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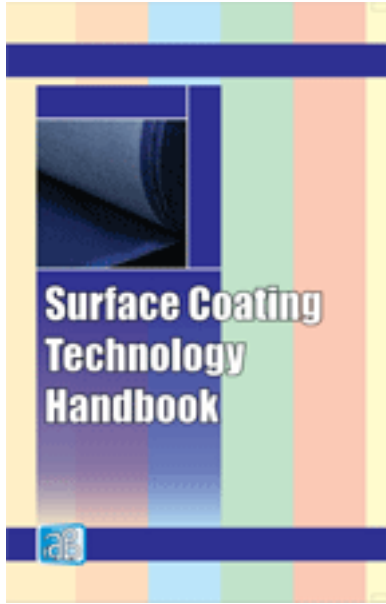
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Surface Coating Technology Handbook



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Surface Coating is in use since long back is rapidly increasing with the development of civilization. There has been considerable impact in this field. Surface coating technology specializes in finding out engineering solutions to all the critical production problems related to coating the products on a continuous and consistent basis in your production plant. Surface coating can be defined as a process in which a substance is applied to other materials to change the surface properties, such as colour, gloss, resistance to wear or chemical attack, or permeability, without changing the bulk properties. Production of surface coating by any method depends primarily on two factors: the cohesion between the film forming substances and the adhesion between the film and the substrate. The development of science and technology revolutionized the surface coating industry in the progressive countries of the world. Surface coating technology involves the use of various types of products such as resins, oils, pigments, polymers, varnishes, plasticizers, emulsions, etc. We have completely replaced costly petroleum solvents with water and we get cheaper finished products with no evaporation loss and fire hazards. Paint is any liquid, liquefiable, or mastic composition which after application to a substrate in a thin layer is converted to an opaque solid film. It is most commonly used to protect, colour or provide texture to objects. The paint industry volume in India has been growing at 15% per annum for quite some years now. Varnish is one of the important parts of surface coating industry. They are used to change the surface gloss, making the surface more matte or higher gloss, or to provide the various areas of a painting with a more unified finish. Plasticizer plays an important role in the formation of polyvinylchloride (PVC). It is also used to plasticize the polymers. Polymers are divided into three different types; linear polymers, branched polymers and cross linked polymers. Polymer Energy system is an award winning, innovative, proprietary process to convert waste plastics into renewable energy. On the basis of value added, Indian share of plastic products industry is about 0.5% of national GDP.

This book basically deals with principles of film formation, evaporation of solvent from a solution, chemistry and properties of drying and other oils, glyceride structure and film formation, the size of polymer molecules, processing of oil and resin, inorganic pigments, classification by chemical constitution, azo pigments, organic pigments in architectural (decorative), organic pigments in industrial finishes, solvent requirements of specific resins convertible systems, molecular structure of polymer plasticiser systems, properties of plasticised polymers, surface active agents, optical properties, rheological characteristics, emulsions and other aqueous media, formation of polymer emulsions, modern methods of analysis etc. The book presents a concise, but through an overview of state of technology for surface coating. This is organized into different chapters like principal of film formation, chemistry and properties of drying and other oils, processing of oil and resin, organic pigment, solvents, plasticizer, surface active agent, surface preparations etc. This book is an invaluable resource to technocrats; new entrepreneurs, research scholars and others concerned to this field.

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The Production of a surface coating by any method depends primarily on two factors the cohesion between the film forming substances and the adhesion between the film and the substrate. These two factors are antipathetic. If the cohesion is at a maximum then adhesion will be nil and (although difficult to visualise) vice versa. The intermolecular forces involved in each case are fundamentally the same but on the one hand the reactions occur within a liquid phase or one derived there from and on the other between two phases.

The forces holding the film together are of the same type as those involved in the adhesion of the film and it is therefore convenient to discuss them side by side.

Cohesive and Adhesive Forces

Mechanical Forces

Granted that the surfaces involved do not yield areas of repellency as in the painting of wet timber a considerable strength arises by interlocking of molecules or polymers. A typical case is that of timber and an oil based primer the oil penetrates into the cellular structure and dries therein and the strength of the bond is determined by the cohesive forces existing within the film. It should be noted that the depth of penetration has no bearing on the strength of the joint once interlocking has occurred.

Similar effects occur on zinc sprayed surfaces phosphate coatings roughened metal and sanded primers. It is not illogical to assume a similar mechanical attachment between pigment particles and the medium.

An oil medium itself must also be subject to a mechanical cohesion by interlocking of polymer chains of the simple glyceride molecules.

Molecular Forces

In any system the tendency to randomness that is the entropy of the system will tend to increase. Any process that may occur to oppose this will therefore result in stability because energy will be required to overcome this stability and so allow the random process to continue.

These forces will operate in the formation of surface coatings and influence the cohesion adhesion balance.

Electrostatic effects

In coating a metal for instance iron with a varnish it is often overlooked that in point of fact the varnish is actually being applied to an iron oxide film. All metals are coated with such an oxide the coating ranging from thin acid resistant adherent transparent layers on the precious metals through oxides of high tensile strength such as that of aluminium to the water soluble oxide layers of the alkali metals. With a completely dry fresh film therefore adhesion should occur between the oxide film and the medium. This may be assumed to occur via polar groups.

However in actual practice the solid oxide is coated with adsorbed gases (air and water vapour).

Employing Langmuir's suggestions the surface of the substrate may be considered as a mosaic of oxide crystals containing elementary spaces from which residual valency forces extend to a distance of approximately 10^{-8} cm. These valency forces yield a chemical union of elementary spaces with molecules of the adjacent gas in a manner that depends upon the specific forces involved the relative sizes of the elementary spaces and the adsorbed molecules and the orientation of the latter. The films so formed have been assumed to be mono molecular but there is no reason to assume that other layers may not be built up by molecular forces such as hydrogen bonding once a water layer has been adsorbed on the surface.

A similar adsorption will occur at the surface of pigment particles hence the cohesion of the pigmented film will depend on how far the medium may be adsorbed on the crystals faces of the pigments.

Hydrogen bonding occurs as a result of the intense unshielded field of the positive nucleus. The effect of hydrogen bonding on solvents is seen in the elevation of the boiling point and an increase in the density in comparison with similar substances. This can be seen in the following list of boiling points and densities (in each case the more highly hydrogen bonded substance is placed first)

This means that whenever a hydrogen bonded solvent is employed considerable energy in the form of latent heat is required to effect evaporation and this is important where the abstraction of the latent heat occurs from the ambient atmosphere hence causing deposition of water in the film.

It must be realised that hydrogen bonding between solvent molecules is a dynamic equilibrium as the molecules are in a constant movement unlike that existing between polymers where a static state arises. Hydrogen bonding between polymer chains as for instance in Nylon 66 leads to orientation of the atoms regularly

If a number of segments of chains are similarly orientated then crystallinity arises in the system.

Now these crystalline sections which may occur more than once on portions of the same chain will remain associated unless solvents having groups with a greater hydrogen bonding tendency are employed so breaking the existing hydrogen bonds and producing solution of the polymer.

An interesting case where polar linkages afford adhesion is the use of an intermediate to bond a surface coating to glass. Methyl acrylate chromic chloride made from chromyl chloride and methacrylic acid is hydrolysed and dehydrated at the glass surface. Ether linkages are produced and the remaining hydrogen atoms attach themselves to the free oxygen ends of the silica tetrahedra network.

The methyl acrylic residues are left at the surface to present an oleophilic interface.

Van der Waals and London forces

When molecules approach each other attraction occurs between them. Normally this gives rise to liquid cohesion that is viscosity. If the chains in a polymer are free to undergo rotation then the polymer is said to be a liquid. If energy is now withdrawn by cooling the substance the chains cease either completely or partially to move and ultimately the viscosity becomes so high that the substance is said to be a solid. If the chains on cooling orient themselves in such a way that regularity occurs by attraction between molecules such as then a crystalline condition as occurs with hydrogen bonding will arise. The forces holding the chains together will however be smaller.

Metallic Forces

In a metal the electrons in the outer orbits are not confined to any one atom and hence metals will conduct electricity. Bonding of the metallic type does not occur in organic surface coatings but does form the basis of deposited metallic coatings. It has been suggested that one function of paint films on metals is to prevent the flow of the electrons in metals and so act as corrosion inhibitors.

Ionic Forces

The crystal lattice of salts is built up from their ions. This type of structure does not occur generally in organic coatings but does occur in such materials as phosphate and thick oxide films.

In each of these cases solution plays an important part by reducing the viscosity of the film forming medium. Except in the case where natural oils are employed as in linseed oil and red lead mixtures most media consist of a high proportion of polymerised material. It is therefore of value to consider the physical chemistry of the solution of polymers. This problem has been dealt with by a number of authors.

The employment of the correct solvents is important because a poor solvent will mean that a thin film will be produced giving low adhesion. The whole economics of cheap poor solvents high viscosity media and pigments with high hiding power can only be worked out experimentally until the rheology of paint systems becomes better understood. For instance differential evaporation may leave a poor solvent in the mixture so that the film medium is no longer soluble.

Dispersion of polymers by solvent occurs in two ways. In the first case crystalline areas are separated and

in the second the random parts of a chain are separated from neighbouring chains by the solvent molecules. Disrupting of crystalline areas formed by hydrogen bonding involves the use of energy either in the form of heat (see below under Transition Temperature) or electrostatic attraction of the hydrogen bonded solvent for the individual atoms in the polymer chains. The crystalline areas formed by van der Waals forces may be disrupted by the entry of solvent molecules. The action of solvents parallels that of heat. When a polymer is heated the chains of molecules remain unaffected until a temperature is reached at which random parts of the chains are free to rotate. This is known variously as the second order transition temperature the glass temperature and the brittle temperature.

If there are no crystalline areas then a change will occur from a glassy solid to a viscous liquid or a rubber. Linear segments become free to rotate further heat causing fresh segments to thaw out . The temperature therefore remains stationary as additions of heat are absorbed as rotational energy until the movement of chains across each other is possible when the substance flows. The glass temperature is exceedingly important in surface coating technology as it will affect resistance to cold shock.

Crystalline segments of the chains will require more energy to overcome van der Waals forces or hydrogen bonding and in these cases a considerable rise in temperature will occur before these areas are disorientated. Within this temperature range considerable flexibility will arise due to the random portions being free to slide and rotate while cohesion is maintained by the crystalline portions.

The term S the change in entropy merits some discussion. It is particularly important in relation to surface coating polymers as these in many cases are in solution or externally plasticised which amounts to the same thing. The entropy of a system is a measure of disorder or randomness. In a gas there is complete disorder in a crystal practically none. Randomness in a polymer system as already pointed out depends on the temperature.

If a wholly amorphous polymer is treated with solvent of the correct type it will swell by absorption of the solvent. This absorption occurs because as the polymer chains rotate spaces are left which the solvent molecules can fill. As more solvent is added the chains are further separated until a viscous dispersion occurs. Further additions allow chains to slide past each other and the mixture is a liquid.

The presence of crystallinity complicates the system because in addition to the simple free energy considerations there are also the energies required to overcome bonding forces.

Light cross linking will also affect the entropy as randomness will only occur in segments of the chains. Complete cross linking reduces the change in entropy to a minimum. This explains why a small amount of cross linking as in an incompletely converted undercoat allows attack by solvents. On the other hand highly cross linked systems such as stoved melamine formaldehyde finishes are resistant to solvent attack.

The solubility factors have also been investigated for alkyd resins.

It is difficult to see how any quantitative ideas can be developed without taking into account the molecular weight distribution in any polymeric system. Two polymer solutions of the same viscosity could be prepared one containing high molecular weight material dissolved in monomer and the other of lower molecular weight but substantially free of monomer. Addition of a poor solvent will result in precipitation in the first case but not necessarily in the second.

An important type of non volatile solvent is the plasticiser. This operates as does any other solvent by separating the chains but the solvent remains in the film indefinitely. The presence of a plasticiser is important as most paint films are subject to stresses which result in the stretching of the chains to take up new configurations and the rotation of the random parts of the chains so increasing the chance of producing crystallinity. This state of affairs is reversible on the removal of stress. On the other hand if too much plasticiser is present the chains become free to slide over each other and the film will flow irreversibly as removal of stress will not cause the chains to slide back again.

The presence of a plasticiser in a cross linked film is necessary to allow some movement of chains across each other to relieve stresses and Jordan has in fact suggested that non drying oils perform such a function in oxidised films.

Internal plasticisation takes place if large groups are introduced as side chains in polymers. These serve the same purpose as external plasticisers in keeping chains apart they also allow increased solubility by acting as centres for their own solution.

Turning now to actual film formation it will be convenient to examine the systems already enumerated.

Evaporation of Solvent from a Solution

If a solid is dispersed in a solvent and the solvent evaporated then the film left will adhere to a substrate providing its adhesive force is high but it will not form a continuous film unless the cohesive force is also considerable. These two forces must also balance.

Some doubt has been thrown on this idea by a suggestion that lack of adhesion is due to the presence of anti adhesive substances. While this is known practically for example with silicone contamination critical opinion will wait for further experimental proof of this thesis.

From what has been said already it will be seen that the ability of a polymer to form a film will depend on its glass temperature. This can be seen by examination of a typical glassy substance rosin. If this be dissolved in alcohol and the solvent evaporated from the film a friable powder is obtained. However if the temperature be raised there comes a point at which adhesion improves. The same result can be obtained by the use of a solvent of high boiling point i.e. a plasticiser which results in a lowering of the glass temperature.

Highly crystalline materials will have high cohesive forces and increase the strength of the film but they will have in consequence low adhesion.

In any film in this class therefore it is necessary to have at least a resinous polymer a plasticiser and probably a crystalline polymer.

Typical Materials

The following are typical of materials used to achieve film formation as discussed in the foregoing.

Bitumen Solutions. These are complicated mixtures consisting of glasses often plasticised naturally or by added fluxes. It is worth noting that those most resistant to atmospheric attack for example the stearine pitches and the blown bitumens both contain oxygen and are therefore likely to be hydrogen bonded. The coal tar pitches also contain phenolic bodies known to be highly polar solvents.

Chemistry and Properties of Drying and Other Oils

The Early development of the surface coatings industry was founded upon the use of unsaturated vegetable oils which have the property of absorbing oxygen from the air when exposed in thin films to form elastic solvent resistant coatings. This property which is possessed by a number of oils of varying importance and especially by linseed oil has also been utilized in the production of printing inks linoleum oilskins and in a number of other industries. Their growth was fostered not by the application of scientific knowledge of the structure of oils nor of the chemical reactions that make film formation possible but by a process of trial and error typical of crafts generally. The vegetable oils came to be classified according to their performance into three groups the drying semi drying and non drying oils. Of these only the drying oils could be used to prepare paints and varnishes of suitable quality and semi drying oils were regarded as extenders or adulterants. Non drying oils could not be used at all.

More recent developments which were begun by the introduction of oil modified alkyd resins in 1929 and were followed by a considerable increase in scientific knowledge have changed the picture completely. It is now true to say that it is possible to produce some form of surface coating from almost any of the known

vegetable oils. The statement might even be extended to include animal fats but they are not generally such promising raw materials and only selected marine oils have actually been used. However any modern account of the oils for surface coatings must cover a very wide field and be based upon scientific principles even although some details are still not completely understood. Space does not permit a full description of the many different types of oil occurring in nature to be given and reference should be made to one or more of the excellent treatises on the subject that are now available.

Vegetable Oils

Origin

Oils are found in a variety of the organs of living plants but the fruits or seeds provide the only sources rich enough to supply commercial quantities. A large number of plants ranging from annuals to trees secrete oil in their seeds to feed the embryo in the early stages of its development and some also produce oil in the fruit coat enveloping them. In the olive oil from the seed closely resembles that from the fruit coat in composition but this is exceptional there being in general no similarity between them. In stillingia for example the fruit coat contains a solid fat and the seed a drying oil and the oil palm has a red semi liquid oil in the fruit coat (palm oil) and a white solid fat in the seed (palm kernel oil). On the other hand many oleaginous seeds are surrounded by tissues containing very little oil and it is advantageous to remove them before milling or extraction process known as decortication.

The main sources of oleaginous seeds are areas of cultivation in many parts of the world although certain wild crops are still harvested in parts of Africa and the Far East. There is an increasing tendency to install oil mills near the plantations and this is sometimes desirable to eliminate deterioration during transit but the majority of oilseeds can be shipped to any part of the world without risk of damage provided that the moisture content is not too high. Where lipolytic enzymes are present as for example in conophor seeds the development of acidity in transit has been prevented by a heat treatment before despatch.

Production of Oils

Commercial oilseeds contain anything from 20 to over 50 per cent of their weight of oil according to variety and vary in size from tiny seeds like tobacco which require 13 000 to the gramme to large fruits like coconuts. Both these factors have a bearing upon the type of treatment employed and this in turn has an effect upon the quality of the oil produced. Two main processes are employed in practice viz. oil milling and solvent extraction.

Milling

Until fairly recently milling was carried out by means of hydraulic presses but these have now been almost entirely replaced by continuous expellers in which increasing pressure is applied between a rotating worm and a barrel housing. Before feeding into this machine the seeds are broken up if necessary further reduced by passing through a set of rollers and the oil cells are then disrupted by cooking with steam. The pre treatment has a profound effect upon both the yield of oil obtained and its quality mild conditions favouring the latter at the expense of the former. In some instances the oil may be recovered in two or more stages as for example with castor beans where a medicinal quality is first obtained by low temperature pressing followed by a firsts quality by hot pressing and seconds by solvent extraction. This however is an exception and requires a plant of special design. Where expellers are used in two stage processes the cake from a low pressure machine may be passed either to a high pressure expeller or to a solvent extractor.

Solvent Extraction

Many devices have been proposed for the production of vegetable oils by extraction with solvents by batch or continuous processes and a number of them are in current use. Most employ the counter current principle the seed being washed successively by an oil solvent mixture or miscella of progressively

decreasing strength so that the final wash is with pure solvent and the strong miscella is removed at the other end of the system where fresh seed is introduced. The oil is recovered from the miscella by distillation and the meal after steaming to remove solvent contains less than 1 per cent of oil. A number of solvents both inflammable and non inflammable are suitable for the process but the one most commonly used is a petroleum fraction boiling between 60° and 80°C rich in normal hexane. Solvent extraction is generally applied to seeds with a relatively low oil content that are easily flaked or to cakes produced by low pressure expelling.

Composition of Crude Oils

Vegetable oils in general consist of mixed triglycerides of the higher fatty acids and the identity and composition of the mixture of acids present together with their distribution amongst the glyceride molecules determines the nature and properties of the various individuals. Although the composition of any given type of oil is subject to variations which may be due to the climate prevailing where the seed was grown to differences in botanical species or adulteration due to careless harvesting the crude oils of commerce are remarkably constant in their properties. Identification or the detection of admixture can generally be made on the basis of the usual constants of oil analysis.

Apart from the glycerides forming their main constituents crude oils contain minor amounts of a number of impurities which include free fatty acids colouring matter phosphatides carbohydrates protein fragments sterols tocopherols hydrocarbons waxes flavours odours etc. in quantities depending upon their nature and method of production. The phosphatides and various resinous and mucilaginous materials of uncertain identity are precipitated as sludge when the oil is heated and are gradually deposited in the form of flocs when it is stored under moist conditions. In order to avoid this raw linseed and soya bean oils are sometimes subjected to a de gumming process in which the precipitation is accelerated by the addition of water. Although the non glyceride components are present in minor amounts and some have little or no effect upon the technical properties of the oil others act as antioxidants which serve the purpose of protecting it against deterioration and give rise to the induction period observed during the autoxidation of drying oils. These materials have been studied in some detail but their nature and mode of action are still imperfectly understood. It is believed that the principal agents are the tocopherols and that their action may be reinforced by phosphatides and other antioxidants of the phenolic type.

Refining

The purposes of oil refining are to remove those impurities the presence of which is objectionable in the particular application for which it is to be used. In the production of media for surface coatings the main object is to remove phosphatides and other break materials as well as waxes which may give rise to film defects and sometimes to reduce the colour without destroying the capacity for further bleaching on heating. Both acid and alkali treatments are practised but alkali refining is now by far the more important. It may be carried out either by batch or continuous processes and methods of refining in solution (miscella) have also been proposed. Many variations are employed to deal with oils of different kinds but the basic principle is to treat with a caustic soda solution of suitable strength in an amount slightly greater than would be required to neutralise the free fatty acids present and to wash out the resulting soap with water. The soapstock is treated with mineral acid to give a mixture of fatty acids and neutral oil known commercially as acid oil. The oil after neutralisation is dried under vacuum and bleached if necessary by heating with a small quantity of activated fuller's earth. It is then filtered and freed from wax by chilling to near the freezing point i.e. 40° 50° F and filtering off the deposit.

Refining with alkali removes phosphatides protein fragments carbohydrates resinous and mucilaginous materials and free fatty acids. The content of sterols tocopherols hydrocarbons etc. which make up the unsaponifiable portion of the crude oil are little affected.

Fatty Acids

The fatty acid mixtures obtained by the hydrolysis of glycerides occurring in natural fats are usually complex and contain a variety of both saturated and unsaturated individuals. Where one particular acid predominates it is often of unusual structure and is typical of the oil concerned as for example ricinoleic acid in castor oil elaeostearic acid in tung oil or licanic acid in oiticica oil. The identity of the vast majority of oils is not however determined by the presence of one typical acid but by the proportions in which a number of common acids are present and the manner in which they are distributed amongst the glyceride molecules.

Fatty acids with chain lengths of from six to twenty four carbon atoms have been isolated in appreciable quantities from natural glycerides and when it is considered that they may be saturated or contain up to six double bonds per molecule the possibilities for complexity are very great indeed. There are however a number of circumstances that reduce the possibilities to some extent. For example it is observed that almost without exception natural fatty acids have straight chains and contain an even number of carbon atoms. This is thought to be due to the biological process by which they are formed from carbohydrates. Unsaturated acids with less than sixteen carbon atoms are unimportant and but few of the large number of possible isomers actually exist in nature. Most of the polyunsaturated acids found in the drying oils have eighteen carbon atoms and those with more than four double bonds are encountered only in marine oils.

Saturated Acids

The saturated fatty acids have the general formula $C_nH_{2n}O_2$ and form a homologous series commencing with the lower members which are liquid at ordinary temperatures and progressing to solids with increasing melting points. Table 1 shows the acids occurring most commonly in natural glycerides together with some of their characteristics. The first three caproic caprylic and capric are never present in more than minor amounts and their principal source is in coconut and palm kernel oils. Lauric acid is the first member of the series to be widely distributed in nature and occurs in practically all of the seed fats of the laurel family from which it derives its name. Coconut and palm kernel oils are however the principal sources from which it is obtained commercially. Myristic acid is found in small quantities in most animal and vegetable fats and forms only a minor component of the oils used in surface coatings. Palmitic acid has been reported to be present in practically every animal and vegetable fat that has been examined but usually in minor quantities. It may however comprise as much as 10 per cent of the total fatty acids present in groundnut soya bean and maize oils 20 per cent in cottonseed and over 35 per cent in palm oil. Stearic acid is also of considerable importance although it is not so widely distributed as palmitic acid. It forms a major component of the saturated acids present in drying oils. The saturated acids with more than eighteen carbon atoms arachidic behenic and lignoceric have comparatively little importance occurring only in minor quantities.

Saturated fatty acids may be regarded as undesirable constituents of drying oils but owing to their distribution in the glycerides it is not an easy matter to remove them.

Monoethenoid Acids

It is widely believed that in the biosynthesis of vegetable fats the products are liquid at the prevailing temperature. If the component glycerides were derived only from saturated acids of the chain lengths normally encountered they would have high melting points and one of the ways of preventing this is by the introduction of unsaturation. In the study of natural fats it is found that unsaturated acids are invariably present and as a general rule the proportion found in a particular species is greater if the plant is cultivated in a cold climate than in a warm one.

The first series of unsaturated acids having one double bond is represented by the empirical formula $C_nH_{(2n-2)}O_2$ and the more important members are shown in Table 2. It will be seen that the series is by no means complete being not only confined to compounds with an even number of carbon atoms from ten to twenty six but very few of the large number of possible isomers have been identified. It has often been

stressed that the majority of monoethenoid fatty acids have the double bond between the ninth and tenth carbon atoms. Too much importance should not be attached to this rule which would be equally true if it were the convention to begin counting from the other end of the chain instead of from the carboxyl group. In other words the tendency appears to be for unsaturation to occur near the centre of the fatty acid molecules. Unsaturated acids are also subject to cis trans isomerisation as shown in Fig. 1 and much has been learnt about this since the development of infra red absorption analysis. With monoethenoid acids the cis form having the lower melting point is most commonly found in nature.

With the exception of crotonic acid (C4) which is present in croton oil no naturally occurring monoethenoid acid with a chain length below C10 is known. Although a number of acids with from ten to fourteen carbon atoms have been identified the first member of the series of any importance is palmitoleic acid which is found in appreciable quantities in marine oils and the fats of cold blooded animals generally. It also occurs in small quantities in vegetable oils from various sources sometimes sufficient to be detected by classical methods and sometimes in traces that become evident only in analysis by gas liquid chromatography. Of the sixteen possible isomers of cis octadecenoic acid only three have been characterised with certainty viz. oleic petroselinic and vaccenic acids of which oleic acid is by far the most important. It has been found in every plant and animal fat to the extent of at least 10 per cent and frequently more than 50 per cent of the total fatty acids. Other isomers are produced during the hydrogenation of fats containing polyunsaturated acids or may be made synthetically. Trans isomers are formed from oleic acid by elaidinisation in the presence of suitable reagents such as oxides of nitrogen sulphur selenium etc. and during fat hydrogenation. Apart from erucic acid which is an important constituent of rapeseed and a few other oils the higher members of the series are confined to marine oils.

Monoethenoid acids may be oxidised but are not thought to take part in reactions leading to film formation under the conditions generally employed. For example olive oil which has an iodine value of 85 and may contain over 80 per cent of oleic acid is almost completely lacking in drying properties or any tendency to become gummy when exposed in thin films.

Polyethenoid Acids

Although the introduction of a plurality of double bonds in the carbon chain increases the possibility of positional isomerism actually fewer isomeric polyethenoid than monoethenoid acids have been detected in natural fats. The principal members of the series are given in Table 3. The diethenoid linoleic acid is the most widely distributed in the plant kingdom and is characteristic of the semidrying oils of commerce including soya bean niger seed safflower sunflower tobaccoseed poppyseed etc. It also occurs in major quantities in liquid nondrying oils such as groundnut maize and cottonseed and is associated with more unsaturated acids in the conventional drying oils. It is believed to be essential to the maintenance of health and normal reproduction of animals at least some species of which are incapable of synthesising it and must obtain the requisite quantities by ingestion from other sources. Linolenic acid is not so widely distributed in nature as linoleic acid but is characteristic of linseed oil and a major constituent of other drying oils such as conophor perilla stillingia and hempseed. Owing to the presence of three double bonds it absorbs oxygen more rapidly and the presence of relatively small amounts greatly increases the drying potential of oils rich in linoleic acid. The conjugated isomer elaeostearic acid is not widely distributed but is of considerable importance owing to its occurrence as the characteristic acid of tung oil. The different arrangement of double bonds gives rise to marked differences in physical characteristics and chemical properties including refractive index absorption spectra addition of halogens mechanism of oxidation and especially in the rate of polymerisation. Natural or elaeostearic acid has a *cis transtrans* configuration but it readily changes to the high melting trans trans trans form. Attempts to produce it by isomerisation of linolenic acid appear to have given rise to a third form known as pseudo elaeostearic acid which differs from the natural material in many of its properties. The other polyethenoid

acids are of considerably less importance but are not without interest. The 2,3,4,5 decadienoic acid found by Hilditch in stillingia oil is believed to account for the fact that it dries more rapidly than would be expected from the iodine value. Parinaric acid is the only authentic acid containing four double bonds that has been isolated from seed fats and they are believed to occupy the conjugated position. Fatty acids with up to twenty six carbon atoms and six double bonds have been isolated from oils of marine origin. Two acids are also known which contain a double bond and a triple bond one of which occurs in ongokea oil.

Substituted Acids

In addition to the members of the simple homologous series of fatty acids mentioned above a number of substituted acids of more unusual structure occur which are often characteristic of the oils produced by plants of a particular species. Only those that are of interest in surface coatings will be considered here. Ricinoleic acid which resembles oleic acid in structure but has an hydroxyl group on the twelfth carbon atom is characteristic of castor oil and is responsible for its unusual and useful properties. The presence of the hydroxyl group enables it to take part in a number of chemical reactions including dehydration which gives rise to a mixture of conjugated and non conjugated isomers of linoleic acid. A less familiar hydroxy acid hydroxy elaeostearic or kamolenic acid has more recently been shown to be the major constituent of kamala oil. Licanic acid or 4 keto elaeostearic acid was first isolated from oiticica oil but is now known to occur in po yoa oil and in number of others. The naturally occurring acid is solid at room temperature melting at 74°-75°C and is readily converted into an isomeric form melting at 99.5°C. It resembles elaeostearic acid in many of its properties but the presence of the keto group provides additional reactivity.

Glyceride Structure and Film Formation

Fatty acids comprise between 94 and 96 per cent of the glycerides occurring in natural fats and therefore occupy a most important position in the chemistry of these compounds. As has already been indicated each fat contains a number of individuals and the analysis of natural fatty acid mixtures has been the subject of a vast amount of work for a great number of years. Fats containing only oleic and saturated acids were the first to yield results of a reasonable degree of accuracy the presence of polyunsaturated acids introducing a complication that was not easily resolved. The thiocyanogen method of Kaufmann followed by the ultra violet absorption technique first proposed by Mitchell have become valuable analytical tools and the introduction of gas liquid chromatography has recently made it possible to check the results obtained by these and other methods. The means are now at hand to analyse almost any natural fatty acid mixture but so wide is the field to be covered that accurate results have not yet been obtained with all known fats and published compositions should never be accepted without scrutinising the methods by which they were determined.

Fatty Acid Composition

Table 5 shows the fatty acid composition and other characteristics of a typical specimen of most of the natural oils that have been used to a greater or less extent in surface coatings. It should be borne in mind that the figures are subject to fluctuation but for purposes of clarity it is preferable to give a single set of figures all relating to the same sample rather than inserting the upper and lower limits. Following a procedure adopted elsewhere the oils have been classified into four sections 1st linoleic oils 2nd linolenic 3rd conjugated oils and 4th miscellaneous oils.

Linoleic Oils

The linoleic oils are derived from a variety of sources and form an important group certain members of which are produced in very large quantities for edible purposes. The linoleic content varies widely between the different individuals e.g. groundnut oil contains roughly 30 per cent maize 40 per cent cottonseed 45 per cent soya bean 50 per cent poppyseed and sunflower 65 per cent grapeseed and niger 70 per cent and safflower and tobaccoseed 75 per cent. Soya bean oil also contains 7-15 per cent of linolenic acid and

is sometimes classified with the linolenic oils although for technical purposes it is employed as a semi drying oil. Together with hempseed and rubberseed (20 per cent linolenic acid) and candlenut (30 per cent linolenic acid) it might be placed in an intermediate group.

The linoleic oils are sometimes up graded by a solvent segregation process using furfural or liquid propane and it has been claimed that the products resemble linseed oil in their drying properties. This is not correct the presence of the third double bond in linolenic acid conferring a considerable increase of reactivity in oxidation and polymerisation reactions. It is only when the acids are combined with a complex structure that is capable of film formation through cross linking as for example in alkyd resins that roughly comparable results may be obtained.

Although a number of oils in the linoleic group are used for technical purposes soya pean oil is the most important owing to the large quantities produced from seed grown in China Manchuria and the U.S.A. The other members that contain over 50 per cent of linoleic acid and are therefore most suitable for use in surface coatings are less readily available although there has recently been an increase in safflower cultivation. Soya bean oil is obtained from the seeds of a leguminous plant which contain rather less than 20 per cent of oil but give a meal of high protein content that is extensively used in animal feeding stuffs. The principal outlet for the oil is in edible products only a relatively small amount being used for technical purposes. The iodine value is generally within the range 125 140 and the variations are due mainly to the linolenic acid content most specimens containing about 50 per cent of linoleic acid. Other members that have been used to a minor extent in alkyd resins include tobaccoseed safflower niger groundnut cottonseed and maize oils. The fatty acid mixture obtained by the fractionation of tall oil has a composition very similar to that occurring in oils of the linoleic group and is sometimes used as an alternative in alkyds.

Linolenic Oils

A group that is comparatively small in numbers but of considerable importance technically is that of the linolenic oils. The only members to have been used outside the countries of origin are linseed perilla and stillingia oils. Others known to contain more than 45 per cent of linolenic acid include chia conophor and lallemantia and many more contain lesser quantities.

Linseed oil is obtained from the seeds of the flax plant extensively cultivated in many parts of the world including the America Russia India and the Far East. The principal exporting countries are Argentina Canada India and the U.S.A. The composition of the oil varies somewhat according to the country of origin and climate appears to exercise the greatest influence the highest iodine values being recorded with oils produced from seed grown under cold conditions. Although it is possible to obtain samples with values below 130 or above 200 the oil produced commercially is generally within the range 175 195. Painter have analysed a large number of oils and shown that the linolenic acid content varies from 20.5 per cent at iodine value 128 to 61.8 per cent at iodine value 203. Commercial samples generally contain between 48 and 57 per cent. Perilla and stillingia oils have been available for limited periods only and are acceptable replacements for linseed oil in surface coatings.

Conjugated Oils

The naturally occurring conjugated oils all contain major quantities of acids with three double bonds in the conjugated position such as elaeostearic acid or a substituted form like licanic acid. Conjugated isomers of linoleic acid exist only in modified oils and are produced by the dehydration of castor oil or by isomerisation. The principal sources of the natural conjugated oils are certain plants of the Rosaceae and Euphorbiaceae families and more particularly of the genera *Licania* *Parinarium* *Aleurites* *Garcia* and *Ricinodendron*. The only members to have been produced commercially are tung and oiticica oils.

Although highly unsaturated the natural conjugated oils cannot be used directly as media for surface coatings because they give frosted films on drying. Their structure gives rise to rapid polymerisation on

heating and the oils gel in a few minutes at 280°C. The principal application is in the manufacture of varnishes using either pure or reduced phenolic resins which are outstanding as regards water and chemical resistance. Tung oil is produced from nuts of two species of the genus *Aleurites* both of which are indigenous to China. *Aleurites Fordii* is generally preferred on account of the fact that it gives an oil with a higher elaeostearic content and greater reactivity than that produced from the *montana* species. Apart from China the principal sources of supply are the U.S.A. Argentina and Brazil. The montana oil comes from Nyasaland. Tung oil is free from phosphatides and is invariably used in the raw state refining with alkali being extremely difficult owing to the tendency to form emulsions. Oiticica oil is produced from the kernels obtained from the fruits of a slow growing tree found wild in Brazil. When freshly expressed it sets to a soft buttery mass that is somewhat sensitive to oxidation but it may be stabilised in the liquid condition by a mild heat treatment.

Miscellaneous Oils

Under this heading may be discussed a number of oils of widely different composition that have found some applications in surface coatings. Apart from the unsaturated oils of marine origin they may be classed as non drying oils suitable for the production of alkyds of the plasticising type. Castor oil is by far the most important member owing to its unusual versatility. Not only can it be used as such or in the fully hydrogenated form in non drying alkyds but it can be converted into a drying oil by dehydration and take part in a number of other reactions associated with free hydroxyl groups. The castor plant grows chiefly in India Manchuria Russia and Brazil and the seeds contain between 40 and 45 per cent of oil which is used entirely for medicinal and technical purposes. Certain marine oils obtained mainly from sardine menhaden whale herring and pilchard or fractions segregated from them by solvent extraction are also used as drying oils.

The whole oils contain a much wider range of glycerides than is normally encountered in vegetable fats including significant amounts of saturated glycerides that may be separated by a winterisation process. The highly unsaturated glycerides containing fatty acids with over twenty carbon atoms and four or more double bonds are also objectionable in surface coatings and segregation processes are generally aimed at producing a fraction of intermediate unsaturation.

Fatty Acid Distribution

The analysis of glycerides or the determination of the distribution of the individual fatty acids amongst the glyceride molecules is a matter of considerable difficulty and the results obtained to date are of doubtful accuracy. The methods used include fractional crystallisation chromatography and the Craig counter current distribution technique. As a result of his own extensive studies Hilditch formulated the principle of even distribution which states that the fatty acids are distributed evenly and widely amongst the glyceride molecules. This principle has been challenged by a number of workers and other types of distribution such as the random theory of Dutton and the restricted random theory of Kartha have been postulated. Evidence that conflicts with the random theory is provided by the fact that the properties of many oils are changed by interesterification which is known to give mixtures of the random type. It is also known that in certain fats like cocoabutter which contain a high proportion of glycerides with one oleic and two saturated groups the oleic acid invariably occupies the position. An attempt to resolve the anomalous situation created by these conflicting views has recently been made by Youngs.

The glyceride composition of drying oils is of particular importance because only polyunsaturated acids are capable of being linked together by oxidation or polymerisation and the observation that the acids separated from polymerised glycerides contain little polymeric material higher than dimers. Individual glyceride molecules may therefore be regarded as non functional or mono di or trifunctional according to the number of polyunsaturated radicals present. In a polymerisation reaction non functional glycerides are non reactive mono functional glycerides can act only as chain terminators di functional glycerides may

form long chains and tri functional glycerides can produce cross linked systems. In a mixture of the different types a solvent resistant coating can be obtained only if sufficient tri functional glycerides are present to introduce the requisite cross linking. In the absence of reliable analytical results no certain forecast can yet be made of the drying potential of an oil on the basis of the fatty acid composition alone. It should be noted however that a random distribution would give a greater amount of trifunctional glycerides than the other current theories of glyceride structure and the figures given by way of illustration in Table 6 can be regarded as showing the situation most favourable for film formation at any given polyunsaturated acid content. They were calculated using the equations for random distribution given by Feuge Kraemer and Bailey. All of the natural drying and semi drying oils have more than 50 per cent of polyunsaturated acids and it will be seen that this is near to the limit below which glycerides capable of cross linking do not occur.

Chemistry of Resin Formation and Its Properties

Introduction

Although synthetic resins have been used in surface coatings for half a century it was not until the 1930 s that scientific method was introduced into their study. The turning point can be identified with the publication in 1929 of papers by Staudinger Kienle and Carothers stating the fundamental concepts of polymer formation and polymer character from which modern polymer science has grown.

Fundamentals of Polymer Formation

Staudinger recognised polymers as very large molecules built up of repeating units derived from the starting materials or monomers. Thus the rubber molecule was seen to be composed of many isoprene units and they are now known to be joined together by a typical 1 4 addition of the conjugated system. It was realised that no special forces were involved in polymer formation and nothing beyond the ordinary operation of chemical valency and reactivity need be invoked to explain the existence of these molecules.

Functions or Reactive Groups

The reacting groups in the molecules are called functional groups or functions following Kienle and a compound is said to be mono di or tri functional depending on the presence of 1 2 or 3 such groups in the molecule. The term poly functional is used generally to describe molecules having more than one functional group so polyfunctional molecules are the fundamental building blocks from which polymers are made.

Familiar reactive groups or functions are

Consequently it can be seen that the following materials are bifunctional are tri and tetra functional respectively.

Bifunctional Reactants

It should be noted that the double bond and the epoxy group each yield two reactive points at which union to other molecules can occur

Each of these groups must therefore be regarded as two functions. Ethylene $\text{CH}_2=\text{CH}_2$ and ethylene oxide CH_2CH_2 each have a functionality of two whilst butadiene has a functionality of two or four according to whether one or both of its double bonds react under the experimental conditions.

Formation of Linear Polymers

Bifunctional reactants can only yield polymers in which the monomer units are joined in a straight chain the so called linear polymers. Thus

Cross linked Polymers

When a reactant of greater functionality than two is present branching and crosslinking can occur leading to three dimensional networks which can attain indefinitely great size and become immobile infusible and

insoluble. This condition is known as gelation. The transition from an open chain to a cross linked structure is fundamental to the curing of convertible coatings and thermosetting resins generally.

As an example we may consider the reaction of glycerol with phthalic acid or its anhydride. This is basically a simple esterification distinguished only in that reaction occurs at several points in each molecule thus representing the glycerol residue by G and the phthalic acid residue by P we can depict the following as typical parts of a glyceryl phthalate macromolecule

In such cases no regular structure can be assigned to the macromolecules for in accordance with Kienle's second postulate reaction between functions occurs in a random manner and a whole range of molecular sizes and isomeric structures is built up as reaction proceeds. Gelation in such systems will occur at an early stage of the reaction if a large proportion of the reacting molecules have high functionalities. On the other hand the presence of monofunctional reactants serves to limit the growth of the polymer molecules and retard gelation a principle which finds wide application in the manufacture of resins for surface coatings which are generally required to retain their solubility at least until some much later stage of their existence.

Classification of Polymers

Polymers may be classified in several ways to facilitate their study and the utility of the system adopted depends on a personal point of view. The terms rubber resin and plastic frequently used to distinguish polymeric materials are associated with certain physical characteristics but with the possible exception of the first have tended to lose through indiscriminate use any precise significance they may have had.

A traditional classification is that into thermosetting and thermoplastic or convertible and non convertible types according to the resin's ability to cure or dry to form insoluble or infusible cross linked products. This is a convenient division when considering surface coating materials. Purely utilitarian in origin it is now seen to be founded on the functionality concept. It should be realised however that whilst polymers which are classified as convertible will dry by chemical reaction in the air or cure when stoved other materials non convertible under these conditions can sometimes be made to cure in special circumstances. Thus polyvinyl chloride which is normally regarded as a thermoplastic can be cross linked by heating in the presence of polyamines.

Perhaps the most generally useful classification is based on the type of chemical reaction utilised in building up the backbone of the polymer molecule. It leads directly to a consideration of the types of linkages uniting the polymer segments and permits a number of practical generalisations concerning the chemical nature of polymers their mode of formation and the properties associated with given types.

Formation of Polymers

The two main divisions of polymer forming reactions are designated condensation polymerisation (or polycondensation) and addition polymerisation (or simply polymerisation). Condensation and addition reactions have exactly the same meaning in polymer science as in classical organic chemistry.

Condensation Reactions

Typical condensation reactions are the formation of an ester from an acid and an alcohol and of an amide from an acid and an amine. By definition a by product of low molecular weight is eliminated in these cases water.

Polycondensation

Application of such reactions to polyfunctional reactants already exemplified in aminocaproic acid glycerol and phthalic acid yields condensation polymers. The mechanism and kinetics are the same for the polycondensation reactions as for the simple condensations the only distinguishing feature chemically is the functionality. The reaction rate depends on temperature and on the concentration of reactants and products at any given stage in the reaction. The last is very important when as in the formation of

polyesters and polyamides the reaction is reversible for in accordance with the Law of Mass Action the forward reaction will only proceed to completion if the reverse reaction is prevented by separation of polycondensate from by product. This is usually accomplished by distilling off the byproduct leaving the polycondensate in the reaction vessel.

When as is usual the by product is water its removal can be facilitated by azeotropic distillation. The best known example of this is provided by the solvent process for making alkyds. Provided the raw materials be not too volatile efficiency of by product removal can be facilitated by applying vacuum to the reaction vessel as is done in the later stages of polyamide manufacture.

Some polycondensations such as the reactions between phenol or urea and formaldehyde are not reversible in the sense that the polymers are not broken down to the starting materials by hydrolysis. As will be seen however water and other by products are evolved in the later stages of the reaction and here also the application of vacuum assists in the attainment of high molecular weights.

Interfacial Polycondensation

Recent work in the laboratories of the du Pont company has revealed an interesting new technique known as interfacial polycondensation. Polyamides of very high molecular weight are formed rapidly at the interface between an aqueous solution of a diamine and a solution of a diacyl halide in a water immiscible solvent. The technique has been extended to the preparation of polyurethanes and materials difficult to prepare by conventional polycondensation methods for example polyphenyl esters and polysulphonamides.

Sequence of Reactions

In all polycondensation reactions the greater part of the starting materials react through one or more of their functions at an early stage to form products of low molecular weight. These then react with one another and with remaining monomers so that mean molecular weight increases as reaction proceeds the precise relationship between degree of reaction and molecular size depending on the mean functionality of the initial reactants.

Addition Polymerisation

The principal form of addition polymerisation is often referred to as vinyl or ethenoid polymerisation and comprises the union of unsaturated monomer molecules by the opening of and interaction between their double bonds. This is a chain reaction of either free radical or ionic mechanism. The former is the more important in the production of surface coating polymers and is similar kinetically to the formation of hydrogen chloride from gaseous hydrogen and chlorine.

Three reaction steps can be distinguished. First free radicals are generated by the thermal dissociation of an added substance known as an initiator such as benzoyl peroxide and these react with monomer molecules to form an active species which initiates the polymerisation reaction. Many unsaturated monomers have structures of the type $\text{CH}_2=\text{CH}$ i.e. they are monosubstituted ethylenes.

Writing the initiating free radical as R. the initiation reaction may then be expressed

The resulting active species is another free radical and this now reacts successively with further monomer molecules in the second step called propagation.

Many thousands of monomer molecules may be combined in this way before the third step termination destroys the active species by elimination of the free radical and the final fully grown polymer molecule results.

Termination may occur by combination or by disproportionation of two growing chains thus

Copolymer Formation

If a mixture of monomers is present they enter the growing chain in a more or less regular manner depending on their reactivities and the product is then known as a copolymer. Styrene and maleic anhydride for example exhibit a strong tendency to regular alternation thus

Rate of Polymerisation

These polymer forming reactions are exceedingly rapid but in the conversion of a batch of monomer to polymer they are only occurring in a very small fraction of the total molecules present at any one time. Thus although the time taken to form one polymer molecule of some thousands of monomer units may be only a few seconds the conversion of all the monomer present may take many hours. The overall polymerisation rate and the molecular weight of the polymer depend on the relative rates of the initiation propagation and termination steps and the relative concentrations of monomer and initiator. The most important feature to remember is that polymer of high molecular weight is present from the very commencement of the process. Molecular weight does not increase progressively with time as in a polycondensation reaction all that happens is the conversion of more monomer into polymer.

Addition Polymerisation in Practice

The practical methods of conducting these polymerisations include polymerisation in bulk in an aqueous suspension of droplets of monomer in solution and in emulsion. Polymers for coatings are usually made in solution or in emulsion. Emulsion polymers have very much higher molecular weights than polymers prepared in solution.

Chain Transfer Reactions

Two of the more recent developments in the chemistry of addition polymers have been the discovery and application of chain transfer and stereospecific polymerisation. The most interesting type of chain transfer occurs when a free radical on the end of a growing polymer chain withdraws a reactive atom from a dead polymer molecule thereby creating a growing centre on the latter. Branching can thus occur in for example polyvinyl acetate which would otherwise be a linear molecule. The phenomenon can moreover be deliberately applied to graft branches of one type on to a backbone of another. Thus methyl methacrylate polymerised in the presence of polystyrene yields a proportion of graft copolymer molecules such as

Materials of this sort may possess a balance of properties different from those of a simple copolymer and it is sometimes possible to prepare graft copolymers of which no conventional copolymer analogue exists. Commercial exploitation of these materials is however still in its infancy.

Stereospecific Polymerisation

In stereospecific polymerisation the reaction is induced by a complex initiator which unlike those of prior art exercises a directive influence on the way the monomer molecules enter the polymer chain. One result is an almost total absence of branching by chain transfer. The other only relevant when the repeat unit contains an asymmetric carbon atom is the introduction of successive segments in the same or a regularly alternating sense in space. If propylene is polymerised by conventional means the dextro and laevo configurations arising from the presence of an asymmetric carbon atom in each segment are disposed at random along the polymer chain. The polymer is said to be atactic. Stereospecific polymerisation however can yield either a syndiotactic polymer with regular alternation of dextro and laevo configurations or an isotactic form in which every segment has the same configuration.

Stereospecific polymers are harder more crystalline and less soluble than their atactic counterparts. They are finding application as structural materials and fibres but whether in view of their reduced solubility they will make an impact on surface coating formulation remains to be seen.

Polyaddition Reactions

Other addition reactions leading to polymer formation are known which do not depend on the foregoing mechanism. Examples are the polymerisation of ethylene oxide in the presence of a trace of water and the reaction between diisocyanates and dihydric alcohols.

These reactions are referred to as polyadditions to distinguish them from addition polymerisations of the ethenoid type. They differ from polycondensations in being unaccompanied by the liberation of by products

but in most other respects they are more akin to polycondensation than to ethenoid polymerisation.

Types of Polymers

Polyesters

Of the condensation polymers used in surface coatings pride of place is taken by the alkyds. These are polyesters the molecules of which contain fatty acid side chains which have the effect of limiting molecular weight imparting solubility in hydrocarbons and otherwise modifying the physical and chemical properties of the material. The traditional polyester modified in this way is glycerol phthalate and a typical structure would be

where L = fatty acid residue.

Formulation of Alkyds

Such materials can be made by simple interaction of a mixture of glycerol phthalic anhydride and fatty acids. Alternatively a fatty oil may be used as starting material when it becomes necessary first to convert this into a monoglyceride by alcoholysis with glycerol before adding phthalic anhydride and esterifying. Formulating variables are manifold. The proportion of fatty acid to phthalic may be varied between wide limits to yield products lying almost anywhere between oil and unmodified glycerol phthalate in solubility and other physical characteristics. The fatty acids or oil may be fully saturated or predominately unsaturated the former yielding plasticising alkyds of maximum colour and gloss retention and the latter convertible coatings which by virtue of their high functionality in terms of unsaturated centres cross link and dry rapidly by oxidation to yield tough durable films. Glycerol may be replaced by pentaerythritol or other polyols. Pentaerythritol is particularly valuable as a component of drying alkyds at the longer oil lengths because the increased molecular complexity resulting from its use leads to increased speed of drying and film durability. Phthalic anhydride can be replaced by other polybasic acids or anhydrides. Adipic acid yields more flexible products whilst isophthalic acid yields somewhat harder materials halogenated acids may be introduced to render the resins more or less fire resistant.

Structures Analogous to Alkyds

It can easily be seen that the older oleoresinous varnishes fit into the same pattern of structure and behaviour as the alkyds. Linseed oil molecules the glycerol esters of the unsaturated acids linoleic and linolenic on heating form stand oils due to the formation of dimeric and trimeric fatty acids by interaction of double bonds.

Here we have an alkyd in which phthalic acid is replaced by more flexible aliphatic structures and some of the unsaturation of the fatty acids is lost. By comparison with a phthalic alkyd of similar degree of polymerisation therefore the product dries more slowly to yield softer films.

In the same way it will be appreciated that many hard resins used in varnish manufacture react with oils by a process of ester interchange to yield structures similar in pattern to the alkyds. Copal resin for example contains polybasic resin acids whilst the rosin maleic adducts are semi synthetic materials produced by Diels Alder addition of maleic anhydride to the conjugated alicyclic acids present in rosin and hence contain tricarboxylic molecules.

Saturated and Unsaturated Polyesters

In the surface coating industry the name polyester is rarely applied to oil modified alkyds and is reserved for types containing no oil or fatty acid modification. These polyesters are of two kinds. The best known are the unsaturated polyesters commonly derived from diols such as propylene glycol or diethylene glycol and unsaturated dicarboxylic acids such as maleic and fumaric. In some types unsaturation is introduced in other ways such as by the incorporation of glycerol monoallyl ether. These polyesters are essentially linear in structure and in use are mixed with an unsaturated monomer commonly styrene which under the influence of a peroxide initiator copolymerises with the unsaturated centres thereby cross linking the

system to a hard glossy film.

The degree of cross linking is controlled by using a proportion of phthalic or other non polymerisable acid in the polyester.

The other type the saturated polyester is derived from saturated or aromatic dicarboxylic acids and mixtures of polyhydric alcohols having an average hydroxyl functionality greater than 2. These polyesters are produced with free hydroxyl groups and are subsequently reacted with polyisocyanates to effect cross linking through urethane groups. For use in coatings it is important to have polyesters substantially free from acidity because carboxyl groups liberate CO₂ on reaction with isocyanates and so cause foaming.

Polyamides

The best known polyamides are the nylons derived from aminocaproic acid or from hexamethylene diamine and adipic or sebacic acid. These are high melting materials of low solubility and their main use as surface coatings is in wire enamels. Many attempts have been made to prepare more soluble types but the major success in this direction was only achieved in 1944 when it was shown that polymerised fatty acids containing predominantly dilinoleic acid could be produced economically and converted into polyamides.

Two classes of such polyamides have been developed. The first is a more or less linear type derived from a simple diamine such as ethylenediamine. These resins are essentially non convertible. The other type is derived from polyamines such as diethylene triamine the molecules are branched and are deliberately made to contain free amino groups. These find their major outlet as curing agents for epoxy resins.

An important recent development has been the incorporation of the ethylenediamine dilinoleic acid type into alkyd resins. When heated together ester amide and other interchange reactions occur leading to a complex resin which yields highly thixotropic solutions in hydrocarbons. Such materials form the basis of jelly or dripless paints and are finding increasing use as formulating tools to control paint structure.

It is easily seen that phenol meta cresol and other materials of functionality greater than 2 can yield cross linked products by these means.

Under acid conditions phenol yields only a bifunctional derivative and the inter unit linkages in this case are essentially methylene groups.

Unless subjected to high temperatures or treated with alkali and formaldehyde these so called novolaks are non convertible.

A wide variety of phenolic resins can be made by varying the nature of the phenol the ratio of phenol to formaldehyde and the conditions of preparation. The use of phenols containing higher alkyl groups promotes solubility in oils and hydrocarbons whilst substitution in the *para* position by a tertiary carbon atom prevents the formation of quinonoid structures on oxidation and renders the resins substantially non yellowing. It may also be noted that the methylol compounds can be reacted with a variety of other materials. An important example is the reaction of methylol phenols with rosin to yield reduced phenolic resins.

Cashew Nut Shell Liquid Resins. A novel resin in the phenolic series is that derived from cashew nut shell oil. This oil obtained from the shell of the cashew nut on refining and steam distillation contains essentially a mixture of substituted mono and dihydric phenols.

The substituent hydrocarbon radical is unsaturated.

The mixture of phenols is capable of polymerising by a variety of routes either by condensation as a phenol with formaldehyde or furfuraldehyde or by acid catalysed polymerisation of the unsaturated residue.

The main use of this type of resin is in the insulating field as the fully cured resin has good flexibility. It is therefore used as a wire enamel and also for laminated board which is later punched or stamped.

Processing of Oil and Resin

The Processing of most synthetic resins stand oils and similar products is carried out under batch working

conditions and the major proportion of existing reaction units are designed for this purpose. The comments and recommendations dealt with in this section apply to this class of equipment generally.

Some work has been done on the design of continuously operating units but apart from the dehydration of some formaldehyde types mainly on large scale continuous production units are generally only suitable for one particular product and as most manufacturers require a wide range the more flexible batch unit has been and is preferred.

General Requirements for Processing Equipment

Although the basic requirements to be achieved in the design of individual process units vary between different classes of resins and stand oils etc. there are certain main factors common to nearly all. The materials being reacted must be combined in a suitable vessel with agitation if necessary heated to a predetermined temperature schedule until the required reaction is completed and then cooled and subjected to after treatment. Also it is usually necessary to supply some sort of vapour condensation system for refluxing condensate or separating part of the condensate and refluxing the residue or removal of fumes and vapour entirely. All these stages must be under control and clearly indicated both for quality of product and safety conditions.

The basic designs for the three main types of process units are shown in the simplified flow diagrams. Fig. 1 shows a typical stand oil unit Fig. 2 typical P.F. or U.F. units and Fig. 3 typical alkyd (polyester) units. There are of course many modifications which can be made and these are discussed later.

Materials of Construction

The choice of material for the construction of the equipment is of prime importance and both economic and product quality factors must be considered. It is generally accepted that an installation should be dealt with on the basis of at least a ten year life and a correctly designed unit which has facilities provided to suit possible modifications can be economically used beyond this life span.

The constructional materials most commonly used in Britain at the present time are listed in Table I although other materials may be employed in specific cases.

Mild steel has not been generally classified as although many installations have been made in this material its life is often comparatively short and many products are precluded. It is however extensively used in those positions in plant where contact with the product is avoided.

Design of Reaction Kettles

The Kettle Body

The first consideration should be given to the shape of the reaction vessel for a particular process and apart from the limitations which may be imposed by the siting of the unit with regard to height etc. the ratios of free surface area and heating surface area to volume and to each other must be realistic. Also to a less extent the use of standard sheet sizes of material is preferred often giving increased capacity at little or no extra cost.

In the case of the manufacture of stand oils dehydrated castor oils and similar products convenient ratios of depth of charge to diameter of vessel are approximately 1.1 : 1 for standard methods and 1.5 : 1 for the Sommer and similar systems. For alkyd or polyester resin types a convenient ratio is approximately 1 : 1 and for most formaldehyde types approximately 1 : 1.25. These are for medium sizes of equipment and typical dimensions are given in Table 2 covering a range of sizes.

The thickness of the vessel walls and dishings can normally be calculated using the standard formulae given in B.S. 1500 and specifications for test pressures of finished vessels should be at least twice the greatest pressure that is to be encountered. It is also advisable to include a safety allowance on the thickness of any reaction vessel to cater for any friction erosion or particular condition which may arise. In most equipment this allowance would be satisfied by approximately 10 per cent of thickness and usually

only implies rounding off the thickness calculated to the next standard sheet thickness.

For example the requirements of a reaction vessel for the production of alkyd resins by the solvent or azeotropic method and having a working capacity of 500 gallons can be calculated. The gross capacity allowing 50 per cent freeboard would be 750 gallons and dimensions of 4 ft 6 in. dia. and 7 ft 3 in. deep on the straight side are convenient as dishings are standard for top and bottom. The material chosen is stainless steel of F.M.B. grade and full vacuum is to be catered for as well as 15 lb/sq. in. pressure.

Branches and Connections

The necessary fittings and branches for the reaction kettle will depend upon its use but it is as well to remember two main points. Firstly when a vessel is being fabricated it is not expensive to have extra branches or bosses provided and blanked off but additions can only be made later at considerably enhanced cost. Secondly an excessive number of connections on a small unit can only lead to difficulties in manufacture and operation thus multi purpose fittings should be used. A good example of a kettle top cover is shown in Fig. 4 all the fittings are accessible and sufficient space is allowed to permit a neat layout of incoming connections to be made. Table 3 gives recommended numbers of branches etc. which can be achieved without difficulty.

Types of Agitators

The combination anchor paddle and foam breaker unit is very commonly used and is particularly useful where vessels with heating and cooling jackets induction heating or external electric jackets are employed. It is suitable for mixing light solids into liquids and gives a gentle agitation to the mass of the charge with emphasis on maintaining a steady movement across the sides and bottom of the vessel. It is usually employed at speeds ranging between 25 and 60 r.p.m. based on a nominal peripheral speed of 300/700 ft/min. and not a standard rate of revolutions.

The turbo type agitator which gives a centrifugal pumping action is more effective for mixing finely divided or flake type solids into liquids but does not give the movement over the outside walls and the bottom of the vessel achieved with the anchor type. It is however of considerable assistance where immersion heaters are employed such as electric elements combustion tubes or flue gas induction tube stacks. The speeds are 80 200 r.p.m. again based on peripheral speed considerations.

More recently the marine type propeller has been employed and for the best effect these are arranged to force the liquid down into a cruciform baffle formed on the bottom of the vessel. These have great advantages in that the volume of liquid moved is greatly enhanced without increase of motive power and also that agitation is achieved by turning the charge over without the normal stirring action the flow pattern being shown in Fig. 5. This type of stirrer is particularly suitable where solids are to be melted as adequate clearances are available and the design lends itself to a robust unit which does not clog. Speeds may vary between 90 and 300 r.p.m. depending upon viscosities etc. and are related to quantities to be moved or more correctly to pumping speeds.

Sealing

Where the shaft of the stirrer enters the kettle it is necessary to provide a suitable gland which must be capable of being repacked quickly and efficiently and lubricated continuously and must be designed to suit the particular conditions. It is as well to be generous in the dimensions of the gland at the expense of some extra power losses in the drive as this will be amply repaid by the added security given. Glands and packings can vary widely but a simple and effective type is shown in Fig. 6.

In the case of small kettles it is often possible to rely on the bearings provided in the reduction gearbox unit with the steadying effect of the gland section but for large vessels it is often preferable to employ a steady bearing at the bottom. This should be supported by a straddle across the outlet and generally the most satisfactory bearing consists of a replaceable section on the end of the stirrer shaft rotating in a renewable

split bush in the bearing housing. Dissimilar materials should be used and a fair clearance allowed 0.020/0.030 in. (Fig. 7).

Drive Units

The selection of suitable drive units for stirring gear is very much a question of preference of individual users and either turret types or pulley drives are employed. The turret type is normally slightly the less expensive in first cost and consists of a reduction gearbox mounted on a support stool and supporting the drive motor.

It is economical in space but is not convenient where variable speed is a requirement or when maintenance of the gearbox is necessary.

If the pulley and belt drive system is employed then a simple and robust system of speed control can be achieved by the use of expanding pulleys. Many other methods of speed control can be used and information is freely available.

The types of drive motors employed may vary but the totally enclosed and fan cooled units are most often employed and these should be specified for high starting torque. When stirrers are first started there may be residues from preceding batches in bearings and glands which will cause extra load and thus if a 170 or 200 per cent starting torque is specified the extra torque available will normally overcome the drag. This also applies to pumps dealing with viscous or sticky materials.

Fume Disposal and Scrubbing

For some types of stand oil and synthetic resin production units vapours evolved during the process can be regarded as waste products and as such the only problem is the disposal of these fumes or vapours.

Unfortunately they are often objectionable either in odour or because they have unpleasant toxic or irritant effects. Normally they must be disposed of without allowing the ingress of free air and several methods of achieving this are possible.

Disposal Systems for General Use

The simplest system of fume disposal where the fumes are readily soluble in water is the water sealed type stack pipe. This is commonly fabricated in cast iron or mild steel and as its construction is cheap it is common to allow fairly large diameters 8 in. being considered a convenient diameter for a reaction kettle of capacity 2 tons.

An alternative scrubbing system which can be usefully employed in disposing of fumes which are not so readily soluble is shown in Fig. 8. In this type of scrubber the fumes are passed through a constant mist of fine droplets of liquid which is held in the base of the scrubbing unit. Additions may be made to the liquid in use to counter acidity or particular components of the fume and a further advantage is that the pressure drop through the system is very small. Depending upon the fume conditions to be met the complete unit can be fabricated in stainless steel which is expensive or alternatively in mild steel and galvanised or metal sprayed internally to minimize corrosion. A mild steel unit can have a good life as the surfaces are continuously washed.

Water Scrubbing of Anhydride Vapours

In the manufacture of alkyd resins by the fusion process a quantity of the particular anhydride being employed will be vaporised and will pass from the reaction kettle with other unwanted materials the fumes being very unpleasant. Some designs have been made of dry condensers to recover the anhydride sublimed for re use but in general it is preferable to use a water scrubbing system for their removal.

Design Considerations

This type of scrubbing unit is very effective but the design and construction for a particular capacity is important for if the unit is too large the water consumption is uneconomic and if too small the pressure loss is excessive besides not giving complete condensation.

The vapour duct should be constructed in stainless steel and should be kept clear of obstructions. It should also be provided with some form of heating to maintain it at a controlled temperature between 140°C and 160°C depending upon the particular conditions which can only be decided by trial in operation. Typical methods of heating are by use of low voltage transformers Pyrotenax heating cable loops steam jacketing or glass woven electric heating tapes. Pyrotenax cable is most convenient as it can easily be rendered flameproof in dual condensing system equipments and also its outer sheath can be effectively earthed for safety.

The sprays used are normally of the double ended type constructed from stainless steel and the sizes of the jets should be such that the spray just reaches the wall of the tower this giving effectively several curtains of water for the fumes to pass through. This also washes the walls of the tower which can be fabricated in mild steel and still have a good life.

Sludge Handling Equipment

The sludge receiver is normally constructed in mild steel and the most important point is that its capacity should be adequate for the quantity of water used the recommended quantities being 300 400 g.p.h. for a typical reaction kettle of 2 tons working capacity.

The sludge pump rating is normally adjusted to the full flow of water from the spray jets and to eliminate any possibility of flooding if the sludge pump should fail it is advisable to fit a level control in the sludge receiver to cut off the water delivery to the jets automatically. The pump is normally constructed in cast iron and gunmetal and must be capable of working against vacuum where the production schedule requires this.

It is not advisable to use isolating valves in fume ducts where this type of process is being carried on as it is almost impossible to adjust temperatures correctly and cleaning operations will be a constant necessity. A simple blocking plate assembly is often used and offers a clean arrangement.

Packed Scrubbers

Alternative scrubbing units can be constructed employing packings such as coke or carbon lightly irrigated with water. These are very effective but tend to clog quickly and are expensive to operate. They are often used however where the simple scrubbers described above do not completely condense or absorb the fumes and where conditions by local authorities etc. render it essential.

Condensing and Refluxing

The correct design of the condensing equipment is one of the most important aspects of synthetic resin process plant and great care must be taken that all the main considerations as below are fully taken into account.

For synthetic resins and allied products it is normally an essential function of maintenance that the condenser must be regularly cleaned. For this reason the standard condenser used is of the tube in shell type with the vapours passing through the tubes and deviations from this standard are rare.

Condensers for P.F. U.F. and M.F. Resins

During the processing of the formaldehyde types of resins the condenser has two main functions first refluxing during the initial stages when it assists in the control of the exothermic reaction which depending upon the mix can be extremely violent and second during the final stages when the excess water is being stripped off. The first duty is normally the greater and the design is based on this premise assuming a nominal rate of 20 lb/min condensate per ton of charge for medium sized batches.

During the exothermic reaction the condensate can be returned to the charge at a relatively high temperature as the latent heat absorbed by the evolution of vapour is the major factor in heat release but when stripping off the water at the end of the run the condensate must be sufficiently cooled to remain liquid under vacuum conditions. To this end it is essential that the entry of the vapour and outlet for the

condensate are at opposite ends of the condensing unit and also that sufficient length of path is available to permit adequate heat transfer to be effected.

Design and Layout of Tubes

Precise calculation of surface areas and cross sectional areas are extremely difficult as the factors to be allowed for dirt coefficients (fouling factors) and similar unknown quantities vary widely between different formulations and also at different stages in the process but convenient ratios between diameter and length of individual tubes vary from 1/80 to 1/120. These ratios must be used with discretion as under normal circumstances the minimum convenient bore is 3/4 in. and the working space available must also be taken into consideration.

A typical condenser layout is shown in Fig. 2 and alternative arrangements are noted for the tubes and to suit differing site conditions. Average condensing surface areas for standard formulations are given in Table 4.

During the main period of exothermic reaction refluxing of the condensate occurs the condensate being returned to the reaction kettle through a three way cock and subsequently when dehydration of the product is required the position of the three way cock is reversed to permit the draining of the condensate to waste. It is essential that the reflux lines should be of ample size for their duty and in order to minimize any possibility of blockages etc. slow bends should be employed. If a sight glass is fitted in the main reflux return feed the operator is able to detect quickly any unusual occurrence and also this can to some extent indicate the state of the process.

Waste Receiver

The waste or dump receiver must be of a suitable size for the particular batch and formulation and the normal system is to allow for the receiver to be two thirds full after dehydration is complete. Plate type sight glasses can be employed to check the final quantities involved.

When designing the receiver and condenser it should be noted that they must be suitable for both vacuum and pressure conditions although normally if the vessels are designed to suit vacuum it will be found that this represents the more arduous duty.

Inorganic Pigments

Introduction

The Conversion of the Rocket type of locomotive into the present day Royal Scot is an object lesson in evolution. Step by step some features have been modified and adapted others have been discarded. Some entirely new characteristics have appeared while certain basic structures have been maintained relatively unchanged throughout.

Although knowledge of this history is perhaps not vital to the users of such transport it certainly helps to explain and understand the particular pattern which has evolved and it demonstrates the extreme changes which may occur by small adaptations.

The inorganic pigments used for surface coatings have in the same way slowly evolved over a series of years by small changes in characteristics until ultimately extreme changes in properties have occurred although the basic structures have been maintained unchanged.

Many inorganic pigments have been evolved from intractable parent material over a period of fifty to a hundred years by gradual modification.

The users of transport have the change in name from the Rocket type of engine to the Royal Scot locomotive to indicate changes of characteristics and progress in design but often confusion is caused by using the same pigment name over a period of years without reference to other changes that have taken place.

For this reason a short evolutionary history is given of all the important pigments described to enable a comparison to be made of both the uses and properties of pigments given the same name at different periods of their history.

Origins of Pigments

Comparison of Natural and Synthetic Pigments

Several of the parent bodies of the inorganic pigments are found in naturally occurring deposits in the earth's crust. The corresponding pigmentary materials are often made synthetically. In general the only characteristic in common between the natural and the synthetic pigments is the chemical compound upon which the pigments are based otherwise their characteristics are quite different and the reason is not far to seek.

The naturally occurring materials are usually stable corrosion products which occur in a macrocrystalline form often associated with silica. In order to be used as a pigment the ore found in the earth's crust is mined crushed washed and classified into particle sizes of different ranges. During the crushing process the crystalline material is broken into fragments the crystals cleaving by way of the cleavage plane. In the case of the disorientated material crushing and grinding breaks the material into fragments and the distribution of the size range in both cases is solely determined by chance. The shape of the particle is also determined by chance even when a crystalline ore fractures mainly along a plane of cleavage.

A synthetically prepared pigment on the other hand can be designed to have the most suitable crystal lattice crystal habit and to a considerable extent particle size and particle size range and to maintain its chemical constitution within any desired limits.

If these two types of material are used as pigments for surface coatings the differences between the natural and the synthetic pigments are greater than the similarities and the natural and synthetic pigments used under such circumstances are distinctly different pigments.

Problems in Producing Natural Pigments

The natural pigments create one problem of which there is no simple solution. After crushing washing classification and drying a very small quantity of oversized particles are entrained in the pigment particle size range. The removal of these few boulders from the main bulk of pigment can be achieved by further grinding which widens the range of particle sizes introducing other undesirable properties. Reclassification will remove these boulders but only by processes giving uneconomical yields.

The presence of even small quantities of oversize pigment particles reduces considerably the output of pigmented pastes and a satisfactory method of removing these large particles has not yet been devised. For this reason an account is given of the basic chemical engineering process used in pigment manufacture.

Pigment Classification

Since in the same way the physical properties of the inorganic pigments depend upon a series of physical characteristics which can be measured no attempt has been made to give a certain pigment name specific surface coating properties but to outline the physical basis upon which such properties depend and to consider each pigment modification as an entirely different pigment belonging to a specific class.

In the beginning of the search for suitable pigments for the surface coating industry any coloured material from whatever origin was considered and tried. This has resulted in a very large number of materials called Inorganic Pigments and a list of such materials is an extremely long one. As the basic physical use of such materials has become known so has the number of pigments in use been reduced and this trend will continue with the search for new pigments directed along specific avenues defined by physical properties.

Pigmentary Properties

An inorganic pigment is a finely divided inorganic substance usually a stable solid which is added to the vehicle to produce a stable surface coating.

These properties are related to particle size and particle size distribution particle shape colour and refractive index at all wavelengths. These four physical properties which are discussed in turn below can be measured and controlled and used to give suitable properties for the pigmented system.

Particle Size and Particle Size Distribution

The particle size and refractive index of an inorganic pigment closely determine the scattering coefficient of the pigment. The refractive index will be discussed later and is of greater importance than particle size but since for any one material the refractive index is fixed and particle size and particle size distribution can be controlled in manufacture the influence of this latter factor will be determined.

The high brightness of a white surface coating material is obtained by having a large number of pigment vehicle interfaces each of which returns a quantity of the light towards the surface of the paint. It can be shown for any one particle that if d is the diameter and the wavelength then as d diminishes the light reflected increases to a maximum and then decreases. It then increases to another maximum before decreasing finally into the colloidal range.

In practice we never achieve a uniform particle size. Instead a white pigment is a mixture of particle sizes grouped around the size of greatest frequency. Thus the wave point of reflected light is the combined point from the various particle sizes. Nevertheless it is possible to define the range of size most desirable. They should be not smaller in diameter than the short wavelength (blue end of the visible spectrum) and not larger than the long wavelength (red end). Unfortunately only in certain cases has sufficient data been collected showing the relation between particle size particle size distribution and opacity but the basic physical quantitative conditions are now known.

Particle Shape

Practically all synthetic inorganic pigments are crystalline showing a well defined crystal lattice but the manner in which the basic unit lattices are built into a crystal may differ during crystal formation. Very small traces of impurities may cause changes in crystal habit without change in crystal lattice. Such changes may be superficially considerable a cubic habit may change into an acicular one or be a partly disorientated (spheroidal) one which is often unstable reverting to a more stable crystal form after ageing.

Influence on Pigment Properties

The geometry of the shape of a particle is of importance for two reasons. The surface area of any shape approaching that of a sphere is a maximum the edges of an acicular shape often offer areas of high surface activity and by their alignment in the surface relieve and reduce surface strain. For example the weathered surface of an acicular zinc oxide surface shows microcracking whilst under the same conditions the other form of zinc oxide shows macrocracking.

Since several pigments show more than one form of crystal habit and more than one form of crystal lattice the physical form and properties of certain inorganic compounds can be widely different. Iron oxide has a minimum of three crystal lattices and three crystal habits offering the possibilities of nine different physical forms.

The influence of the different physical forms upon the properties of the surface coating material although not known quantitatively is often considerable changing both flow properties and colour of the product. Such changes will be considered under the appropriate pigment name.

Colour

The colour of a pigment is an important property indeed certain pigments are selected for that purpose alone and often a certain type is referred to by a colour name e.g. yellow iron oxide since iron oxides have a wide range of colours. It is not possible to record a colour by words alone and the only way is to plot

the spectrophotometric curve of the colour over the visual spectrum under standardised conditions. The spectrophotometric curve is the record of the reflection of light plotted wavelength by wavelength continuously over the visual spectrum.

If the method of presenting the coloured material to the light source is standardised then the spectrophotometric curve will uniquely define the colour. Typical curves are given as representing typical white pigments (Fig. 1).

Refractive Index

In section 1 the importance of the refractive index has already been stressed. Probably due to the fact that the refractive index of a particular pigment cannot be changed the subject has received little attention from the systematic workers.

Indications of Opacity

Little data is available of the refractive index of any pigment over a wide range of wavelengths so it is not possible to use this data for purposes of calculation but isolated measurements are readily available and are often used as a guide for opacity. Since the measurements are usually made at a wavelength in the yellow region of the spectrum the measurements give some indication of opacity but for a complete understanding the change in the refractive index over the whole range of the visible spectrum must be known.

The refractive index of the pigment in relation to that of the medium determines the opacity of the surface coating layer. The smaller the change of refractive index at an interface the greater the intensity of light transmitted.

Influence of Wavelength

Although little systematic work has been done upon change in refractive index with wavelength it is known that the index varies near an absorption band falling rapidly on the short wavelength side and rising rapidly on the long wavelength side. The blue and green hue pigments having absorption bands in the long wave region possess relatively low refractive indices for the effective light they reflect. Iron blue has a R.I. of 1.56 for the blue end of the spectrum and since the medium used has a R.I. of 1.5 this pigment will be relatively transparent in such a medium. The iron oxides reflect in the red and yellow region and absorb in the green and blue region. The R.I. of iron oxide in the wavelength region of high reflection has a R.I. of 2.8 3.1 and such a pigment will be highly opaque in a medium of R.I. 1.5. As a general rule the blue and green hue pigments have a low R.I. and the yellow and red hue pigments a high R.I. for the effective light they reflect.

Control of Opacity

It is desirable to have control over the opacity (and transparency) of pigments over the whole hue range. This is usually achieved by adding a non selective reflecting pigment of high R.I. to the blue and green pigments to increase opacity and decreasing particle size in the yellow and red pigments to increase transparency. Examples of this are the addition of titanium dioxide to iron blue to increase opacity and decrease of the particle size of the iron oxides to decrease opacity.

In the past the desire to have available pigments of varying hues and opacity has led to an extensive search for inorganic pigments of a wide range of hues and with varying degrees of opacity. With an understanding of the principles of the optical properties given above it is now known that the desired hue and degree of opacity can be achieved by mixing relatively few pigments. The ultimate effect will be to concentrate development upon these few pigments and only search for new products along well defined avenues.

Following a brief outline of unit processes used in pigment manufacture the remainder of this chapter will be devoted to an account of the important classes of inorganic pigments.

Chemical Engineering Processes of Manufacture

The four main unit processes used for the preparation of pigments are discussed in the following.

Precipitation

Such processes presuppose the formation of the pigment in the presence of electrolytes. By choice of radicals or addition of electrolytes and conditions of concentration of soluble compounds and temperature the crystal form habit and size can be controlled. If in the first precipitation an intermediate compound is produced then similar conditions apply and control of both form and size of the intermediate can be obtained.

Vapour Phase Oxidation

Many elementary metals melt at low temperature and may be oxidized to a controlled degree which is dependent upon the injection of a stream of metal vapour into a stream of air or oxygen.

If the oxygen is in excess then oxidation is complete and by varying the concentration of the element vapour crystal habit can be changed from growth under starvation conditions (resulting usually in acicular habit) to growth under conditions of excess metallic oxide (often producing a disorientated mass which after ageing gives the most stable crystalline form). It is possible then by changing the metallic vapour/oxygen ratio to change the crystal habit from one extreme form to another often without change of crystal lattice. The consequent changes in physical properties are also wide since many such properties are dependent upon crystal habit and particle size.

Heterogeneous Surface Reaction (Corrodibility and Corrosion)

This is the historically basic process for the preparation of all pigments. Naturally occurring pigments are all the ultimate corrosion products naturally produced by the exposure of elements to natural favourable conditions. Although chemically they may appear to be complex they are in all cases the most permanent compounds which can exist under such an environment. They are therefore the most permanent of pigmentary materials showing stable crystal lattice and crystal form.

The processes of natural exposure are often reproduced artificially in order to produce suitable pigments. Sheets of metal are exposed to the natural components of our climate water vapour and carbon dioxide (sometimes reinforced by additions from other sources) and the corrosion processes allowed to proceed until a condition of equilibrium is established thus producing under the conditions employed the most stable compound. The process is allowed to proceed until corrosion is complete and no quantity of unchanged metal remains. Chemically the products are nearly always coordinate compounds of the metal i.e. a molecular structure with a central metal atom surrounded by other groupings usually carbonate and hydroxyl coordinately linked. Rarely are other elements involved.

Solid Phase at Elevated Temperature

The reactions that take place at the interface of solid materials are often used in preparing inorganic pigmentary materials. Such reactions depend upon surface area temperature and so are often very slow demanding many hours at high temperature for completion.

The products are in all cases complex in structure and usually based upon a skeleton of silica. They are often very stable to all other physical changes.

The unit processes used for filtering washing drying disintegration and size classification are those used normally for such purposes.

Organic Pigments

Surface coatings were originally used to impart protection to the objects on which they were applied. The inclusion of coloured pigments gave decorative effects also but this was of secondary importance. Over a period of time the emphasis has changed so that the decorative effect obtained by the application of a

surface coating is of equal importance and in some cases of greater importance than the protective action. In consequence demand has changed from the dull functional shades obtainable with inorganic pigments to the brighter more varied hues only provided by the use of organic types and particularly in the post war period consumers have been encouraged to expect surface coatings to provide a complete range of hues comparable to the gamut obtainable on textile materials for a long time.

This change can be seen in many aspects of colour usage in the field of house paints the once popular full shade greens browns and creams have been replaced by brighter more varied pastel shades accompanied by a range of strong shades of clear pure tone. A comparison of British Standard 381C (1948) shades with B.S. 2660 (1955) or the House and Garden range of colours will illustrate this point. A second example appears in car finishes where the once predominant black together with a few strong shades have been replaced by a wide variety of colours. Organic pigments are being used in increasing quantities to fulfil these demands and in some cases have been specially developed for the purpose.

Important Properties of Organic Pigments

The type of surface coating the method of application and the intended use of the finish all impose conditions varying in severity which must be withstood by the coloured pigments present if the coloured effect is to be retained during application and subsequently. The ideal pigment would withstand all treatments and would be usable in all types of surface coating irrespective of the severity of the conditions but such ideal products are rare and compromise is frequently necessary.

Four properties of organic pigments are of major importance in determining their ultimate use namely fastness to light solvents heat and chemicals.

Light Fastness

A coloured finish is required to maintain its coloured effect during its useful life.

Inorganic pigments such as iron oxides or carbon black give effectively permanent coloration but organic pigments need not approach this performance except where resistance to outside exposure is involved since for interior use a lower level of light resistance is acceptable.

The light fastness and durability of coloured finishes is dependent to some extent on the medium used but the controlling factors are type of pigment used and its concentration. Although the light fastness and durability of a finish containing an organic pigment alone e.g. a full shade may be satisfactory if the same pigment is used with opaque white to give a reduced shade the performance may not be adequate and in fact the tint produced may be quite fugitive. The type of opaque white used will be a factor in determining the resistance of tints to exposure but it is primarily the type of organic pigment which governs the performance over a wide range of depths of shade. Because the behaviour of organic pigments varies more widely in pastel than in full shades the result of tests in pale shades is a more valuable yardstick to use in assessing the resistance of a pigment to light and weathering. In addition a fastness rating based on pale shades is of direct value because of the predominance of pastel shades in surface coatings and because it enables a prediction to be made of the performance of a pigment when used as a component of mixtures. Only a product of high light fastness should be used as the minor component of any mixture otherwise rapid change of hue can occur on exposure caused by loss of the fugitive component.

Fastness to Solvents

A wide range of solvents is employed in the various types of modern finishes to produce satisfactory coloured finishes organic pigments must be capable of resisting the effects of solvents in order to avoid defects such as hazing blooming bronzing and bleeding into adjacent white or pale coloured finishes. The degree of solubilisation of a pigment is dependent on both the type of solvent and temperature and different results can be obtained between tests on pigment powders and on pigmented compositions. However the examination of the resistance of pigment powders to a range of solvents gives an overall

indication of the performance to be expected in use.

Heat Fastness

Where the finish is cured by the application of heat the coloured pigment must withstand the conditions of stoving which are applied. This may be a relatively low temperature for a long time e.g. 1 hour at 100°C or a much shorter time at higher temperatures e.g. 8 minutes at 180°C or with infra red stoving temperatures around 300°C may be obtained. Repeated stoving schedules may also be experienced in for instance two or three tone finishes or in tin printing. It is essential to consider heat fastness as a function of the whole system as different fastness can be obtained depending on the medium used.

Chemical Fastness

With the extension of the use of decorative effects to industrial equipment pigmented finishes are in some cases required to withstand chemical attack and to maintain their colour in the presence of acids alkalis and other reagents. Tests on the dry pigment can indicate stability or otherwise according to the degree of colour change occurring but the medium used in a chemically resistant finish will afford a degree of protection to sensitive pigments some of which can be used in very resistant media. In order to make use of the widest possible range of pigments selection on a basis of tests on pigment powders should be supported by trials on pigmented finishes.

Tinctorial Strength

A further property of pigments which is of importance when appraising products is tinctorial strength. When pastel or reduced shades are made in paint from organic pigments and opaque white such as titanium dioxide it is found that different organic pigments give different depths of shade even though the proportion of coloured pigment to white is the same in each case. This visual difference is caused when the organic pigments differ in tinctorial strength. The relative amounts of two coloured pigments which with the same quantity of opaque white give pale shades of equal visual depth is a measure of their relative tinctorial strengths the stronger pigment is that which requires the smaller amount to give the visual match. The cost of making a pastel shade is therefore dependent on the tinctorial strength of the pigment used as well as its cost per pound.

In the discussions which follow on the properties of organic pigments and their selection for particular uses verbal ratings are employed to describe the fastness of a pigment to light solvents heat and chemicals and to indicate its tinctorial strength. A five step scale P = poor F = fair M = moderate G = good and E = excellent is used. The use of a verbal scale simplifies the task of comparing the products of different manufacturers since their own methods of assessment differ widely. The term excellent implies that the pigment is virtually unaffected by the particular treatments. In the case of heat fastness the selected treatment is in a stoving medium for 10 minutes at 180°C. A rating of excellent given for heat fastness does not guarantee no change at temperatures higher than this e.g. in silicone resins at temperatures appreciably greater than 200°C.

Types of Organic Pigments

The group of organic pigments used in surface coatings is a large and expanding one and includes a wide variety of chemical types. In comparison with the natural and synthetic inorganic pigments the main advantages of the organic group are the availability of a wider range of hues brighter shades and higher tinctorial strengths. Their basic fastness properties to light solvents heat and chemicals vary widely necessitating careful selection for any particular end use.

General Classification

Organic pigments may be divided into three main groups according to their composition Pigment Dyestuffs Toners and Lakes.

Pigment Dyestuffs

Pigment dyestuffs are wholly organic water insoluble compounds produced by a wide variety of chemical reactions. This group is easily the largest and includes the azo phthalocyanine and vat pigments.

Toners

This description is applied to water insoluble products made by the precipitation of water soluble dyes the final product being free from inorganic base (e.g. alumina) or extenders (e.g. barytes). Precipitation is effected either by heavy metal salts such as calcium barium or manganese with anionic (sulphonated) azo dyes or by complex mixtures of phosphoric tungstic and molybdic acids with cationic (basic) dyes. Usage of the latter group is primarily in printing inks.

Lakes

These are similar in constitution to the toners i.e. they are derived from watersoluble organic compounds by precipitation but in the presence of a base such as alumina or a co precipitate of alumina and blanc fixe where the base is an essential and integral part of the product. The presence of the base ensures complete insolubilisation of the dye and a satisfactory degree of water resistance in the lake. The type of base used will depend on the final application of the lake e.g. alumina/blanc fixe for surface coatings alumina for printing inks. Water soluble dyes which do not give water insoluble toners can be converted to lakes. While commercially available toners are usually prepared from organic compounds made specially for the purpose lakes can be prepared from any watersoluble dye and potentially the entire range of anionic water soluble textile dyes is available for use. The fastness and tinctorial properties of lakes however are in general inferior to those of pigment dyestuffs and the group is of declining importance.

Extended or reduced pigments can be made from products in all the three previous groups by mixing pigments with extenders such as blanc fixe. These derivatives are frequently erroneously classed as lakes. They are however merely intimate physical mixtures of the parent product and extender and although extended pigments frequently show some advantage in ease of dispersion over their concentrated counterparts the fastness properties of the latter remain unaffected.

Usage of the terms toner and lake differs in the United States there toner implies a concentrated organic pigment i.e. it includes both the pigment dyestuffs and toners of the present classification lake implies the presence of extender or base and hence in the U.S. lakes comprise both extended pigments and the true precipitated lakes defined earlier.

General Properties of Organic Pigments

The three groups of organic pigments differ in the range of properties which they possess these are summarised in the following table.

It will be noted that although in resistance to such agencies as heat and solvents toners and lakes compare well with pigment dyestuffs it is only in the latter group that the highest general resistance occurs.

Classification by Chemical Constitution

As pointed out earlier many chemically different organic compounds are used as pigments. The second edition of the Colour Index lists and numbers dyes and pigments in a systematic manner based on chemical constitution. In the present treatment the pigments will be examined under the two main headings of azo and non azo and within each group individual pigments will be arranged in order of C.I. numbers.

Azo Pigments

Azo compounds are characterised by the presence of the azo chromophore $N=N$ joining together two aromatic nuclei and the basic reaction has been known for about a hundred years. Aromatic primary amines when treated at low temperatures with nitrous acid form an extremely reactive diazonium salt which is capable of combining with other aromatic compounds to form the azo linkage. The reaction producing the diazonium salt is termed diazotisation the combination of diazonium salts with other aromatic products (second components) is the coupling stage.

If either the first component (diazotised amine) or second component contains sulphonic acid groups the resulting azo compound will possess water solubility and can be isolated as a sodium salt by salting out where such groups are absent the resultant product will be water insoluble but may be somewhat soluble in oils or solvents. The presence of other substituent groups in either part of the molecule will affect tinctorial properties and non aqueous solubility.

Since the above reactions are typical of those used in the manufacture of azo pigments a brief description of the manufacturing cycle of one important product Toluidine Red will suffice to illustrate the processes used for the whole group.

Typical Manufacturing Process for a Monoazo Pigment

Meta nitro para toluidine is made from toluene by the following series of reactions

The second component naphthol is derived from naphthalene as follows

A solution of meta nitro para toluidine in dilute hydrochloric acid at 10° 15°C is stirred and sodium nitrite solution run in so that an excess of nitrous acid is maintained. The diazo compound formed is filtered and excess nitrous acid removed. Naphthol is dissolved in caustic soda solution sodium acetate is added as a buffer salt and hydrochloric acid is added to precipitate the naphthol in a finely divided state. The diazo solution is then run in over a period with stirring and a red insoluble pigment is formed which is maintained as a slurry. When coupling is complete as judged by the presence of excess diazo component the slurry is filtered the pigment washed to remove impurities and the filter cake dried in a stove. The dried lump is then ground to powder.

Since tinctorial properties vary from batch to batch because of slight variations in processing conditions or variations in purity of the coupling components used selective blending of batches is carried out to maintain manufacture within accepted limits of a standard.

Formation of Disazo Pigments

Toluidine red is a monoazo pigment i.e. only one azo linkage is present in the molecule. If an aromatic primary diamine is diazotised on each amino group coupling with two molecules of second component is possible and a disazo pigment is formed

Disazo pigments can also be prepared by coupling two molecules of a diazonium compound with the same second component.

Monoazo Pigments

Couplings with Acetoacetaryl amides

These monoazo arylamide pigments are yellow to orange in hue and have the general characteristic of poor resistance to heat and solvents. Their light fastness varies from good to moderate and Yellow 1OG is outstanding in this property. Although their tinctorial strengths are in the group poor to moderate there are important variations between individuals. For example Arylamide Yellow 1OG is the weakest of the series a property most unfortunately associated with high light fastness.

Couplings with 2 Naphthol

These examples of couplings with 2 naphthol range in hue from orange to bluish red Para Red being the bluest in shade. As is evident from the table the fastness properties with the exception of chemical resistance are very variable. Only Dinitraniline Orange and Parachlor Red possess any measure of light fastness in tints the latter contrasting sharply in this property with the inferior performance of its isomeric compound Chlorinated Para Red. Part of the increased light fastness of Parachlor Red may be an ancillary effect of its lower tinctorial strength. Some degree of increased colour retention on exposure is to be expected since fading is produced by a photochemical reaction and the degree of fade will depend on the amount of light and the amount of coloured pigment in addition to the rate of degradation of the coloured pigment under constant conditions of illumination.

High tinctorial strength with only fair light fastness in tints shown by Para Red is a property of little value to the paint industry and inadequate durability in strong shades together with insufficient heat fastness are the reasons for the declining importance of the pigment.

The most important naphthol pigment Toluidine Red owes its position to its excellent heat fastness and very good colour retention in full shades. It is capable of producing bright strong red shades with a reasonable degree of hiding power although the solvent resistance is poor.

Couplings with 3 Hydroxy 2 naphthanilides

A comparison of Tables 3 and 4 shows immediately that pigments based on naphthanilides offer a higher level of fastness properties than is available in the naphthol series. The hue of the naphthanilide pigments is bluer than that of the naphthol derivatives there is no true orange in the products tabulated and the bluest gives bordeaux shades.

The light fastness in tint shown by naphthanilide couplings is superior to that of all naphthol pigments except Parachlor Red and Dinitraniline Orange and the former series has the added advantage of higher tinctorial strength.

The solvent fastness of the products listed in Table 4 is in general only equal to that of the naphthol pigments and here lies the main disadvantage in terms of current requirements. Where the molecular weight is increased by greater structural complexity in both components as in Carmine FB the solvent fastness rises to moderate. This level of performance is sufficient to give freedom from bloom in stoving finishes but not sufficient to prevent bleed into white stoving overspray enamels.

The naphthanilide pigments were developed to give bright shades with high light fastness in tint properties which were accompanied by high tinctorial strength. Their shortcomings in solvent fastness and the fact that no light fastness rating of excellent can be given led to the search for other products pigments resulting from this search are discussed later.

Couplings with Heterocyclic Hydroxy Compounds

Yellow R gives very similar fastness properties to Arylamide Yellows G and 5G. Its main interest lies in its redder shade produced by coupling with a pyrazolone instead of an acetoacet arylamide (d. Benzidine Orange and Benzidine Yellow).

Nickel Azo Yellow on the other hand is a unique product. Although duller in shade than Arylamide Yellow 10G but of comparable strength and light fastness the major deficiencies of Yellow 10G poor heat and solvent fastness are absent. The resistance to solvents is sufficiently high to give freedom from bloom in stoving enamels but the product will not give enamels or lacquers which are non bleeding when oversprayed. The performance under these conditions is however satisfactory for all but the most critical applications. The high level of fastness exhibited by Nickel Azo Yellow is very largely due to the presence of ionic nickel as a coordination complex since the free dye base is of poor resistance to solvents and light. The pigment is however not fast to acids because demetallisation occurs with liberation of the dye base.

Couplings containing Sulphonic Acid Groups

The toners are listed in Table 6. It will be seen that their principal virtues are high heat resistance high strength and good solvent resistance but that there are exceptions to this generalisation in the case of each fastness property. Their chemical fastness is poor the principal reason being that alkalis are capable of destroying the metal salt present liberating the parent water soluble azo coupling.

The light fastness of toners in reduced shades is inadequate for them to be used in most surface coatings their full shade light fastness is of a higher order ranging from good to very good. In durability however even in full shades the products do not give very satisfactory performance for under the combined action of light and weather colour fading and pigment solubilisation occur simultaneously. In weathering resistance the manganese toners show better performance than the corresponding calcium and barium types even though all these products give the same order of light fastness.

Bordeaux BL is a toner of very high hiding power and although below the average of the remainder of the toners in resistance to solvents gives lacquers which are non bleeding when oversprayed.

Pigment Scarlet 3B is an example of a dye lake giving similar fastness properties to the toners. Its tinctorial strength however is low and this is due in part to the diluting effect of the alumina base present.

Disazo Pigments

The properties of the disazo pigments can be compared with those of the arylamide yellows listed in Table 2 which contain similar second components and the contrast is immediately apparent. The disazo pigments possess much superior resistance to heat and solvents and are of much higher tinctorial strength. Unlike the arylamide yellows therefore the disazo pigments can be used in industrial stoving finishes their light fastness however does not in general equal that of arylamide yellows. Disazo products such as Yellow GR 2G and NCG have however sufficient light fastness in full shade and when used as the major component of mixtures with opaque white to make them useful in medium quality stoving enamels.

Non azo Pigments

The group of azo pigments was extended more rapidly in the early stages of the development of organic pigments than were the non azo types. Several non azo pigments have been known for a long period and are still in use and because of their historical importance they will be discussed first.

Miscellaneous Products

The three products listed in Table 8 as being lakes on alumina show quite typical behaviour very good fastness to heat and solvents moderate light fastness lack of resistance to acids and alkalis and poor tinctorial strength. They do however still find use in strong shades because of good colour retention on exposure coupled with economy.

Aniline Black has the general inertness to be expected from a highly oxidised product its chief virtue lies in intensity of shade compared with carbon blacks i.e. a deeper black is produced.

Pigment Green B is an organo/iron coordination complex and shows typical acid instability. The pigment is very dull in shade being much duller and weaker than Phthalocyanine Green. However it offers an economic means of making olive greens particularly in water paints.

The demand for pigments of higher all round fastness than are obtainable with the azo group has been met in the modern additions to the non azo pigment group. It is not possible to classify these non azo pigments in the formal manner of chemical constitution as was used for the azo series. For convenience the compounds studied which are of extremely diverse constitution will be divided into three groups i.e. Phthalocyanines Vat Pigments and Miscellaneous Heterocyclic Compounds.

Phthalocyanine Pigments

The first pigment in this group Phthalocyanine Blue B was marketed over twenty years ago. The products have been continuously improved in brightness of shade tinctorial strength and ease of dispersion and in addition a large number of specialised forms have appeared each suited to a specific application.

Phthalocyanine blues are produced by a condensation reaction from relatively simple intermediates. Phthalic anhydride urea and cupric chloride are fused together or alternatively heated together in a suitable high boiling solvent to give the crude blue compound which has the structure.

The crude blue compound produced by the condensation reaction requires further treatment before it can be used most effectively as a pigment. For example by dissolving the crude in concentrated sulphuric acid and reprecipitating by controlled dilution with water a product of useful pigmentary form is obtained.

Compared with the crude material the pigmentary form gives much brighter shades is stronger tinctorially and possesses enhanced ease of dispersion. This need for a separate pigment conversion stage following the formation of the required chemical compound is typical of the group of non azo pigments being discussed and contrasts sharply with the formation of azo pigments where the useful pigmentary form is

obtained directly in the aqueous coupling suspension.

Copper Phthalocyanine

Copper phthalocyanine can exist in two crystalline modifications and the latter being the more stable. Pigmentary Phthalocyanine Blue B (the form) in the presence of certain solvents particularly aromatic hydrocarbons will recrystallise into the form of large crystal size. In a paint or lacquer this change results in loss of tinctorial strength and brightness. The use of unmodified form copper phthalocyanine pigments is therefore restricted to those uses where crystallising solvents are not present e.g. water paints. A slightly chlorinated copper phthalocyanine does not crystallise in solvents and is the product used in paints lacquers and enamels.

By special processing in the presence of solvents it is possible to prepare copper phthalocyanine in the modification with small crystal size. This product which is not further affected by solvents is greener brighter and somewhat weaker tinctorially than the form and is of interest mainly because of its superior brightness of shade.

The copper atom is so strongly coordinated with the organic molecule that it cannot be removed by acid treatment. Other metal phthalocyanines can also be produced but they are not commercially of value giving either inferior tinctorial properties or unstable products from which the metallic nucleus can be removed quite simply.

Copper phthalocyanine can be chlorinated so that substitution of chlorine occurs in the peripheral benzene rings of the molecule and 14-15 chlorine atoms can be introduced. The product is Phthalocyanine Green a bright bluish green pigment.

Metal free Phthalocyanine

It is also possible to obtain a metal free phthalocyanine which is much greener in hue than the copper compound. It also tends to crystallise in strong solvents and a modified form is necessary to give adequate stability in paint media. The metal free phthalocyanine is considerably more expensive than the copper derivative.

From their tabulated fastness properties the virtues of phthalocyanine pigments are obvious and their properties are much superior to the azo pigments listed earlier. The restriction of available hues to the blue and green portions of the spectrum led to a search for reds and yellows of comparable fastness properties.

Vat Pigments

Vat dyestuffs widely used in textile dyeing and printing are water insoluble compounds capable of being solubilised by alkaline reduction (vatting) and when reconverted to the oxidised form on a fabric give a wide range of shades of excellent fastness. Though of varied chemical constitution they are polynuclear compounds comparable in complexity to the phthalocyanines. Because they are chemically inert except to reduction and of very low solvent solubility efforts were made to exploit these properties in the pigment field.

Vat dyes as used on textiles are not directly suitable for use as pigments and physical treatments similar to those employed on phthalocyanines are necessary to give a powder product of adequate ease of dispersion in paint media. In addition purification is frequently required to remove by products of the manufacturing processes which otherwise could lead to bleeding in solvents.

The selection of vat dyes for use as pigments has been reviewed by Vesce it is apparent that not all vat dyes can be converted to give highly durable pigments and among those now in general use there are important variations in performance.

Extenders

Introduction

It is not easy to devise a clear simple definition but extenders known also by the alternative name of fillers are essentially inorganic compounds usually with limited opacity in non aqueous media and limited staining or colouring properties. There are exceptions more particularly in respect of colour where the extender may have too much self colour to permit its use in whites or delicate pastel shades.

The limited opacity of the extenders is in line with their refractive indices which are invariably notably lower than those of the regular pigments and low refractive index may be regarded perhaps as a feature of extenders which distinguishes them from the pigments as such.

Bradley (Jun.) suggests that extenders would be found in the refractive index range of 1.45-1.70 by contrast with the opaque pigments from 1.94 to 2.70 the former range of figures being very near the refractive index of oleoresinous media. In aqueous media by contrast with the performance in non aqueous media some extenders demonstrate a useful if not an entirely satisfactory degree of opacity and a good example of this is the almost traditional use of whiting in water paints and distempers where it often constitutes a large proportion of the total pigment extender.

Many extenders are natural minerals suitably pulverised and are used as such or they may be subjected to processing to provide more generally acceptable products or to enhance certain properties. These natural extenders have been greatly augmented in recent years by types which have been specially synthesised.

Whereas it might have been true in the past that extenders were used to provide weight or bulk to a paint the myth that weight alone has any merit as been largely dissipated and the exploitation of extenders to provide bulk only has become much less important. The selection of extenders has become much more discriminating.

The practice of selling paint on a weight basis has almost disappeared and most paints are sold in gallons or other unit of volume and the area covered by a unit volume (gallon) is often quoted. This leaves no doubt in the mind of the purchaser of the true value of the paint or of the amount he will need to cover a given area after making due allowances for the nature of the surface involved.

Production and Manufacture

Extenders may be derived from the natural mineral which is ground in different types of mills and the powdered products may be classified by dry or wet means into finer or coarser particles the latter being reground as necessary. Dry classification may be by screening or air floatation wet classification may involve settling tanks the finer particles being carried farther through the systems and the coarser particles being settled out at an earlier stage.

Micronising of extenders using superheated steam is becoming a popular way of producing extenders in the finer ranges of particle size and increasing numbers of extenders are being supplied in micronised form.

Some natural minerals as mined are not sufficiently white in colour for general use in all types of paints and the agent responsible for the discoloration often an iron compound is washed out by acid treatment. The efficiency of this process depends upon whether the iron or other coloured agent is present as free oxide which may be conveniently soluble in dilute acid or whether it is in chemical union as part of a complex compound. When the iron or coloured agent is part of the complex compound itself this may remain fixed and will control the improvement of colour which can be achieved.

Opacity

This subject is dealt with more extensively in other Chapter but it is perhaps of interest to compare the refractive indices of extenders and pigments as in Tables 1 and These figures show clearly the distinctive groupings of the two types of material.

Amongst the higher refractive index extenders would be included barytes and blanc fixe barium carbonate some calcium and magnesium carbonates calcined china clay (aluminium silicate) calcium metasilicate

(wollastonite) and perhaps asbestine. The lower refractive index types include the synthetic silicas diatomaceous silicas some being reported as low as 1.40 and some precipitated calcium and aluminium silicates. From the lower refractive index types would be found extenders suitable for producing mattness in clear lacquers with minimum effect on transparency for grain fillers which are not readily distinguishable and for pigmented products where minimum colour change is required.

Natural and Synthetic Extenders

The extenders which are mined as natural minerals are likely to contain more insoluble impurities than the synthesised types where sometimes the main possibility is the existence of water soluble salts retained as the result of a precipitation process. It must not be concluded from this that the natural mineral extenders are free from soluble impurities for small amounts of soluble impurities may be found in them also a fact which is recognised in official specifications.

It is obvious that the amount of water soluble matter in both natural and synthesised extenders will depend on the degree of washing which they receive before they are delivered to the consumer.

Surface Coating Agents

It is becoming very popular to provide natural and synthetic extenders with a surface coating consisting of fatty acid fatty acid soap or resinous matter in order to facilitate wetting or dispersion especially in oleoresinous media. This means that grinding or milling times are reduced a most important factor in processing costs and in production from a given milling unit. The presence of a surface coating may also be helpful in providing the required compatibility with certain types of synthetic resin especially when the proportion of extender used is high. The actual bond between particles of extender and the synthetic resin (or other type of medium) may have a very important effect on the general physical properties of the applied coating.

The amount of surface coating agent used is usually less than about 3 per cent of the weight of the extender but it could be somewhat higher. Generally speaking it is desirable that the amount of surface coating agent does not exceed that necessary to provide a more or less continuous layer of active material on the surface of the individual particles at the minimum thickness. Larger amounts may begin to have other effects on the properties of the medium which are undesirable.

Oxides

Silicas

By far the most important member of this group is silica or silicon dioxide which is found in several forms naturally as quartz crypto crystalline quartz and diatomaceous silica (diatomite kieselguhr infusorial earth) or it is also produced synthetically the latter often being distinguished by its extremely finely divided condition.

The differences between the chemical compositions of the various forms of silica (natural and synthetic) are shown in Table 3.

Where several grades of an extender are available from one source the analytical and physical figures quoted may apply to the range as a whole and not to an individual member. This method of recording applies throughout this chapter.

Analysis of Silicas

Consideration of the analytical figures for the various types of silica indicates that natural quartz silica and some of the synthetic types may be very rich in silicon dioxide (SiO_2) indeed the figure being in excess of 99 per cent for the dried material.

The diatomaceous silicas may contain notable amounts of other metallic impurities such as compounds of iron aluminium calcium and magnesium which may be significantly absent from synthetic silicas.

The amount of water soluble salts in the synthetic silicas is likely to vary appreciably according to their

method of preparation degree of washing and ease or difficulty of removal and whilst for some applications their presence may be acceptable there are others for example in anti corrosive primers where it is usually advisable that they should be at the minimum possible level.

Chemically held water is also likely to vary depending upon the source or method of preparation of the silica and whether or not it has been calcined.

The pH values of the aqueous extracts from the various forms of silica vary appreciably. The synthetic silicas yield pH figures from 9 to 2.4 and appear to be more often on the acid side of neutrality. By contrast a group of proprietary diatomaceous silicas all fall within the range 7.0 9.9.

Physical Properties

Perhaps the most distinctive feature of the whole group of silicas is the extremely fine particle size of some of the synthetic varieties which is reflected in considerable surface areas per unit weight and in very high oil absorptions.

It is clear that apart from breaking down the loose agglomerations of the particles no real grinding is necessary with some of the synthetic silicas. The high oil absorption (adsorption) figures of both the diatomaceous and synthetic silicas suggest their value as matting agents and their potential influence on the rheological characteristics of media and these are fields in which they are of special interest.

As matting agents even the addition of only 1 per cent by weight of a fine synthetic silica has a significant effect on gloss 5 per cent may produce a semi gloss and 12 15 per cent practically a dead matt result depending upon the nature of the medium.

The surface areas per unit weight are not necessarily in direct proportion to their oil absorptions which suggests that some of the surface area presented may be inaccessible to medium. This may indicate the possibility of arranging for voids in the pigmented coating which could allow for breathing of the coating if desired.

Applications

When particles of infinitely irregular shapes are required the diatomaceous silicas are a good choice because they represent the siliceous skeletons of aqueous diatoms or tiny plants of which many thousands of varieties are possible. The fine synthetic silicas are very useful agents for inducing thixotropy in coatings especially where these are required to remain on vertical surfaces without curtaining and one special application in this category is for polyester finishes where it is necessary to apply the equivalent of several normal thicknesses of coating in a single application and to achieve this without affecting transparency.

They are also useful in the production of one coat decorative finishes where controlled thixotropy is essential and in paint removers where the object is to retain a substantial thickness of coating on vertical surfaces long enough for the active agents to penetrate and soften the old coatings. The very small particle size and large surface areas indicate that these might be used as pigment suspending agents.

The water absorbing types of fine silica have been used to remove free water from aluminium paints and thus prevent development of pressure and loss of leafing properties.

The diatomaceous silicas are also used as matting agents in flat finishes which do not gloss up when rubbed and their effect is claimed to be due to their capacity for causing light to diffuse in all directions and it is to this feature that their opacifying power is attributed. Some of the mattness obtained from diatomaceous silicas is achieved because some of the odd shaped particles in heavily pigmented systems are believed to project through the upper surface of the coating.

Their heterogeneous forms prevent tight packing which allows greater freedom of movement of moisture in coatings and this reduces blistering and peeling more particularly on absorbent surfaces. Similarly better solvent release is obtained in highly pigmented sealers and undercoats and to their unique multivarious structures is attributed their reinforcing action on coatings which results in better toughness flexibility and

resistance to cracking when exposed to weather influences.

In emulsion paints the diatomaceous silicas are claimed to give better washability. The presence of voids in the individual particles makes them of interest in fireproofing paints where heat insulation is of importance. Improved adhesion especially on soft surfaces such as wood is provided by diatomaceous silicas which tend to anchor to them.

Ordinary natural powdered silica is used in grain fillers for wood because of its transparency which preserves the natural colour of the wood and avoids muddiness for conferring adhesion it is often used in undercoats to provide a key both to the primer and for the finishing coat and in finishes where abrasion resistance is important such as in road line paints paints for airplane runways and floor paints.

Coarse silica or sand is a good constituent in deck paints for reducing slip and in sound deadening coatings or compounds for motor cars and metal domestic equipment.

Hydroxides

Alumina

Hydrate of alumina $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or in its calcined form Al_2O_3 together with grades containing intermediate amounts of combined water are available in very pure state having less than one per cent of impurities. Some grades are colloiddally dispersible in water.

The specific gravity varies from 2.45 to 3.9 according to the combined water content.

The aluminas have not yet found many direct applications in surface coatings although they are used as a basis on which dyes are precipitated. Some grades have a marked livering tendency with fatty acids such as may be present in paint media and this has limited their possibilities but there are types of coating where a measure of thickening is desirable and they are worth consideration for these specific purposes.

Solvents

Introduction

The Primary function of solvents in surface coatings can be stated very simply. They are incorporated in order to make it possible to apply the film forming material to the required surface by anyone of a number of methods so as to obtain a uniform film of specified thickness. Once the coating has been applied the solvents must evaporate as completely as possible. The solvents in fact may be said to convey the film former to the surface.

Simple though this function may appear in principle there are many factors to be considered when selecting a suitable solvent mixture for a particular composition. This is because the function is not simple in practice the solvents being called upon to contribute much more than is implied by their primary function. As in all broad classifications there are exceptions and they arise in this case because of certain convertible resins which by their nature are soluble only in a much narrower range of solvents and in which the solvents play some part during film formation. Notable examples of such systems are the amine cured epoxy resin coatings and the urethanes where the curing reaction is rapid and is taking place during the evaporation of the solvents.

Characteristics of Solvent Groups

This section deals with groups of solvents from the aspect of their suitability for the various types of resins consideration being given to those characteristics which are appropriate in each particular case. For instance when choosing hydrocarbon solvents aromatic content is an important factor. In the case of oxygenated solvents their polarity gives a clue to their suitability as solvents for a particular resin since in general resins of high polarity require highly polar solvents whereas those of low polarity are dissolved by solvents of low polarity. This matter of polarity and the other factors which must be considered in choosing the most suitable solvents for a particular type of coating are discussed in detail later.

The Terpenes

These consist mainly of hydrocarbons obtained largely directly from the pine tree by distillation or extraction or as by products of paper pulp manufacture the most widely used solvents in this range being turpentine dipentene and the pine oils.

There are four grades of turpentine commercially available three of which are obtained from various species of pine trees by steam or destructive distillation and the fourth from sulphite liquor a by product of the paper industry. Two grades are covered by British Standards Specifications Type I B.S.S. 244 and Type 2 B.S.S. 290 whilst all four grades are included in the American Society for Testing Materials specification ASTM D.13 51. The three grades obtained from the pine tree consist essentially of pinene and boil in the 150° 170°C range that obtained from sulphite liquor has a variable composition and a somewhat wider boiling range.

Until the advent of petroleum hydrocarbon solvents of the white spirit type turpentine was the principal solvent used in paints and varnishes. Dipentene has similar solvency characteristics to turpentine the commercial product consisting mainly of dl limonene and boiling in the 170 190°C range. It has an appreciably lower evaporation rate than turpentine and is normally used in minor proportions only. It improves flow and brushing characteristics and also acts as an anti skinning agent.

The pine oils are complex mixtures largely of terpene alcohols boiling in the 195° 225°C range. They are useful constituents of brushing compositions where they improve flow and brushing characteristics but are used only in small quantities because their evaporation rate is very low.

Hydrocarbon Solvents

The hydrocarbons as a class are of low polarity and strongly hydrophobic and are solvents for non polar or weakly polar materials amongst which are oils bitumen coal tar and many of the resins used in surface coatings. The aromatic hydrocarbons are solvents for a wider range of these materials than the paraffins or the naphthenes. The hydrocarbons are not solvents for nitrocellulose but some of the cellulose ethers are soluble in aromatic hydrocarbons.

There is a very wide range of hydrocarbon solvents available to the surface coatings industry derived from petroleum or coal tar and these solvents range from purely aliphatic to wholly aromatic materials and cover an extensive boiling range. It is not easy to classify them in a logical manner and in practice the technologist will select from a list of properties those which meet his requirements in such respects as boiling range flash point and aromatic content. There is however an accepted terminology in the trade in this country which makes it possible to put most of the solvents into groups and the following descriptions deal with them on this basis. At the same time American equivalents have been included and reference is also made to some solvents which are available in various parts of the world but not necessarily in the United Kingdom.

White Spirits

These are petroleum fractions boiling in the 150° 210°C range and are the most widely used solvents in the industry. They are also sometimes referred to as petroleum spirits or mineral turpentine or turps substitute and are known in the United States as mineral spirits. The grade used on the largest scale has an aromatic content of about 15 per cent and it is this material which is referred to simply as White Spirit in this country and as Mineral Spirits Regular in the United States. In some countries a high aromatic white spirit is also available with an aromatic content in the region of 45 per cent. High flash white spirits are also available which resemble ordinary white spirit except that the lower boiling fraction is not present.

In addition there are the low odour and odourless white spirits with special characteristics. The low odour white spirits are distillation products from which practically all the aromatics have been removed whilst the odourless white spirits are produced synthetically by an alkylation process. The reduced odour of the low

odour grades and the virtual absence of odour in the odourless grades are real advantages in paints used for interior decoration. The virtual absence of aromatics poses certain problems on solubility of alkyds but these can be overcome by modification of the resins. At the same time there are certain advantages in physical characteristics which can be obtained by using these purely aliphatic solvents such as reduction of sinking of flat wall paints.

Special Boiling point Spirits

These are petroleum fractions of lower boiling ranges than the white spirits frequently closer cut and with aromatic contents for the most part in the 2-15 per cent range. These fractions are referred to in many parts of the world as SBP solvents with a suffix to indicate type or boiling range. In the United States the solvents in this range are known as VM & P naphthas or just as naphthas. There are a few exceptions to this generalisation a limited number of cuts with higher aromatic contents between 35 per cent and 60 per cent being available.

Aromatic Solvents

Under this heading are included all hydrocarbon solvents with aromatic contents of 80 per cent and over which is a fairly well recognised definition in the paint trade. Whereas all these solvents originally came from coal tar in recent years the petroleum industry has become a major producer of these materials. From coal tar they are obtained by distillation but this is not the case with petroleum derived aromatics.

Petroleum products are predominantly aliphatic or naphthenic and various ingenious chemical processes have had to be devised to reform the molecules. One such process called hydroforming dehydrogenates the naphthenes to aromatics and cyclises some of the paraffins.

Aromatic hydrocarbon solvents are available either as cuts or as single hydrocarbons of a high degree of purity both from the petroleum and the coal tar industry. The petroleum cuts which are normally used in surface coatings rather than the pure hydrocarbons are sold under various proprietary names and are specified by boiling range and aromatic content. The coal tar solvent cuts are referred to in various ways such as 90's toluene 5° solvent xylene solvent naphtha and heavy naphtha.

Ketones

The aliphatic ketones with the general structure $R-CO-R$ are intermediate between the hydrocarbons and alcohols in polarity. The lower members of the series are strongly hydrophilic but they lose this characteristic rapidly as the size of the hydrocarbon groups increases. Thus whereas acetone is miscible with water in all proportions methyl isobutyl ketone is soluble in water only to the extent of about 2 per cent. This rapid change in the hydrophilic nature of ascending members of the series is reflected in solubility characteristics but not to as great an extent as might be expected from this factor alone. The ketones are solvents for a wide range of resins including many for which few solvents exist. In addition to their widespread use in nitrocellulose lacquers they are the principal active solvents used in lacquers based on cellulose acetate and on copolymers of vinyl chloride/vinyl acetate vinyl chloride/vinylidene chloride and vinylidene chloride/acrylonitrile. They are very stable under normal conditions and cover a wide range in evaporation rate from acetone to isophorone. Acetone has too great an evaporation rate to be used to a major extent in nitrocellulose lacquers of the normal type but methyl ethyl ketone and methyl isobutyl ketone figure prominently in a very large proportion of nitrocellulose and vinyl resin lacquers. Of the cyclic ketones the most widely used are cyclohexanone and methyl cyclohexanone which are similar to the aliphatic ketones in their solubility characteristics.

Esters

The esters with their typical $R-CO-OR$ structure are similar to the ketones in polarity but are less hydrophilic. Methyl acetate is soluble in water to the extent of 24.5 per cent whilst the figure for butyl acetate falls to 0.68 per cent at 20°C.

With the exception of ethyl lactate the esters used as solvents are the acetates. The lower molecular weight esters the formates are unsuitable because of instability being readily hydrolysed by water and are too volatile. Whilst the acetate esters are less stable than the ketones they are quite satisfactory in this respect for all normal lacquer applications and are in fact used widely especially in the nitro cellulose lacquer field. The members of the series used most extensively are ethyl acetate isopropyl acetate and the butyl acetates. In the higher boiling range ethyl lactate and the acetate of ethylene glycol monoethyl ether figure prominently the latter particularly in the epoxy resin field.

Glycol Monoethers

These solvents possess interesting structures in that they have both the strongly polar hydroxyl group and the less polar ether group in the same molecule.

Of the glycol ethers the methyl derivative is the only one which will dissolve cellulose acetate whereas both the methyl and ethyl ethers of diglycol are solvents. It would appear that the influence of the larger non polar hydrocarbon group has been counteracted in the diglycol ethyl ether by the presence of the second ether group.

These solvents form an extremely useful series of solvents for many resins including nitrocellulose alkyds and shellac. They are all completely miscible with water at normal temperatures and with most hydrocarbons and have a very mild odour. They are in the medium to high boiling range but are much slower in evaporation than would be anticipated from their boiling points compared with most of the other solvents and the proportion which can be incorporated in air drying compositions is therefore limited to some extent.

Ethers

The aliphatic ethers such as ethyl and isopropyl are solvents for relatively few of the resins used in coatings although in conjunction with ethyl alcohol they dissolve nitrocellulose. In fact one of the earliest nitrocellulose solutions known as collodion cotton still used for certain specialised applications makes use of an ether/alcohol solvent mixture. The cyclic ethers such as 1,4 dioxane and tetrahydrofuran in contrast to the aliphatic ethers are solvents for a very wide range of resins in which respect they are similar to the ketones. Both are solvents for cellulose acetate and the various vinyl copolymers whilst tetrahydrofuran is also a solvent for polyvinyl chloride. With the exception of 1,4 dioxane these ethers are too volatile for use in coatings and are prone to peroxide formation.

Alcohols

The hydroxyl group renders the alcohols highly polar and strongly hydrophilic methyl alcohol ethyl alcohol and the propyl alcohols all being completely miscible with water. The hydrocarbon portion of the molecule makes its presence felt sharply in the higher alcohols for normal butyl alcohol is soluble to the extent of only 7.7 per cent in water at 20°C. This marked reduction in the hydrophilic nature of the molecule with increasing molecular weight is reflected in solubility characteristics. Thus whilst linseed oil is only partially miscible with methyl alcohol it is completely miscible with butyl alcohol. Castor oil with its hydroxyl groups is however completely miscible with methyl alcohol.

The alcohols as a class are very stable compounds and are to be found in many types of surface coatings. The higher members of the series such as the butyl alcohols improve flow and inhibit blushing tendencies in nitrocellulose lacquers and spirit varnishes and impart stability and good flow to alkyd/amino resin compositions. Certain resins such as the higher molecular weight epoxy resins where there are polar and non polar groups in the same molecule can be brought into solution in mixtures of the highly polar alcohols and the non polar aromatic hydrocarbons although they are not soluble in either of these solvents alone.

Halogenated Compounds

In spite of their reduced inflammability the chlorinated compounds do not find widespread use as solvents in surface coatings. Whilst they are not solvents for nitrocellulose they will dissolve many of the resins used

in coatings including a number of the other cellulose derivatives. However they suffer from a number of disadvantages being less stable more toxic and generally more costly on a volume basis than many of the other solvents. One field where they figure prominently is in paint removers methylene chloride frequently being the major constituent.

The only other halogen compounds of interest in the coatings field are the chloro fluoro compounds used as propellants in aerosol paint packs which are becoming increasingly popular. These have similar solvency characteristics to the chlorinated compounds.

Nitroparaffins

The commercially available nitro paraffins i.e. nitro methane nitroethane 1 nitropropane and 2 nitropropane are solvents for a wide range of resins including nitrocellulose. Cellulose acetate is soluble in nitromethane and nitroethane whilst the vinyl chloride/acetate copolymers are soluble in nitroethane and the nitropropanes. They are all similar in evaporation rate and fall in the medium boiling range close to butyl acetate. They are stable compounds with a mild odour and have proved useful in cellulose acetate and vinyl copolymer lacquer formulations.

Evaluation and Selection of Solvents

The paint formulator is faced with a large number of commercial solvents and an even larger number of commercial resins each with its own solvent requirements and solvents must be selected carefully if good results are to be obtained at minimum cost. Selection is far from simple and the general problems involved will now be discussed.

The viscosity of a resin solution is therefore of great importance or to put the problem in a more realistic way it is imperative to know what proportion of solvent must be used to obtain the best results.

The above five headings cover all the important factors involved in solvent selection and these factors and the test methods employed in their evaluation will now be described in more detail. One general point to be noted is that these methods of evaluation should be considered as sorting tests only and are no substitute for practical evaluation under specific conditions of use.

It must also be noted that many of the test methods for solvents were worked out in the sphere of nitrocellulose lacquers. This was because solvents represent a relatively high proportion of the total cost of these lacquers and also because they greatly affect their performance. Results thus obtained for nitrocellulose lacquers cannot be assumed necessarily to have any significance for other resin systems but the basic principles of the test methods used can often be applied.

Although the primary object is to consider the scientific background of use of solvents it would be unrealistic not to recognise that the problem is to choose suitable solvents at the lowest possible cost. In a clear lacquer based on high viscosity nitrocellulose the cost of solvents may be over half the total cost and whilst this is admittedly exceptional solvent cost is significant in all cases and there is always an incentive to reduce it. Psychologically the fact that solvents are not present in the final film reinforces the wish to reduce their cost. This must not be taken too far however because of the essential function which they perform in film formation.

Solvency

In the first place it is essential to remember that there is a fundamental difference between resin solutions and solutions of simple crystalline solids such as common salt. Resins do not give saturated solutions except in one or two special cases usually as more resin is added it becomes progressively more difficult to dissolve it owing to increasing viscosity but there is no critical point at which no more resin will dissolve. Similarly during film formation as solvent is lost the viscosity rises progressively but there is no critical point at which the resin crystallises. The final film can be regarded as a highly concentrated solution of resin in solvent and indeed its properties are those of a liquid a supercooled liquid and not those of a crystalline

solid.

In fact so far from forming saturated solutions corresponding to an upper limit of solubility some resin solutions show the opposite behaviour that is they show a lower limit of solubility below which the solution goes cloudy. On standing the cloudy solution forms two layers the upper of which is solvent alone. A well known example of this is the solubility of solid grade epoxy resins in many of the aliphatic ketones and esters where solutions can be obtained at higher concentrations but are precipitated on further addition of the same solvent. However solubility limits (minimum solids contents) can be determined. An alternative way of expressing the same effect is the white spirit tolerance of short oil varnishes. This depends on the maximum number of volumes of white spirit which may be added to one volume of varnish without precipitation or cloudiness.

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