and any solvents considered hazardous air pollutants (HAPs)[2]. For instance, liquid coatings formulation must simultaneously meet VOC limitations and HAP restrictions by shifting to high solids, low-solvent coatings as well as water-borne coatings. Although a lot of research is now concentrating on water-borne systems, non-aqueous systems will still be with us for a while. So, non-aqueous formulations that meet existing and pending VOC and HAP regulations and offer the performance customers are willing to pay for are important to the industry. Switching to environmentally-friendly

coatings involves more than simply replacing organic solvents with VOC-free ingredients such as water. This paper highlights some of the current and future challenges in the paints and coatings industry with emphasis on the chemical aspects.

## 2. Definision and Composition of Paint/Coating

Paint, in its simplest form, is made up of the pigment and binder. Strictly speaking, a "coating" is broader term, and includes formulations without pigment. However, good quality paints are made up of four components: pigment, film former, thinner (solvent) and additives [3]. Varnishes, which form transparent or semi-transparent films, are made up of the last three components, with coloured varnishes containing small amounts of pigment.

*Pigment.* This is possibly the most obvious part of paint. Pigments are fine powders that give the film its colour and help it to hide the surface underneath. They may provide other properties too such as altering the way paints flow or providing corrosion resistance. Not all coloured powders are suitable as pigments. They must be insoluble in water. It is helpful if the pigment is chemically inert and colourfast when exposed to light.

Similarly, not all white powders are useful as white pigments. Not only is insolubility and inertness being sort, but also they should be opaque in use. If they are not opaque, however, they may still be of value in paint for other reasons than opacity. We call these transparent white pigments "extenders". They may help to prevent pigment settlement in the can, act as a matting aid, and provide a micro-toughness of the surface to assist adhesion of the next coat or act as reinforcement to strengthen the film.

Coloured pigments range from simply inorganic compounds such as red iron oxide ( $\text{Fe}_2\text{O}_3$ ) to complex organic pigments, for example, dioxazine violet. By far the most commonly used white pigment is titanium dioxide ( $\text{TiO}_2$ ) although zinc oxide ( $\text{ZnO}$ ) and lithopone ( $\text{ZnS} + \text{BaSO}_4$ ) find small use.

Many of the extenders used are naturally occurring minerals such as whitening marble ( $\text{CaCO}_3$ ), barytes ( $\text{BaSO}_4$ ), silica ( $\text{SiO}_2$ ) and china clay ( $\text{Al}_2\text{SiO}_5 \cdot 2\text{H}_2\text{O}$ ).

*Film former (binder, resin or polymer).* As the name suggests, this component holds the pigment particles together and to the surface to be painted. It is invariably either a natural or synthetic polymer. These polymeric or polymerisable components provide the cohesion of a coating composition. The choice of binder is paramount and decides so many of the fundamental properties of the paint film such as hardness, toughness, flexibility, durability

and speed of drying. In other words, it is the material that forms the film, giving protection to the substrate and keeping the pigment in place and evenly dispersed. It may be made up of a single polymer, or a combination of polymers. These include polyesters (which include the alkyds), the acrylics and the vinyls, epoxies and polyurethanes, phenolic and amino based resins, etc. (see Box 1) [4]. Paints are usually classified according to the binder present, for example, an alkyd gloss paint, a polyurethane car finish, a polyester wood finish, or a polyvinyl acetate latex paint. The binder may be dissolved in a solvent, or in the form of an emulsion or colloidal dispersion in water, which results in solvent-borne and water-based paints, respectively (see Box 2) [4]. A mixture of resin and solvent is called the “vehicle” for the pigment.

*Thinner (solvent).* These may be organic liquids or water, or a mixture of both. Thinners are chosen particularly for the solvency and evaporation rate. Commonly a blend of solvents is used. For instance, mild-odour aliphatic hydrocarbons might be used in a gloss paint for home whereas quick evaporating esters find use in car touch-up aerosols. Water would be used more widely except for its slow evaporation especially in humid atmospheres. They may be added to improve the spreading properties of the vehicle. The carrier thins the paint or varnish, allowing it to be brushed, sprayed, dipped or rolled. Once on the substrate, the solvent evaporates, leaving the dry film coating. The term ‘liquid carrier’ is preferable because the liquid may not be a true solvent for the binder. The function of paint solvents, therefore, are to keep the pigment and resin apart until the coating has been applied, to allow adhesion to the surface, and to lower the viscosity to allow spraying and levelling.

*Plethora of additives.* These are not strictly essential but can be used, in small amounts, to develop formulations with improved properties and assist the coating’s application. They are added to modify the film or paint. Examples are driers, which promote the drying time of some coatings; flow-control agents, which give a smooth surface; deformers, which prevent the formation of bubbles that could dry in the film; and anti-skinning agents to prevent the paint from a ‘skin’ in the can (see Box 3) [4]. Therefore, additives are often used as “improvers” to a basically satisfactory paint.

A coating material is a composition applied in a layer to all sorts of surfaces to decorate, protect, or in some way modify them. The term ‘paint’ can be taken to include all types of surface coatings that are used for decorating and protecting substrates as well as for various special applications such as fire protection. Even in general terms, most coatings cannot easily be defined and include not only several different and distinct classes of

conventional liquid paint formulations, but also stains and clear vanishes, as well as powder coatings and various other solid systems. It is clear that paints and coatings not only make our surroundings more attractive but they also protect and preserve them. Even the simplest form of coating is very complex in chemical terms and involves blending together of several different components in varying proportions.

### 3. Paint Formulation

As mentioned earlier, paint contains three classes of material namely a resin or mixture of resins, pigment and solvent (thinner). A mixture of resin and solvent is called the “vehicle” for the pigment. Most paints also contain small quantities of various additives e.g. driers to speed up the drying process, substances to adjust pH of the paint, etc. This section describes the way the paint chemist blends the “vehicle” and pigment together to make paint (see Figure 1 for the flowchart).

Pigments are supplied in the form of dry powders. These consist of “primary particles” which are sized to give the best results in paint films. For example, white pigments (titanium dioxide,  $\text{TiO}_2$ ) scatters light most efficiently (whiteness and opacity) when the particle size is 0.22 microns [5]. Some pigments are much smaller, some larger. The small primary particles of pigment clump together when the powder is dried and stored to form relatively large clumps (A ‘clump’ of titanium oxide may contain 5,000,000 primary particles). These clumps are known as aggregates and it is in this aggregated form that the pigments are supplied. To produce good paints, it is necessary that the pigment be in its primary particle size when mixed with the vehicle. Otherwise most of the expensive coloured pigment will not be used efficiently and the dry film will not be smooth, glossy, opaque or have the correct colour.

It is therefore necessary to break down the aggregates of pigment particles in the presence of the vehicle and prevent them from re-aggregating. For this reason, it is not normally possible simply to stir the pigment into the vehicle, but rather work has to be done on the mixture in order to break down the aggregates and ensure that the resin coats the small particle surfaces. This process is known as “pigment dispersion”, in which the following must occur:

- “wetting” of the pigment surface by the vehicle;
- de-aggregation of the pigment aggregates to small primary particles; and
- “stabilisation” of these small particles by the resin to prevent re-aggregation.

A resin which is to perform well as a pigment dispersant must therefore be composed of molecules consisting of two parts [6]:

- an “anchor group”, which wets the pigment surface and becomes

- associated with it; and
- a “stabilising chain” which is soluble in the solvent used and therefore stretches out into it.

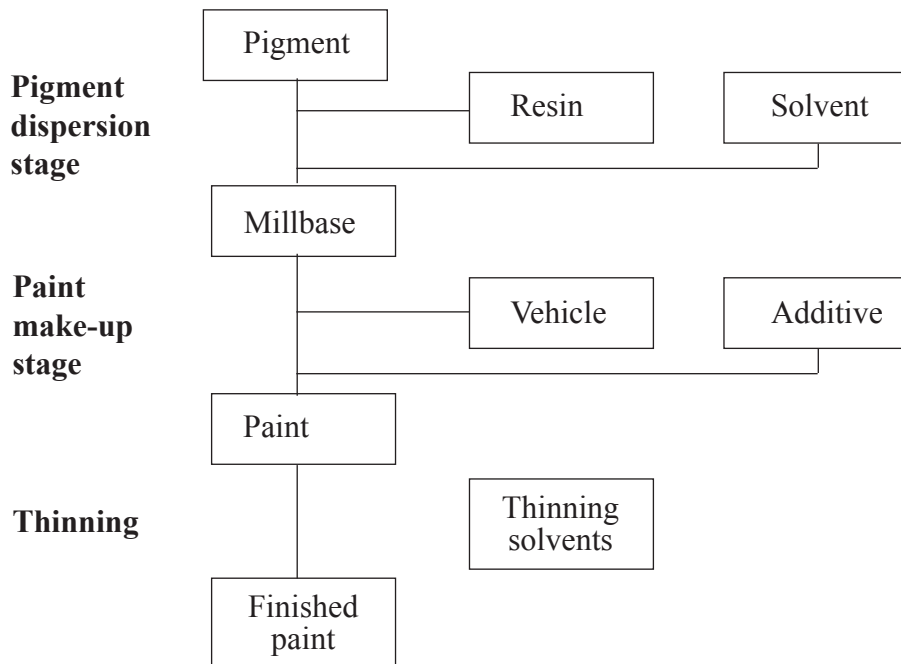
Pigment particle surfaces contain areas of electrical charge. The “anchor group” in a dispersing resin is chosen for its ability to be attracted to some of these charged areas. In this way, during dispersion, the original surface of the aggregate, and the new surfaces exposed during grinding are covered by molecules of the dispersing resin. This process is known as “wetting”.

Many different types of dispersion machinery have been developed but they all use one or both of two mechanisms to break up aggregates. The machinery falls into two groups:

- 1) Those that use “dispersion media”, usually ceramic balls 9 to 12mm in diameter or glass beads 1 to 3mm (like marbles) in diameter. Dispersion occurs where the balls touch each other by a combination of impact and shear depending on the conditions.
- 2) Those that do not use media - these disperse entirely by shear.

Pigments are always dispersed at the highest concentration possible for technical and economic reasons. Finished paints contain only enough pigment to give the desired properties for the same reasons.

Millbases are, therefore, converted to paint by mixing with film forming resins, solvents and any necessary additives. This must be done carefully such that the mixing of the ingredients is in the right order to get the best results. Obviously the resins and solvents must be compatible but problems may arise if components with large differences in resin solids, viscosity or temperature are mixed - “pigment shock” – reaggregation of the pigment particles may occur. For these reasons pigment dispersions are usually “second staged” when dispersion is complete - they are diluted with resin and solvent to give a recipe which is still more concentrated than the final paint but much easier to use than the dispersion recipe. Waterborne millbases and paints must have the pH adjusted at this stage. The stages involved in paint making are summarised Figure 1.



**Figure 1:** Flowchart showing different stages in paint making

It may be a long time between the manufacture of a paint and the day that the tin is opened for use. The paint must therefore remain stable in the can and the ingredients must not react with another chemically under storage conditions. Some paints do not dry by chemical reaction, but solely by the evaporation of the liquid carrier. In such cases, the polymer is fully formed in the liquid state and does not change chemically on drying. Soon after application, it is expected to form a film. The way this happens differs with different paints but generally it might be as result of drying by either evaporation (lacquer drying) or chemical reaction.

The evaporation of thinner leads to a film deposition on a surface that is painted with a paint containing a binder dissolved in thinner. In this case the binders have high molecular weights in the order of 80,000 atomic mass units [4]. The high molecular weight is necessary in order for the binder to have good paint properties. Artists' water colours are a simple example. Here a gum is dissolved in water and this solution is pigmented. When the water evaporates, pigment bound with gum is held to the paper. If you take some more of the original thinners (in this case water) you can, of course, re-dissolve the paint and wash it away. Bitumen, chlorinated rubber and nitrocellulose are examples of binders that dry by evaporation of their thinners [7].

Emulsion paints” exhibit a slight variation to drying of paints by evaporation described above. More accurately these are latex paints wherein the binder consisting of tiny rubbery spheres is suspended in water. As the water evaporates the particles pack closely and then fuse with each other to form a continuous film. The pigment becomes embedded as the particles pack close together. Since a latex is not a solution, the application of water to the dry film does not dissolve it or remove the pigment [3].

Modern latex particles are always man-made polymers. One of the original ones was built up from vinyl acetate monomer by opening the double bond to form polyvinyl acetate. More usually “copolymers” are used these days where two or more different vinyl or related acrylic monomers are reacted together to provide just the right balance of mobility, hardness and flexibility [8].

When films dry by evaporation alone, only a physical change that derived from the high molecular weight properties of the resin takes place. However, many films dry by a chemical reaction. It is true that even these must first evaporate their thinners, but in these cases they merely deposit a wet or sticky layer. They must undergo further chemical changes that result in increasing the molecular weight of the resin and thereby forming a hard film. Broadly these are the three alternatives:

- The sticky film may react with the oxygen of the air and the binder converts to a plastic solid. Decorative paints based on drying oils react by this so-called “autoxidative” process. It is rare to find a house paint based on, say Linseed oil alone. These days the oils are modified with synthetic resins such as polyesters to give alkyd resins, e.g. the Dulux Gloss Finish paint is based on an alkyd resin.
- Alternatively, two or more components within the binder can react together to change from liquids to a solid. Obviously this must not happen in the can. The film is in some way initiated into reacting. The simplest way to do this is by heating the painted object in an oven. Infrared lamps have also been used. Some speciality paints for the factory finishing of wood are hardened by ultra-violet light or by a beam of electrons.
- The third alternative is to have two reactive binder components which you keep separate, only mixing them immediately before application. Two pack epoxy paints use this principle, (a similar principle is found in two-pack epoxy adhesives, namely Aradite). Two-pack isocyanates are finding increasing use in the car finishing industry. They tend to be used wherever excellent resistance to chemicals and solvents is required.



The thin films of paint applied on various surfaces are called upon to work small miracles. A few  $\mu\text{m}$  thickness of paint must protect the steel of a drilling rig from a most aggressive atmosphere. Elsewhere, a manufacturer expects to be able to decorate a thin sheet of aluminium and then to stretch and shape it into cans and lids without the paint cracking or flaking off. For domestic use, house paints are made with such a complex pattern of flow that they are near solid in the container, fluid under the brush, remain fluid to allow brush marks to smooth away, but then set to prevent even over-heavy applications from sagging.

#### 4. Rheology

The quality of paint to a very large extent is determined by its flow (rheological) properties. For instance, good quality paint will have the following properties [9]:

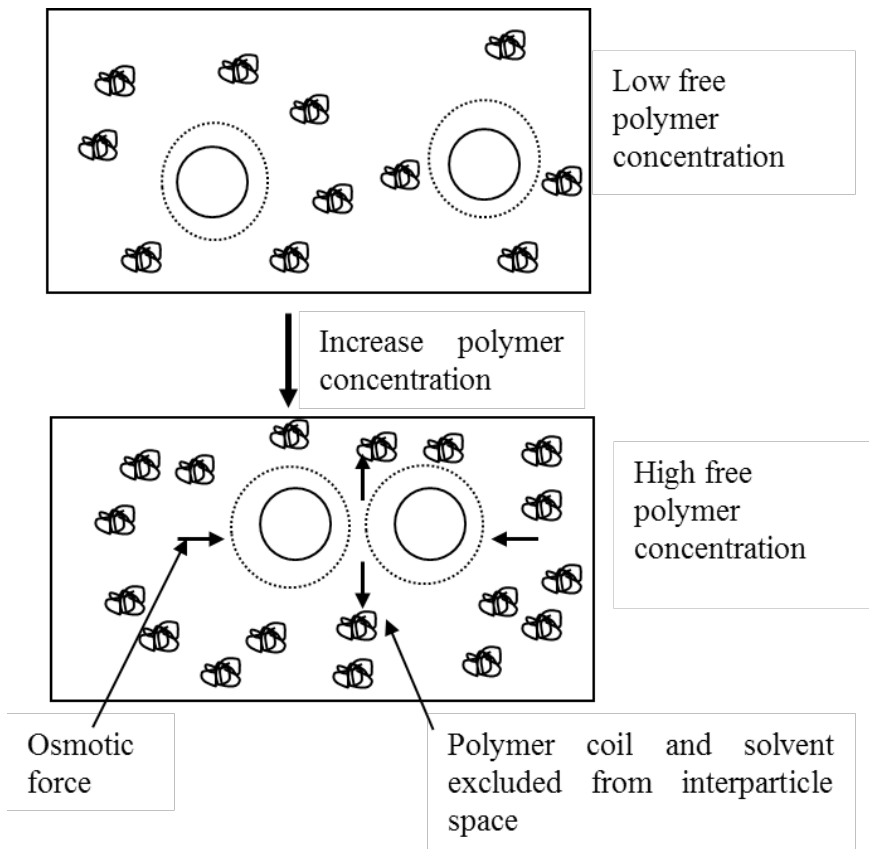
- easy of application (much of the paint is made for use by non-professionals);
- must remain stable in the can without settling too much;
- if it does settle, it must be easy to re-disperse by stirring;
- must stick to the brush without dripping off;
- but must flow freely from the brush onto the surface when it is sheared by the brush-stroking action and;
- must flow sufficiently to allow the brush marks to disappear, but not so much that it will sag under the influence of gravity.

Therefore, the important rheological characteristics are time dependence of the viscosity, shear rate dependence of the viscosity and the elasticity [10].

All the above characteristics reflect the type of interactions between the particles in paints and coatings dispersions. The main aim of colloidal dispersion rheology is to understand and quantify the effects of interparticle forces on the bulk properties of concentrated colloidal dispersions. In order to achieve such an aim one needs to obtain, among other studies, rheological (flow) data for model colloidal dispersions that are sufficiently well characterised for the particle interaction forces to be estimated. A lot of researcher have used this approach to relate rheological properties to interparticle forces of model colloidal dispersions, i.e. from the knowledge of rheological properties the interaction forces have been estimated or vice versa [11]. They conclude that the complex rheology of colloidal dispersions indicates the interplay of the full range of forces at microstructural level. The shear viscosity, the shear modulus and the extent of shear thinning all increase as the interparticle potentials, either attractive or repulsive, become strong relative to Brownian motion. The low shear viscosity and modulus,

which derive from small perturbations of the structure at rest, provide the most sensitive probes of these particle potentials.

In many paint formulations, thickeners such as hydroxyethylcellulose are added to control the rheology of the dispersion. This is to reduce settling and ease of the application of the formulation. In certain formulations, the paint must be pseudoplastic or shear thinning and possibly thixotropic. It is now well established that addition of non-adsorbing (free) polymer to paint dispersion can cause several “things” to occur depending on the type, molecular weight and concentration of free polymer. Three types of flocculation have been documented and these are bridging flocculation, depletion flocculation and depletion restabilisation [6]. Experiments and theory have shown that concentrations of free polymer comparable to that at which overlap begins to occur (i.e. near the semi-dilute concentration,  $c^*$ , of the polymer solution) can induce flocculation, while relatively higher concentrations can impart stability. The experimental and theoretical studies of the phase separation, viscosity and viscoelastic properties have been studied for non-aqueous polymer latices especially sterically stabilised polystyrene (PS) and poly(methylmethacrylate) (PMMA). They have been used as “model” systems because they have a well-defined shape, and can easily be prepared with high degree of monodispersity over a wide particle size range. For instance, Goodwin et al. [12,13] and Kwaambwa et al. [14] studied PMMA model latex particles dispersed in poly(isoprene) (non-adsorbing) polymer solution. The solvent for the free polymer was dodecane. One of the solutions to the problem of VOCs is to use highly concentrated dispersions containing free polymer of low molecular weight (to minimise the viscosity) and low functionality (nearly non-interactive). The latter is to maximise the fluidity of the system and also insures that the build-up of structure by uncontrolled and irreversible bridging flocculation is minimised if not stopped completely. The shear-wave propagation measurements (or pulse shearometry) were used to determine the shear wave rigidity modulus or high frequency limit of the shear modulus and these measurements compared with those calculated using the depletion volume model. The model is based on simple considerations of the resulting depletion force (osmotic pressure) due to exclusion of the polymer from interparticle spaces (see Figure 3) [15]. The depletion interaction occurs in a colloidal dispersion when either (i) non-adsorbing polymer is added or (ii) adsorbing polymer is added to well above the adsorption saturation point or (iii) the added polymer is poorly (or weakly) adsorbed. The depletion force is taken as the work done in pulling flocculated particles apart to infinite separation (i.e. separation distance whereby added free polymer molecules can sit freely in the interparticle space) [15].



**Figure 3:** Schematic representation of depletion flocculation phenomenon for sterically stabilised latex particles with added free polymer [15].

## 5. Coatings Prevent and Protect

Although the number of end-uses of paint is virtually unlimited, it is usual to divide them into three distinct groups namely architectural (also referred to as decorative or building), product line (also referred to as original equipment manufacture - OEM) and special-purpose coatings.

We rarely see a 'raw' product. Our domestic and work spaces are certainly more pleasant and more conducive to good work when the interior decor is attractive. The millions of paint-protected cars on the roads, for example, benefit from years of coating research – giving products that reduce fading

from sunshine, damage from rain, snow, road chippings, oil, petrol, ice and car-wash machines, not forgetting ever greater protection from rust. In the supermarket, meanwhile, we are confronted with shelves of coloured inks and coatings on all kinds of packaging. Food safety and labeling information depend on packaging and coatings. Packing must keep the right things in while keeping the wrong things out. Special internal coatings prevent interaction between the metal and the contents, ensuring the wholesomeness of the food.

It goes without saying that an object with protective coating will last longer than one that has none. It does not have to be replaced as often, reducing the demand for raw materials. Taking the car again as an example, uncoated cars would last only a year or two before rust rendered them unsightly and unsafe. The paint on a car, which costs less than half of one percent of its showroom price, adds many years to its life and saves steel and other materials as well as the energy that would be needed to produce and distribute its replacement.

Tree-lovers should also be grateful to paints and coatings. Coatings not only make wooden objects last longer, but also enable us to use less of the precious hardwoods by substituting coated renewable-forest softwoods that would otherwise be unsuitable for construction. Millions of tons of fuel are also saved by the world's shipping companies through the clean 'slippery bottoms' of their vessels, made possible by modern anti-fouling paints [16].

Coatings also help to ensure that major structures like bridges, buildings and industrial plants are built to last. Without them, the maintenance of structures can be extremely costly. Even on a much smaller scale, however, coatings have an impact on our daily lives. Carrying home several bottles of wine, for example, is now easier with widespread use of lighter glass containers. By applying a thin coating to the bottles, the neck and walls are made thinner without losing strength. Such coatings are now saving the glass packaging industry thousands of tons of glass a year. Added together with savings in energy, transport and so forth, and the result is a substantial saving a year. Already established and growing fast is another glass market for coatings – fibres for telecommunications. Glass fibre cables can carry infinitely more information than copper wires and every glass strand needs a protective coating. The two layers of UV-cured coating not only identify, protect and waterproof the cables but they also help launch the laser light pulses on their path through the fibre core [17].

## 6. Driving Forces for Change to New and Improved Types of Coatings

After centuries of exploitation and degradation, we have finally learned that the destruction of our environment will lead to probable demise of our own species. In contrast to past environmental solutions, modern systems need to be effective, low cost, sustainable, and add value to the environment.

There is a continuing and insatiable demand for new and improved types of coatings, not only for competitive reasons but also to meet the increasingly stringent regulations designed to protect the environment. There are, therefore, three main driving forces that affect the development of new types of coatings:

- i) *environmental* -the need to reduce the amounts of solvent emission to the atmosphere in the light of increasing concern over pollution;
- ii) *economic* -reflecting the necessity for, say car, manufacturers to remain competitive in an industry suffering from world-wide over capacity; and
- iii) *quality* -both of appearance and performance standards as major promotional and selling features.

New environmental regulations, particularly designed to minimize waste and encourage material recovery and recycling, will undoubtedly result in more widespread use of new coatings technologies over the coming years. Hence, although the markets for the coatings are likely to grow only moderately, the demand for new and improved systems will increase considerably.

While environmental pressure is the major driving force for the introduction of the new types of coatings, notice also has to be taken of their effect on the appearance and costs of application. Coatings producers are therefore now required to develop products that not only offer aesthetic appeal and a higher resistance to adverse atmospheric and service conditions, but that are also acceptable to the environment. The latter tends to restrict the choice of type of materials, as well as the nature of the process by which they are applied [18].

The paint and coatings industry is literally and figuratively 'on the move'. Influenced by increasing environmental legislation, raw material price hikes, emerging new markets and consolidation in the industry, development of new products that are both more cost-effective and better for the environment has become more important than ever. On quality, it is clear that the paints and coatings that are now available on the market must achieve complex technical specifications in terms of rheology (flow properties), finish, material constituents and paint performance. In terms of the technology needed to make coatings, the basics of the wet paint production – requiring pigments,

resins/binders, a solvent/carrier and various additives – still apply. However, this description conceals a wealth of research by chemists, physicists and other specialists to match the changing needs of coating users in many fields discussed above.

There are three specific types of pollution arising within the coatings industry: air pollution, contamination by biologically active materials, and plant effluents [19]. Of these, air pollutants arising from the evaporation of organic solvents is the most important. Many of the paints and coatings formulations have traditionally contained aliphatic and aromatic organic solvents, among them xylene, toluene and mineral spirits, which dry quickly to leave a smooth paint finish. These solvents are the VOCs, which are damaging to both human health and the environment. Many governments are now pushing for restrictions in the use of VOCs and any solvents considered HAPs (see Box 3) [5,10]. Liquid coatings formulations must simultaneously meet current and pending VOC limitations and HAP restrictions by shifting to the new technologies. Newer technologies that are finding increasing use include water-borne systems, high-solid solvent-based systems, powder coatings and radiation-cured finishes.

Other factors contributing to the shifts in technology include the level of any involvement by the competition (companies often need to follow suit to maintain technical parity), the availability of the necessary raw materials, relative capital and operating costs of the different methods, the performance of the product and the timing of the investment cycle. Bearing these factors in mind, it is predicted that the growth of most types of high technology systems will be strong to the middle of this decade.

## 7. New Technologies

Several new types of coatings technologies have evolved over the past decade that offer the possibility of replacing traditional coatings with alternatives that can give improved performance at lower costs and without the danger of excessive and unacceptable environmental pollution. These technologies relate not only to new application and curing processes and equipment, but also to modifications and improvements in established practices.

The technologies concerned can be most conveniently categorized into seven distinct groups:

- Improved low-solids (less than 70%) solvent-based systems (the compliance solvents)
- High-solids solvent-based systems (more than 70%)
- Powder coatings
- Radiation-cured (ultra-violet and electron beam)
- Reactive (plural-component catalysed) systems

- Water-borne electrodeposition coatings
- Other water-borne coatings including emulsions, latices and colloidal dispersions

The rate of acceptance of all these coatings methods will depend not only on the rate of successive development of acceptable and economically viable techniques, but also on the overall state of the economies. In addition to these generic high technology coatings systems, there are certain specialized types of coatings that are under continuing technical and commercial development. As an example, three technologies, namely water-borne, powder and radiation cured coatings, are discussed here in more details.

### **7.1 Water-borne coatings**

Switching to environmentally friendly coatings involves more than simply replacing the organic solvents with a VOC-free ingredients, such as water. Water-borne formulations have proved to be acceptable for decorative usage and for this application water-based paints are now the norm. But for industrial application, the paint and coating industry has encountered problems [20]. Despite the fact that by the mid-1990s all of the major industrial paint manufacturers had produced solvent-free/low-solvent content alternatives, they found that these formulations were compromising quality and so did not gain acceptance among the customers, who were reluctant to switch to a more expensive, poorer quality product.

While VOC-free products might represent a valuable marketing tool and offer good financial returns, they have also come in for a considerable amount of criticism. Life-cycle analysis techniques are showing that some of the 'environmentally friendly' components that need to be added to the coatings to achieve the same technical sophistication are, in fact, more damaging to the environment than the solvent that they are replacing [21]. For instance, water-borne paints require a number of chemical additives (thickeners) to maintain a stable dispersion during storage. Some of these additives are toxic, and because they are water soluble, they are potential water pollutants.

Another problem of water-borne paint is drying which results in increase in viscosity [22]. At high volume fractions, the behaviour may change from shear thinning to shear thickening (or dilatant) behaviour common for very concentrated systems. This can result in 'sticky', partially dried paint which cannot be worked for long enough to produce smooth overlap into the next brush-load of paint.

Water-borne paints require more energy to remove the solvent. As compared to solvent-borne paints where the solvent flashes at ambient temperature, water-borne ones require a heated flash.

The swap from solvent-borne to water-borne is not simple for some bigger industries such as the coil and can coating industry. Here there is a big trade-off between potential water-borne advantages and the economics of the solvents used in the formulations that are then oven cured. These solvents are driven off in the ovens and are subsequently re-circulated into the ovens and burnt providing the energy to drive the ovens [23]. Just over a decade ago in Europe, there were conversions from water-borne to solvent-borne for this very reason.

## 7.2 Powder coatings

Almost an industry in itself, powder coating is growing fast despite its higher capital costs in manufacture and application. Powders are virtually VOC-free and manufacture is different from liquid paints. Resin, pigments and other additives are dry-blended to give a homogeneous mixture, which is then heated and extruded before being ground to a fine powder. Spray application uses electrostatics so that the powder adheres to the earthed workplace. After coating, the item is stoved at fairly high temperatures, generally 150–180°C, when the powder melts and flows out to a level, integral coating. The presence of any organic vapour in stoving would necessitate increased ventilation with consequent loss of energy efficiency [24].

Polymers for powder coatings are based on epoxies, polyesters, and occasionally, acrylics. Powder cross-linkers include dicyandamide and its derivatives (for epoxy resins), carboxylic anhydrides and acids. Acid tipped polyesters are cured with epoxies, most notably the weatherable triglycidylisocyanurate (TGIC), catalysts being selected from a wide range of amines, amidines, and phosphines.

The method has its own disadvantages such as [24]:

- TGIC is the stable curing agent for weatherable powder coatings but concerns about its toxicology are causing the industry to look for replacements.
- The need to stove at relatively high temperatures prevents their use in air-drying markets, and limits their use on temperature sensitive substrates such as wood and plastic films.
- The relatively high film builds that are necessary for good film coalescence has limited their use in can coatings and improvements in appearance, durability, and colour styling capabilities still need to be demonstrated before wide acceptance can be expected as car body coatings.
- As in water-borne coatings, it is very difficult in many applications to get customer acceptability because of inadequate post application and levelling.



So, a technology change allowing thin film powder coating application with excellent flow and levelling, gloss levels, and so forth would, for instance, be acceptable for automotive finishing.

### **7.3 Radiation cured coatings**

As with powder coatings, radiation cured coatings do not require the use of solvents and produce virtually no VOCs. They can either be liquid or powder radiation cured coatings. Radiation cured powder coatings are less likely to irritate the skin of workers in factories, a possibility with radiation curable liquids.

Radiation cured coatings contain reactive diluents which reduce the application viscosity but which are reacted into the polymer structure during the curing process thus substantially reducing the emissions to atmosphere resulting from the use of conventional solvents in 'conventional' paint systems. However, radiation cured systems require fixed energy sources and cure rates vary according to the distance between the energy sources and the substrate. Thus, whilst these systems can result in reduced VOC emissions, their use is largely limited to the coating of sheet or flat web substrates in industrial processes, and is certainly not appropriate for coating car bodies nor for decorative air drying coatings [18]. In other words, they are only practical on specially adapted, original equipment manufacturers' (OEM) product-coating lines.

Conversion from liquid coatings to alternative systems can be quite expensive, so paint users are generally eager to continue using newly developed low- or no-VOC liquid coatings on their existing paint production lines. However, paint additive manufacturers are working on new technology of radiation-curable powder coatings to extend the use of ordinary powder coatings [17]. Manufacturers of radiation curing additive initiators are working with resin producers and paint formulators to harness ultraviolet (UV) radiation to apply powder coatings to otherwise heat-sensitive substrates such as wood and plastics. Liquid UV-curable coatings generally are used over paper and paperboard.

## **8. New Challenges**

Nowadays, there is the issue of 'sustainable development' that chemists and formulators should consider carefully. The original definition of sustainable development was that given by the World Commission on Environment and Development in 1987: 'Development that meets the needs of the present without compromising the ability of future generations to meet their needs' (quoted in Keatings [25]). Sustainable development usually refers to some

form of modern technological society, with business taking responsibility for its impact on society and the environment. Since chemistry is the hub of modern society, it is also essential part of sustainable development. But sustainable development is about more than the environment. It is based on four components: prudent use of resources, protecting the environment, economic growth and social progress. The target is better quality of life for everyone now and for generations to come.

In general, the following challenges for the paint and coating formulators are to find effective, non-VOC alternatives to solvents such as xylene, toluene and other aromatics and to develop technologies that exclude the use of solvents entirely, such as powder coatings, UV/radiation-cured coatings and high solid coatings. These challenges for the formulators may be summarised as finding new materials, developing modified chemical materials, finding alternative solvents, developing new formulations and new methods of application.

In short, product developers should formulate coatings that meet existing and pending VOC and HAP regulations and offer performance that customers are willing to pay for. The future may lie in the development of the green chemistry philosophy.

## 9. Green Chemistry

The term green chemistry was first defined by the US Environmental Protection Agency (EPA) as the 'utilisation of a set of principles that reduces or eliminates the use of generation of hazardous substances in the design, manufacture and application of chemical products' [26]. The EPA issued 12 principles of green chemistry (see Box 6), which go some way in explaining what the definition means in practice. The principles cover such concepts as:

- the design of processes to maximize the amount of raw material that ends up as product;
- the use of environmentally-benign solvents where possible;
- the best form of waste disposal – aiming not to create it in the first place.

Green chemistry is essentially chemistry for the environment; it is most definitely apolitical. In many ways green chemistry is a philosophy and a way of thinking. It is not a new branch of chemistry but is pulling together of tools, techniques and technologies that can help chemists in research and production to develop more eco-friendly and efficient products and processes.

The with regard to paints and coatings industry, only five areas are discussed here whereby the principles of green chemistry may be applied.

*(a) Resins are one key to lower VOC*

The development of new resin technology will make all the difference in the formation of low-VOC coatings. Winning resin technologies include acrylic, polyester, epoxy, and aliphatic urethane formulations - all of which can be formulated as high-solids, low-VOC coatings or water-borne coatings. Losing technologies will be those that require a large amount of solvents (up to 70% by volume) for application, including nitrile, chlorinated rubber, neoprene, polyvinyl chloride and alkyd formulations. Another possibility is put to considerable effort into the development of water-borne systems as well as of high-solids, low-solvent systems. For instance, developing water-borne polyurethane coating such that you get the isocyanate cross-linker in the coating to disperse in water yet not react too quickly in water. In solvent systems, urethane formulators are making an effort to stay away from HAPs. It has been found that when formulators move to low- or no-VOC systems, they also are able to remove HAP solvents from their systems. The efforts to reduce or eliminate HAPs and VOCs go hand-in-hand.

*(b) Substitutes*

Look for substitutes, for instance, tributyltin, used in marine anti-fouling and triglycidylisocyanurate, used as a cross-linker in powder coatings, are considered to be toxic. Partly in anticipation of concerns over health risks associated with certain paint ingredients such as certain surfactants. For example, manufacturers of nonyl phenol ethoxylate surfactants need to offer alternative surfactants. Nonyl phenol ethoxylates are believed to be estrogen mimics and pose some health concerns.

*(c) Additives*

We need highly efficient coatings additives that perform the functions required of them, namely to enhance performance, cut costs, and open up new applications.

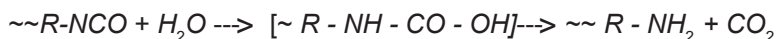
*(d) Solvent suppliers*

Solvent suppliers face VOC and HAP rules. For instance, customers of solvent suppliers in North America are expected to choose solvents based on propylene glycol ether over ethylene glycol for both solvent-borne and water-borne formulations [27]. Ethylene glycol solvents appear on the list of HAPs. However, it should be pointed out that propylene glycols could seldom be one-for-one replacements for the ethylene glycol solvents. Notably on pound-for-pound basis, propylene glycols contribute the same VOCs to a coating formulation as do ethylene glycols. Regardless of this propylene glycols are "more efficient" because often a paint formulation requires less propylene glycol than ethylene glycol and thereby resulting in lower VOC formulation.

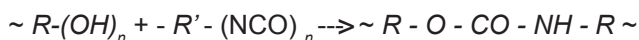
*(e) Reactive diluents*

Switching to water- and powder-based systems is not always feasible. Yet another approach is to increase the concentration of solids in solvent-based coatings, which has an advantage that it leaves the basic composition unchanged. Crucial to the success of these high solids formulations are so-called reactive diluents, added to reduce product viscosity. Adding a reactive diluent does not alter the performance of the coating, but markedly reduces volatile emissions.

Polyurethane (PU) coatings are notable for their durability and resistance to chemical agents, abrasion and weathering. They are extensively used for car topcoats as well as in military and aerospace applications. Polyurethane paints are sold as both one pack and two pack systems as shown below [28].



One component PU reaction



Two component PU reaction

Two pack systems require the user to mix a polyisocyanate with a polyol before applying the coating. In one pack systems the polyol and isocyanate come pre-reacted, in the form of a low molecular weight prepolymer. On applying this prepolymer to the object being painted, the coating hardens or cures by reaction with moisture in the atmosphere. One pack systems have a drawback that carbon dioxide is released as a by-product – often producing pinholes or bubbles in the coating. Two component systems are less prone to producing pinholes, but this can occur when reaction conditions, humidity and formulation parameters are not optimal. This can result in pin-holing defects in the coating and hazing problems with clear lacquer finishes.

For the past 20 years or so, industry formulators have known that a possible solution to this problem is to use polyols derived from bisoxazolidine structures. In the presence of moisture, bisoxazolidines hydrolyse by ring opening to reveal hydroxyl and amine groups that can react with diisocyanates to form the coating. By mopping up any water, bisoxazolidines therefore effectively prevent the reaction with diisocyanates that leads to the release of carbon dioxide.

Researchers found out that bisoxazolidines confer another advantage on some systems. Uptake of many polyurethane coatings – those based on aliphatic compounds – has traditionally been hampered by the slowness with

which the coating hardens or cures. In a bisoxazolidine in the formulation typically speeds up the curing process by three to four times. This is because the ring-opened bisoxazolidine reacts rapidly with diisocyanates [4]. On a car assembly line, for example, two pack polyurethane systems incorporating bisoxazolidines can reduce drying times to as little as two minutes.

Fuelled in part by growing pressures to reduce VOCs, companies such as ICL, began work to develop a reactive diluent for its range of polyurethane applications in the late 1980s. All of the company's one and two pack systems relied on polyols dissolved in VOCs such as butyl acetate or toluene. Unlike other additives and diluents, bisoxazolidines effectively lock themselves into the polyurethane backbone during the reaction process and therefore do not contribute to VOC emissions as the paint dries. This led to the first successful commercial oxazolidine diluent, Incozol. But still there was room for improvement. Although Incozol 4 helped to reduce VOC emissions, the compound is highly viscous. This meant including a large proportion of solvent in the formulations. The answer was to create a solvent-like version whose trade name is Incozol 4 – in other words a version with extremely low viscosity. Not only would such an additive be unable to evaporate to the atmosphere itself, but it could also reduce the amount of solvent required in the coating formulations. The original bisoxazolidine systems were so viscous because of the NH(CO)R group linking the bisoxazolidine together. This is able to form hydrogen bonds not only intramolecularly within itself, but also intermolecularly with other compounds in the mixture – increasing the viscosity of the system in either case. The answer was to form an alternative carbanato (-O(CO)O-) bridge. The resulting compound, now sold as Incozol LV, is incapable of hydrogen bonding and dramatically reduces the viscosity of the system. Commercialised in 1996, Incozol LV allows formulators to use a true reactive diluent that reduces solvent use and VOC emissions. Incozol LV possesses the key properties demanded of a good reactive diluent [29]:

- good polyol and solvent compatibility;
- low intrinsic viscosity (50 mPas at 20°C);
- reasonably high equivalent weight (90);
- virtually colourless (essential for clear lacquer finishing);
- workable pot life and good cure response; and
- no adverse effect on coating properties (including film hardness development and resistance, gloss and weathering properties).

## 10. The Future

And what does the future hold? On a global scale, it is difficult to predict the future but the paints/coatings industry certainly is on the move. There is no

doubt, however, that the industry will continue to thrive and evolve, even if the growth rate is unspectacular. New advances in paints and coatings are brightening up our lives and will continue to do so. The race to reformulate liquid coatings has opened up new opportunities for both coatings formulators and material suppliers. Formulators who can sell paints that meet regulatory limits and still provide performance comparable with or even better than older products will have a marketing edge. New coatings formulae and application methods have been developed to increase throughput, augment durability, reduce environmental impact, and buffer against rising oil prices.

Material suppliers have an opportunity to introduce new- and frequently higher priced components that allow the production of low- or no-VOC coatings. Material suppliers thus have an opportunity to gain entry or market share even as they are introducing value-added higher profit products into the market.

Paint is a very complex and versatile material, offering more challenges to the chemists, physicists, engineers and other specialists than most other products. New generic resin systems are certainly to be developed to suit the changing requirements of the users and to enable future coatings systems to conform to increasingly stringent environmental regulations. There are ample opportunities for the chemical innovations making the coatings industry an exciting place for future generations of scientists. The challenge set for the future is for all paints to be waterborne which requires dedicated scientists to understand paint chemistry and create innovative new products. The chemists should consider the issue of 'sustainable development' carefully. As for the companies, the way forward is the so-called '**triple bottom line**' approach which focuses on understanding and measuring a company's value according to its environmental and social performances as well as its economic performance.

## 11. References

- [1] Prieto J (2010). Painting the future green. *European Coatings Journal*, 4, 20-25.
- [2] Joshi R, Provder T and Kustron K (2008). Green coatings: a trend that is becoming the rule rather than the exception. *JCT Coatings Tech.* 5(1), 38-43.
- [3] Lambourne R and Strivens TA (1995). *Paint and surface coatings: theory and practice*, 2<sup>nd</sup> edition, Woodhead Publishing Ltd., Cambridge, UK.
- [4] Marrion AR (ed.) (2004). *The Chemistry and Physics of Coatings*. Royal Society of Chemistry, London, UK.
- [5] Tablert R (2007). *Paint Technology Handbook*, Grand Rapids, Michigan, USA, ISBN 157447033.
- [6] TadrosThF (ed.) (1987). *Solid/Liquid Dispersions*. Academic Press, London, UK.
- [7] Spurgeon A (2006). Watching Paint Dry: Solvent Syndrome in the late Twentieth – Century Britain. *Med. Hist.*, 50(2), 167-188.
- [8] Hare C (1994). *Protective Coatings: Fundamentals of Chemistry and Composition*. Technology Publishing Company, Pittsburgh, USA.
- [9] Eley RR (2005). Applied rheology in the protective and decorative coatings industry. *Rheology Reviews* 2005, 173 - 240.
- [10] Tadros TF (Ed.) (2010). *Colloids in Paints*. Wiley VCH Velag GmbH.
- [11] van der Werff JC (1989). *Rheology of Hard-sphere Dispersions*. John Wiley & Sons.
- [12] Goodwin JW, Hughes RW, Kwaambwa HM and Reynolds PA (2000). The phase separation behaviour and the viscoelastic properties of particles with non-adsorbing polymers, Part I - Experimental study. *Colloids & Surfaces A: Physicochemical Engineering Aspects* 161, 339-359.
- [13] Goodwin JW, Hughes RW, Kwaambwa HM and Reynolds PA (2000b). The phase separation behaviour and the viscoelastic properties of particles with non-adsorbing polymers, Part II - Theoretical study. *Colloids & Surfaces A: Physicochemical Engineering Aspects* 161, 361-376.
- [14] Kwaambwa HM, Goodwin JW, Hughes RW and Reynolds PA (2004). The viscosity behaviour of particles with non-adsorbing polymers, Part III - Experimental study. *Colloids & Surfaces A: Physicochemical Engineering Aspects* 233, 163-170.
- [15] Kwaambwa HM (1995). Rheological characterisation PMMA lattices with added non-adsorbing polymers. Ph.D. Thesis, University of Bristol, UK.

- [16] Daniliuc A, Deppe B, Deppe O, Friebel S, Kruse D, Philipp C (2012). New trends in wood coatings and fire retardants *European Coatings Journal*, 07/08/2012, 20-24.
- [17] Schwalm R (2007). UV Coatings: Basics, Recent Developments and New Applications, Elsevier, Amsterdam, The Netherlands.
- [18] Tullo AH (2005). Automotive coatings. *Chemical & Engineering News* 80(42), 27-30.
- [19] Randall PM (1992). Pollution prevention methods in the surface coating industry. *Journal of Hazardous Materials*, 29 (1992) 275-295.
- [20] Challenger C (2006). Environmentally friendly paints and coatings: Making the world a greener place. *JCT Coating Tech.* 3(7), 28-34.
- [21] Pianoforte K (2007). Low and Zero VOC Coatings. *Coatings World* 34-39.
- [22] Procopio LJ, Larson GR and Rosano WJ (2007). Low VOC Waterborne Coatings for Use in Industrial Maintenance Painting. *JCT Coatings Tech* 4(2), 50-59.
- [23] Berejka A J (2003). Electron beam curing of coil coatings. *Radtech Report* (September/October), 47-54.
- [24] Misev TA and van der Linde R (1998). Powder Coatings Technology: New developments at the turn of the century. *Progr. Organic Coatings* 34, 166-168.
- [25] Keatings M (1992). Agenda 21: The Earth Summit's Agenda for Change, Centre for Common Future, Geneva, Switzerland.
- [26] Anastas P and Warner J (1998). Green Chemistry: Theory and Practice. Oxford University Press, New York, USA.
- [27] Stoye D and Frietag W (eds.) (2007). In Paints and Coatings, 2<sup>nd</sup> completely Revised Edition, Wiley-VCH Verlag GmbH, German.
- [28] Daniels L and Gorick L (2001). Emission Control. *Chemistry in Britain* 37(1), 42-44.
- [29] Moore DP and Carter NG (Sept 1997). The Versatility of Oxazolidines as Reactive Diluents in Two-Component Polyurethanes", *Pittura & Vernici - Paints and Varnishes*, 20.



## 12. Appendices

### Box 1: Types of binders (Marrion, 2004)

*Alkyd*: Produced by condensation reactions between polycarboxylic acids and polyhydric alcohols - often phthalic acid or anhydride and glycerol. Further reaction with an oil (e.g. soya bean oil) or fatty acid gives a resin suitable for use in decorative gloss paint.

*Vinyl*: These are usually based on copolymers of vinyl acetate with vinyl chloride, acrylic or methacrylic esters or styrene, produced by addition polymerisation. Decorative vinyls are generally based on emulsions in water, whereas heavy duty and industrial finishes may use solution vinyls (in organic solvents) or as dispersions in plasticiser (organosol/plastisol).

*Acrylic*: Many monomers are used in the preparation of thermosetting, thermoplastic and dispersion acrylic polymers for coatings. Examples are ethylmethacrylate, styrene, acrylonitrile, ethyl acrylate. These are often reacted by addition polymerisation, and by ionic group transfer and coordination catalyst polymerisations. Different functionality may be introduced by using comonomers such as methacrylic acid (carboxylic acid groups) or hydroxy ethyl acrylate (hydroxyl groups). These can later be reacted with other polymers during curing.

*Epoxy*: Epoxy resins are actually oligomers, which must be reacted with other polymers such as polyamines, polyamides and polyesters. The most important epoxy resin series is formed by the condensation polymerisation of Bisphenol A with epichlorohydrin.

*Polyurethane*: Polyhydroxy materials can be reacted in a rearrangement polymerisation with diisocyanates to form polyurethanes.

### Box 2: Water-based coatings vs solvent-based coatings (Marrion, 2004)

Water-borne

Solvent-borne

Non-flammable  
 Clean up with water  
 Quick drying in good conditions  
 Low VOC content  
 Low odour  
 Non-yellowing

Better drying in cold, damp conditions  
 Better low-temperature storage  
 No can corrosion problems  
 Less wood-grain raising  
 Higher gloss

\*The terms solvent-based and water-based are not strictly accurate. The coating is not 'based' on water or solvent, but is either dissolved or suspended in it. "Water-borne" and "solvent-borne" would be more accurate descriptions.

**Box 3: Examples of functions of additives**

(Tadros, 2010; Tablert, 2007)

Biocides – in-can preservatives as a result of a shift to water-borne organic resins which can support bacterial growth whereas dry-film biocides help preserve paint that has dried on a substrate i.e. discourages growth of algae or fungi.

Thickeners – aid brush and roller paint pickup and application.

Plasticisers – give paints better chip resistance.

Defoamers/Antifoamers – aid in mixing paint and reducing film imperfections.

Surfactants – pigment dispersants in water (anionic surfactants) and pigment stabilisers (nonionic surfactants). Some have thixotropic properties that help to thicken paint while allowing the user to spread the paint easily on a substrate, whereas some provide hydrophobic properties to dry-paint films, giving the paint water resistance under long-term exposure.

Corrosion inhibitors – forms a monomolecular barrier to protect the metal surface from water and improve coating adhesion.

Ultraviolet light absorbers – stabilise the paint film and preserves it against breakdown under exposure to sun e.g. benzotriazole-based film additive.

Miscellaneous - anti-skinning agents, deglossing agents, stabilisers, surface modifiers, adhesion promoters, rheology control agents.

**Box 4: Three main paint categories****Product coatings**

Appliances

Automotive

Electrical insulation

Factory-finished wood

Film, paper &amp; foil

Machinery &amp; equipment

Marine

Metal containers

Metal furniture &amp; fixtures

Non-automotive transportation

Pipe

Sheet, strip &amp; coil

Toys &amp; sporting goods

Wood furniture &amp; fixtures

Miscellaneous consumer &amp; industrial products

**Architectural**

Exterior &amp; interior house paint

Stains

Undercoaters, primers &amp; sealers

**Special-purpose coatings**

Aerosols

Arts &amp; crafts

Automotive &amp; machinery refinishing

Bridge maintenance

High-performance maintenance

Metallics

Multicoloured roof

Swimming pool

Traffic marking

**Box 4: Three main paint categories**

**Product coatings**

Appliances  
 Automotive  
 Electrical insulation  
 Factory-finished wood  
 Film, paper & foil  
 Machinery & equipment  
 Marine  
 Metal containers  
 Metal furniture & fixtures  
 Non-automotive transportation  
 Pipe  
 Sheet, strip & coil  
 Toys & sporting goods  
 Wood furniture & fixtures  
 Miscellaneous consumer & industrial products

**Architectural**

Exterior & interior house paint  
 Stains  
 Undercoaters, primers & sealers

**Special-purpose coatings**

Aerosols  
 Arts & crafts  
 Automotive & machinery refinishing  
 Bridge maintenance  
 High-performance maintenance  
 Metallics  
 Multicoloured roof  
 Swimming pool  
 Traffic marking

**Box 5: Some of HAPs used in paints (USA Clean Air Act of 1990)**

Acetamide	1,2-Dichloroethane	Hexachlorobenzene
Pentachlorophenol	Acrylamide	Dichloroethyl ether
<i>n</i> -Hexane	Phenol	Acrylic acid
Diethanolamine	Hydroquinone	Propylene oxide
Acrylonitrile	Dimethylaminoazobenzene	Isophorone
Styrene	Allyl chloride	Dimethylformamide
Maleic anhydride	1,1,2,2-Tetrachloroethane	Aniline
Toluene	Dimethyl phthalate	Methanol
Benzene	Epichlorohydrin	Methyl ethyl ketone
2,4-Toluene diisocyanate	Ethyl acrylate	
1,3-Butadiene	1,1,1-Tetrachloroethane	Caprolactam
Methyl isobutyl ketone	Methylene chloride	Trichloroethylene
Ethylbenzene	Ethylene	
Catechol		
dibromide		
Naphthalene	Ethylenimine	
2,4,6-Trichlorophenol	Vinyl acetate	Formaldehyde
Cumene	Vinyl chloride	Xylenes ( <i>m</i> -, <i>o</i> -, <i>p</i> -)
Nitrobenzene		
2-Nitropropane		

**Box 6: The 12 EPA principles of green chemistry** (quoted in Lancaster, 2000)

1. Prevention – it is better to prevent waste than to treat or clean up waste after it has been created.
2. Atom economy – synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Less hazardous chemical synthesis – wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.
4. Designing safer chemicals – chemical products should be designed to effect their desired function while minimizing their toxicity.
5. Safer solvents and auxiliaries – the use of auxiliary substances (e.g. solvents or separation agents) should be made unnecessary whenever possible and innocuous when used.
6. Design for energy efficiency – energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimised. If possible, synthetic methods should be conducted at ambient temperature and pressure.