Additives For Coatings

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Apart from the three main components of coatings i.e. film former, pigment and solvent, there are other ingredients, which are essential for better performance of the coatings. Although the quantity in which these ingredients are incorporated in the formulation is very low (less than 1% of total formulations), their presence is significant for overall performance of the coating. Every additive has a unique and vital role in the formulations. These additives are included in paint formulations for improving the manufacturing efficiency, consistency of the paint, its stability on storage, application and flow properties of paint and enhancing overall properties of coatings. Using additives can enhance almost all the desirable properties, although not necessarily all at a time. In short, these few % components affect the rest 99% population in the coating formulations.

Since a single additive can be multifunctional, their classification based on their chemical composition is difficult. Secondly most of their chemical composition is proprietary. Instead they are classified according to their functions. The additives used for solvent based and water based coatings are different. However some of the functions are common for both the systems.

Dispersing Agents

Pigment dispersion plays a very important role in the manufacture of paints. Properties like covering, opacity, color development in case of colored pigments, gloss, finish, brushability, adhesion, stability and chalk resistance are dependent upon the stability of the pigment dispersion. There are three stages in the dispersion process namely;

- Wetting of the powder, which also involves the displacement of air and adsorbed water from the internal surfaces between particles in pigment clusters.
- Breaking of the pigment clusters, normally accomplished by mechanical energy
- Stabilization - the dispersed particles have a natural tendency to flocculate. To resist this, a particle-particle repulsive force must be introduced into the system.

Wetting Agents

The main function of wetting agents is to decrease the time and energy required for the completion of the dispersion process and stabilizing the dispersions. The inorganic pigments, which have a natural hydrophilic surface and organic pigments, which have a very large surface area and hydrophobic nature, adsorb moisture during manufacture and storage and become so hydrophilic that they do not have affinity for the hydrophobic vehicle. So the dispersion becomes difficult and time-consuming process. A wetting agent whose active pigment seeking end readily absorbs or penetrates the surface moisture on the pigment and also orient to get along with the continuous medium can help in uniform dispersion of the pigment.

Two main destabilization phenomena exhibited by pigment dispersion are flocculation, a loose accumulation of primary particles and settling, an ability of a pigment to sink in a medium. Wetting agents eliminate both these undesirable properties by imparting affinity at the ends oriented away from the pigments for the surrounding phases, thus minimizing selective coupling and decreasing differential mobility of pigments respectively.

Following are five classes of wetting agents :

a) Anionic wetting agents: fatty alcohol sulfonates, alkyl sulfonates, fatty, benzoic, crotonic and naphthenic acids and their salts etc.

b) Cationic wetting agents: Salts of fatty amine and quaternary ammonium salts.

c) Amphoteric wetting agents: Compounds having organic groups of the same size as cation and anion e.g.oleyl amino oleate.

d) Bifunctional, not electrically neutral wetting agents: amino acids, betaines etc.

e) Nonionic agents: polyalkyl ethers.

The wetting agents are used at 0.5 to 2 % baseon pigment, depending upon the surface area of the primary particles.

Rheology Modifiers

Modification of flow properties of paints is important for obtaining optimum application behavior of the paint material, good leveling and no sagging at the desired film thickness. Rheological modifiers include thickening agents, thixotropes, antisettling agents etc.

Thickening agents : Thickening agents are used to provide paint consistency, prevent pigment settling and to assist in applying adequate thickness of paint. In addition to their use as viscosity control agents, they are useful for good dispersion, stabilization and improved brushability of paints. So they are also known as protective colloids. Thickening agents are fairly high molecular weight materials that dissolve by formation of hydration layers along their polymer chains. In solvent based systems gelling-kind agents like aluminium stearate, soya lecithin are used while for water based system, proteins such as casein, cellulose derivatives, water-soluble acrylic polymers, alginates, polysaccharides etc, are used.

Protein based thickening agents like casein, ammonium caseinate give good flow, leveling and fair water resistance. However they are susceptible to yellowing with age, spoilage and putrefaction. Cellulose derivatives include hydroxy ethyl cellulose, methylcellulose, and carboxy methylcellulose. Water-soluble acrylic derivatives like sodium or ammonium salts of polyacrylic acid are largely used for acrylic latex paint systems. Polysaccharide polymers are nonionic in nature and they may be used in surface treated form to avoid agglomeration. Metallic soaps like aluminium stearate, aluminium octoate, and calcium linoleate are used as thickening agents for solvent based systems. They develop a gel structure with the solvent and tend to improve viscosity, pigment suspension and sag resistance. However they are sensitive to other components in the system like free acids, driers etc.

Thixotropes : Thixotropy is the property of becoming lower in viscosity temporarily under the influence of shear, such as the action of mixing or brushing, and then returning to the original viscosity when the shearing action is removed. Thixotropy is useful for good brushability and good resistance to excessive flow at the same time. Additives, which show such shear dependent behavior, are called thixotropes. Thixotropes include acrylic based polymers and organoclays. Organic thixotropes provide viscosity, sag control and pigment suspension. They thicken through macromolecular entanglement. Upon shearing these entangled molecules are pulled free from one another and viscosity increases. When the shear force is removed, the molecules become entangled again. Their main disadvantage is their temperature sensitivity. Their use level is 0.2- 1.0 % based on solid content.

Unlike organic thixotropic agents, organoclays are relatively temperature insensitive and they maintain their thickening efficiency even at elevated temperature. Organoclays used are typically reaction product of smectic clay like bentonite, hectorite and a quaternary fatty amine. Presence of -OH groups on their platelet edges are responsible for their rheological activities. Clays are hydrophilic in nature. By reacting them with quaternary amines such as dimethyl benzyl hydrogenated tallow ammonium chloride, they can be rendered hydrophobic and used for solvent-based systems. Their low thixotropy is advantageous for sag control. Their use level ranges from 0.2% by weight of total system to a maximum of 1.5-2% in linseed oil based systems since linseed oil tends to inhibit the gelling efficiency of organoclays.

Antisettling agents : The main function of antisettling agents is to control pigment suspension, i.e. to prevent settling. They are usually polyolefin in carrier solvents, polyolefin modified with castor oil derivatives. Generally they show some viscosity build-up and improvement in sag resistance. Organic antisettling agents are not effective at high temperature but they regain their property once the system is cooled. They are used at 0.2 to 0.7 % based on weight of the solids.

Leveling Agents

Leveling is the measure of ability of a coating to flow out after application so as to obliterate any surface irregularities such as brush marks, orange peel, peaks or craters, which have been produced by the mechanical process of applying a coating. Leveling agents influence the surface forces thereby limit or prevent flow defects such as pinholes, fisheyes, crawling, edge crawling, sagging etc. They influence the viscosity throughout the bulk of the film. Leveling agents can be solvents or solvent blends having a good solvent power and a graduated evaporation rate, hence influencing the open time necessary for leveling. They can be pigment-dispersing agents, which prevent flocculation of pigments and cause a more newtonian flow even at high pigment concentration. Solvents include cyclohexanol, decahydronaphthalane, dipentene, pine oil, diacetone alcohol, isophorone, n-methyl pyrrolidone, butyralactone, dimethyl formamide etc.

Defoamers and Antifoaming Agents

Defoamers and antifoaming agents are used in aqueous formulations. They are extremely important in minimizing excessive foaming during the manufacturing process and in eliminating the bubble formation in the paint during brushing. Defoamers aid in collapsing of foam already formed in the system, while antifoaming agents prevent new foam creation. Antifoaming agents spread generally over the foam interface and displace the surfactant responsible for stabilizing the foam. Thus they reduce the surface elasticity and / or surface viscosity at the foam-liquid interface. Defoamers and antifoaming agents are usually polysiloxanes, metallic soaps, fatty acids and their esters, fatty alcohols, polyalkylene glycols, high molecular weight polyglycols etc. They are used normally at less than 0.1 to 1% of total weight of the system. Some antifoaming agents, which are effective in small amounts, produce the reverse effect when the optimum concentration for foam control is exceeded.

Grinding Agents

Grinding agents are used in roller-mill grinding that, at a given setting of the mill, increases the rate at which the mill base passes over. They act by giving the vehicle more cohesive strength which makes the paste transfer more readily from one roller to the next roller without any part being carried back. They are effective when the solids in grinding vehicles are low in viscosity and tend to increase the tack of such vehicles, e.g. heavy-bodied oils, rubber solutions. They are used at a level of 0.5-2% based on dry pigment.

Slip-Aids

Slip aids are used for formation of a smooth surface by reducing the coefficient of friction, by providing lubricity or by reducing the number of contact points. Slip-aids include waxes, silicones, PTFE. They are used at 1 to 3% of the total weight of the formulation.

Waxes include paraffin wax, microcrystalline wax, polyethylene and polypropylene wax. Paraffin wax is one of the higher molecular weight petroleum distillates having melting point range of 50-60 oC. Because of their low melting points, they form a barrier film that is impervious to moisture. However upon long term rubbing they tend to lose their effectiveness.

Microcrystalline waxes are derived from the residual fraction during the refining process after other lower boiling points compounds have been distilled off. Because of their crystalline nature, these waxes exhibit harder surface properties than paraffins. They give a less greasy, harder films and good mar resistance.

Polyethylene waxes are saturated compounds having molecular weight between 1000 and 3000. Because of their higher molecular weights and more insolubility, they are preferred when good lubricity and mar resistance are required. Due to their fine size, they are easy to incorporate into a coating. Compared to polyethylene waxes, polypropylene waxes are not very good slip additives. However they are used when a hard wax with high melting point is required.

Silicone additives improve the slip properties of the dried coating which then exhibit improved blocking and scratch resistance.

PTFE is quite inert in most coatings and is insoluble in most of the solvents used in paints. PTFE, owing to its high density, cannot be used in low viscosity systems. So it is generally used in combination with polyethylene wax. The PTFE-PE combination imparts high gloss, good slip, good scuff and antiblocking properties.

Heat and Light Stabilizers

The main function of the coating is to provide protective barrier against external agencies like oxygen, moisture, light, heat and pollutants. Coatings should maintain their useful properties such as adhesion, flexibility, water resistance and impermeability throughout their useful life. However polymers on their own can not give adequate resistance to the external environment. So external additives like UV stabilizers, light stabilizers are incorporated to give protection against degradation due to weathering.

High energy UV light is detrimental to the performance of polymers because each polymer material can be damaged particularly easily at one or more wavelengths in the UV range. Pure polymers like PMMA, PE, aliphatic esters are stable to UV light, as they do not contain chromophores that can absorb light in this range. However they do degrade when exposed to sunlight. This is because commercial polymers contain catalyst residues, d processing aids, oxidation products, and adsorbed atmospheric pollutants. Other polymers like aromatic polyurethane, epoxy resins contain UV absorbing chromophores as part of their basic structures and do not require additional impurities to promote degradation.

Reactions that produce free radicals are particularly harmful because they can initiate photooxidation, photolysis as shown below:

Initiation:

$$\text{Polymer} \xrightarrow{\text{light}} \text{P}\cdot$$

Propagation

$$\text{P}\cdot + O_2 \longrightarrow \text{POO}\cdot$$

$$\text{POO.} + \text{PH} \longrightarrow \text{POOH} + \text{P.}$$

Termination

$$\text{P}\cdot + \text{P}\cdot \longrightarrow \text{P}-\text{P}$$

$$2\,\text{PO}\cdot \longrightarrow \text{POOP}$$

$$\text{P}\cdot + \text{PO}\cdot \longrightarrow \text{POP}$$

The radicals such as .OH and .RO formed in the photolysis reactions are very active and attack the polymer to produce alkyl radicals that can initiate new chain reactions as follows;

$$\text{PH} + \cdot\text{OH} \longrightarrow \text{P}\cdot + H_2C$$

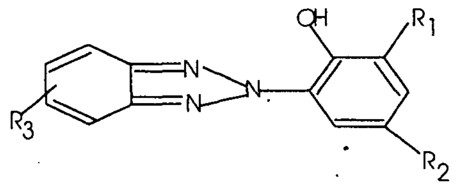
$$\text{PO}\cdot + \text{PH} \longrightarrow \text{P}\cdot + \text{POH}$$

Termination of oxidative chain reaction by coupling of free radicals can result in crosslinking of the polymers. Thus photooxidation can lead to chain scission and / or crosslinking. Any change in physical properties due to such degradation reactions can result in deterioration of properties and lead to embrittlement, color change, change in tensile strength, increase in hydrophilicity, and change of glass transition temperature of polymer network.

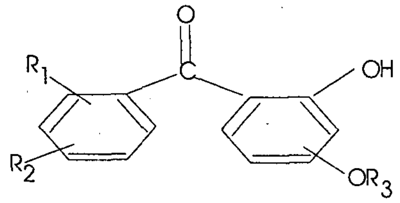
Ultraviolet screeners : Certain pigments like carbon black and titanium dioxide absorb light and can increase UV stability of the coatings. However some screeners that absorb UV light can become sites for degradation, e.g. titanium dioxide upon absorption of UV light can eject electrons forming electron holes. Interaction of the holes with hydroxide ions or the electrons with oxygen and water can form free electrons.

Ultraviolet absorbers : UV absorbers, like UV screeners are designed to work by absorption of UV light and thus interrupting the first step of degradation process. However unlike the pigments used as screeners, these are colorless additives, which absorb light very intensely in the UV region, and they dispose the absorbed actinic energy safely as heat. There are four different classes of UV absorbers as follows,

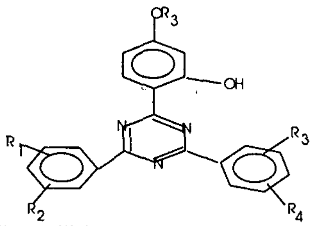
1) Hydroxyphenyl benzotriazoles



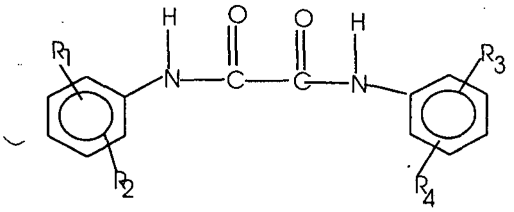
2) Hydroxy benzophenone



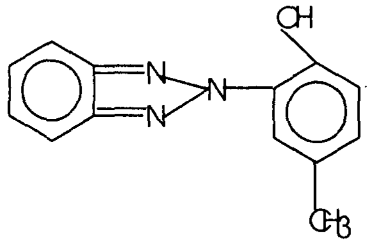
3) Hydroxy phenyl -5-triazines



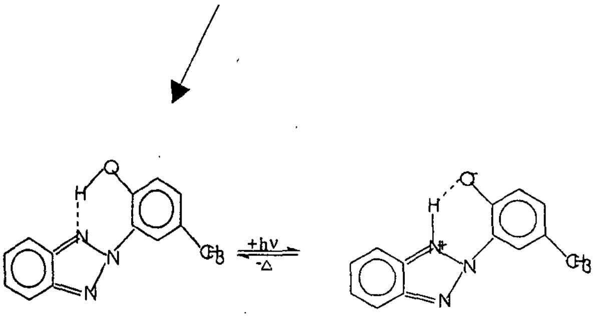
4) Oxalic anilides



An ideal UV absorber will absorb all radiation from 290 to 400 nm but will absorb no light in the visible region of the spectrum. Absorption of light with wavelengths longer than 400 nm will cause discoloration of the coating. Derivatives of compounds like 2-hydroxy phenyl benzotriazoles such as 2-(2'-hydroxy-5'-methyl phenyl) benzotriazole (I) approach the requirement of an ideal absorber.



(I)



(II) (III)

Before the absorption of light, the UV absorbers exist in the phenolic form (II), since the electron density on the oxygen atom is much greater than the triazole nitrogen atoms, making it a stronger base. Absorption of light causes a major shift in electron density away from the oxygen to the nitrogen atoms of the triazole ring. The proton is very rapidly transferred to the nitrogen atom of the triazole ring forming the tautomer (III) and thus making the phenol more acidic and the nitrogen more basic. Being unstable, this tautomer disposes of its excess energy safely as heat, whereupon it returns to the more stable ground state (II). The overall process is extremely efficient and can be repeated almost indefinitely accounting for the compound's photostability.

Hydroxy phenyl -5-triazines have the broadest absorption band and higher photochemical resistance. Compounds like 2-hydroxy phenyl triazole and 2-hydroxy benzophenone are multifunctional additives. They not only absorb light, but also are capable of quenching photoexcited chromophores in a variety of polymers. UV absorbers are used usually at a concentration of 1-2% based on binder solids.

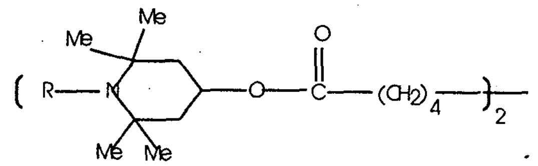
Light stabilizers : If due to the absorption of light by the coating, a molecule is taken to its excited state, and if there is no other mechanism by which it releases energy, bonds can break homolytically to form free radicals of various types.

$$R \longrightarrow R^{*} \longrightarrow R^{**}$$

Once at this stage, if the radicals are not terminated, they can combine with oxygen and the autooxidation chain reaction begins.

Additives such as hindered phenols and hindered amines are designed that can terminate free radicals. Since phenolic and hindered amine antioxidants, unlike UV absorbers, do not depend on the thickness of the sample for effectiveness, they are especially useful for substrates that have a high surface to volume ratio such as thin coatings. Hindered phenols are able to inhibit oxidation by scavenging most of the oxygen-centered free radicals such as RO", ROO" before they are able to attack the polymeric substrate to form an alkyl radical. Conventional phenolic antioxidants used to protect polymers against thermally induced oxidation provide limited protection against photooxidation, since they are degraded in a short time when exposed to sunlight. Thermal antioxidants derived from hindered phenols are used to protect coatings that are baked at high temperature. They inhibit the development of color and the buildup of hydroperoxides and carbonyl groups. Oxidation derived products from these stabilizers can act as photosensitizer and decrease the light stability of the coating e.g. esters of 3,5 di-tert-butyl-4- hydoxybenzoic acid.

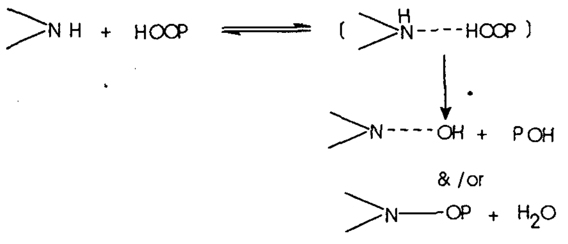
Hindered amine light stabilizers (HALS), used at a concentration of 1% based on binder solids, are outstandingly effective in extending the outdoor aging life of polymers that are susceptible to photooxidation, such as polyurethanes, acrylic coatings. Two typical sterically hindered amines are as shown below;



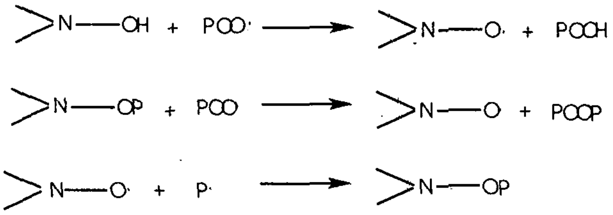
HALS I R- CH_3 HALS II R- -O-C_6H_{17}

Tetramethylpiperidine group is responsible for the stabilizing action. HALS I having pKa value of 5.5, is used in the systems that are not catalyzed by strong acids while HALS II, having pKa value of 10 is used in acid catalyzed system as it does not undergo undesirable interactions with acid catalysts.

They function primarily as highly effective light-stable antioxidants. The hindered amines do not absorb in UV region but can contribute to photostabilization by trapping alkoxy and hydroxy radicals produced by light-induced dissociation of hydroperoxides. The trapping efficiency of hindered amine may be enhanced in nonpolar polymer by association with the hydroperoxides.



HALS are capable of retarding thermal oxidation. Polymers stabilized with HALS contribute to resistance to photodegradation even after the starting hindered amines have been completely consumed as against hindered phenols, which oxidize to products that are potential photosensitizers. This is because hindered amine oxidation products such as hydroxylamines and hydroxylamine ethers as shown below are also inhibitors of photooxidation.



Combination of UV absorbers and HALS has been found to provide synergistic protection. In fact this combination is the single most powerful tool for coating known today.

Biocides

The microbes of concern to the paint and coating industry are bacteria, yeast and fungi. Each of these organisms has a particular set of environmental conditions that it requires for optimal growth. The bacteria require relatively high moisture levels in their environments so are found in water-based paints and other fluids containing water. The fungi grow upon the surface of paint film and coatings, as they do not require such high levels of moisture. The yeasts, which seem to be mid-way between the bacteria and fungi in many of their environmental requirements, inhabit water-based systems and also the surfaces of coatings. The microbes can effectively change many thousand of substrate molecules to undesirable products. This ability, coupled with the fact that the enzyme is not consumed in the process, allows for extremely minute amount of these substances to trigger viscosity loss, the major economic problem of paint industry. Other undesirable problems are malodors, discoloration and on occasions gas formation.

Biological active compounds that cause the death of the degradative organism are called biocides. There are three classes of biological active materials for use in coatings; bactericides and bactriostats, fungicides and fungistats, and microcides, the materials that are generally toxic to all microbial life.

Bactericides kill bacteria at a specific concentration and may be inhibitory at low concentration whereas bacteriostats act as inhibitory at use concentration and may not kill organisms even at much higher concentrations. Similar is the case with fungicides and fungistats. Fungicides have little effect on bacteria. This difference stems from basic physiological and biochemical differences between these two types of organisms. Bactericides are also known as in-can preservatives while fungicides are known as film preservatives. The third class of biocides is effective against both bacteria and fungi. In most cases, there will be a difference in the levels required, but both are in a practical cost/ dosage range.

The selection of biocides depends upon the system to be used for, e.g. for water-based indoor paints, in-can preservative is needed while exterior water-based paints require both in-can and outdoor microbial protection. Solvent-based coatings may not need in-can preservatives but require fungicide to prevent mildew growth in an exterior environment. Liquid biocides are added generally with the solvent at an additional stage of manufacture, whereas insoluble additive is added after thickener but before the addition of primary pigments. There are some interactions of biocides, which are known and can be avoided.

e.g. mercury compounds will be inactivated in formulations containing iron pigments or sulfur compounds ; vegetable oils in coatings supply the main nutrition for microbes and the degree of bodying or polymerization of the oil directly correlates with microbial growth.

Bactericides: 3,5 dimethyl tetrahydro-1, 3,5- 2H thiadiazine-2-thione, phenyl mercuric acetate, di (phenyl mercury) dodecenyl succinate, phenyl mercury oleate, zinc dimethyl dithiocarbamate, hexahydro-1,3,5-triethyl-5-triazine.

Fungicides: tributyl tin salicylate, tributyl tin oxide, 2-(4- thiazolyl) benzimidazole, zinc napthanate, copper napthanate

Adhesion Promoters

Adhesion promoters are used to improve the adhesion of polymers to inorganic substrates. Bituminous paints and those based on natural resins have great wet adhesion qualities. Organofunctional silicone additives, by virtue of their dual reactivity and being hybrid organic-inorganic coupling agents react with both the polymer and mineral component forming durable covalent bonds across the interface. Being hydrolysable and reformable, these bonds provide a means of stress relaxation at the organic/inorganic interface, resulting in improved adhesion and durability. Only handful of organofunctional silanes (with the general formula X3Si (CH2)nY; n=0-3, Y- organofunctional group and X- easily hydrolysable group) have the balance of characteristics such as polymer reactivity, covalent bonding to inorganic substrates, water solubility, hydrolyzability, wetting control, surface activity, etc. required in successful adhesion promoters.

Incorporation of silane adhesion promoters result in number of advantages such as ;

a. Improved mar resistance and adhesion of coatings

b. Improved retention of properties after exposure to moisture, water immersion and salt-spray.

c. Improved dispersion of fillers and pigments, often resulting in less air occlusion, giving fewer voids

d. Improved bond durability

e. Minimization of filler/pigment cure inhibition.

The effective use concentration is in the range of 0.05 to 1% of the total system. However use of optimum level is necessary otherwise the excess quantity may result in other problems such as low shelf life due to tendency of silane to hydrolyze readily, loss of coating adhesion due to absorption of the silane by the filler or pigment.

Corrosion Inhibitors

Corrosion is a wet oxidation process and occurs when both oxygen and water are present. Corrosion inhibitor reduces the aggressive nature of the corrosive medium by reaction at the metal-to-metal or metal- to-coating interface. Inhibitors can be classified as oxidizing agents (chromates), nonoxidizing inorganics (phosphates), metallic cations (zinc salt), sacrificial pigments (zinc dust) and organic compounds (amines).

Chromate, incorporated on the surface of the inhibited metal as chromium oxide or hydroxide, protects the underlying metal by its very low solubility. The nonoxidizing inhibitor ions apparently do not participate directly in the formation of oxide film, but their function is limited to the discontinuities in the oxide film. Pore plugging of the defective areas in the film is provided by precipitation of the anion. Metallic cation inhibitor mechanisms include; 1) altering the cathodic reaction (2) affecting morphology of the corrosion product or the corroding metal (3) changing the nature of the metallic oxide on the surface (4) formation or precipitation of an insoluble barrier layer at the metal surface 5) formation of complex intermetallic compounds and (6) adsorption of cations or metal atoms on the metal substrates. Metal cation can change the catalytic activity of the steel surface and decrease the rate of cathodic reaction. Sacrificial pigments such as zinc function initially by cathodic protection of steel and subsequently by the sealing action of the corrosion products on the coating surface.

Organic inhibitors provide protection by various methods depending on the compound's functional group and they include amines, carboxyls, ring nitrogen, hydroxyls, mercaptans, sulfonate and acetylenic compounds. As a result, organic inhibitors function by chemisorption electrostatic adsorption or p-bond orbital adsorption.

Apart from these corrosion inhibitors, there are some pigments which also act as corrosion inhibitors like zinc phosphate, calcium barium phosphosilicates, molybdates, borates etc. Zinc phosphate is not basic so can be used in paint media of most types. Phosphosilicates are particularly useful in water-based coatings as their low solubility provides package stability in combination with good performance against corrosion. Borates are water-soluble and have high pH so they are very effective in many resins such as alkyd resins. Because of their high alkalinity, borate pigments buffer coating-metal interface at alkaline pH, above 9, at which iron is passivated.

Molybdate pigments passivate iron and steel through the development of a protective film of ferric molybdate, which stops corrosion of metal substrates.

Amongst organic corrosion inhibitors, basic alkaline earth sulfonates are the mostly widely used for improving corrosion resistance of coatings on steel.

These sulfonates are available as lubricants dispersed in petroleum oils. They are specifically useful in asphalt type of automotive underbody coatings, as the compatibility problem does not exist whereas they are not very effective for high performance coatings. Zinc, barium, calcium and magnesium salts of dinonyl naphthalene sulfonic acids are used as inhibitors due to their strong tendency to be adsorbed on iron oxide. Zinc, calcium and sodium salts of aliphatic or aromatic acids have been used as corrosion inhibitors for various coatings. Organic compounds containing nitro groups are oxidants that passivate iron surfaces. Of the nitro-carboxylic acid salts, Water-soluble nitrites are particularly effective in water-based coatings. Zinc and lead salts of nitrogen heterocyclic organic compounds offer improved dispersion and antisettling properties. The extremely low water solubility of the salts provides an improved stability and extended protection of the corrosion protective coating or lacquer films prepared with them, since these salts can not easily be washed out of the lacquer film e.g. zinc or lead salts of mercaptobenzothiazole as well as mercaptopyridine.

Amine and amine salts of carboxylic acids are well known as corrosion inhibitors for steel. Cyclic amines are better inhibitors than aliphatic amines since the electron density at the nitrogen atom; the atom constituting the main reaction center, in the latter is considerably low. Highly alkaline quaternary ammonium hydroxide may control corrosion in organic systems by forming salts with chloride ions, which serves to reduce their availability for corrosion.

By maintaining coating adhesion to a metal substrate during exposure to adverse environment, corrosion can be prevented. It would be ideal to have a coating system with a corrosion inhibitor that protects the passive surface of the metal from chloride ions diffusing through the coating and at the same time provides a compound that will form a bond between the metal oxide layer and the organic coating. Since corrosion is a wet oxidation process, it is important that the additive provides adhesion retention under high humidity or wet conditions. Silanes are preferred for such applications. Other corrosion inhibitors include organotitanates, chelation additives like benzotriazole.

Antirust Agents

Rusting in container is a problem in emulsion paints based on polyvinyl acetate homo- or co polymers, which must be stored for considerable period of time. They are supplied in the acidic pH range. This acidic pH becomes instrumental in promoting rusting in a container. Rust inhibitors are added to reduce the rust in the cans e.g. ferrous ammonium phosphate, barium potassium chromate, lead cyanamide, sodium benzoate etc.

Antiskinning Agents

Skinning is a formation of thick layer or a skin as a result of autooxidation when paint is exposed to the air. Enamels based on oil highly susceptible to oxidation, highly polymeric alkyds when exposed to air form a skin as a result of oxidation. Driers when used in excessive level have a tendency to aggravate skinning. Other factors that will produce skinning are gelation by loss of solvent, combination of surface oxidation and gelatin by solvent loss to upset the colloidal balance of the product. Antiskinning agents like oximes, phenols and antioxidants are added to control skinning. These additives are volatile antioxidants which tend to hold back the preliminary oxidative gelformation in the can but which volatilize when the paint is applied and allowed it to dry in a normal manner.

Oximes (used at 0.1-0.6 % of total paint) like methyl ethyl ketoxime, butyraldoxime, function by temporarily complexing the active drier. Phenols like cresols, guaiacols and o-isopropyl phenol are also used as Antiskinning agents at a level of 0.05 to 0.2% of total paint. Antioxidants are also very effective in controlling skinning; the most common being substituted phenolic compounds. Their use level must be evaluated as excess use may retard drying considerably. Strong solvents like dipentene, pine oil are used to provide some anti-skinning benefit.

Surface Tension Depressants

Surface tension is developed within the paint during drying. This surface tension difference results in material transport from the low surface tension region to higher surface tension. This movement manifests into defects such as fat-edge, picture framing etc. Silicone additives lower the surface tension of coatings and minimize the surface tension differences.

Coalescing Agents

Coalescing agents (at a level of 2% based on the total weight of the system) are used in water-based systems to soften and solvate partially the latex particles in order to help them flow together and form a more neat continuous film, particularly at low temperature. They are temporary plasticizers, which promote the coalescence by increasing the amount of plastic flow. The materials used are ether-alcohols such as butyl glycol, butyl cellosolve, butyl carbitol, tributyl phosphate, pine oil or other strong solvents. Most coalescing agents volatilize slowly but eventually evaporate from the film.

Wet-Edge Extenders

During the application of paint, if a solvent evaporates rapidly, the wet coating becomes very viscous under the brush and leaves lap brush marks in the final dry film. Wet-edge extenders are compounds, which maintain the longer wet-edge time i.e. longer time before the wet coating becomes viscous, and enable formation of uniform films. In emulsion paints, rapid removal of water by any of the factors like temperature, humidity, wind and substrate leaves the latex particles stranded. These latex particles are unable to approach neighboring particles and merge to form a film. Water is an intractable material because it is extremely difficult to modify its properties like evaporation rate, boiling point etc. Control tools available to the formulator are the co-solvents such as glycols, alcohols and ether-alcohols, which reduce vapor pressure and therefore reduce evaporation rate. The low volatility of these wet-edge extenders lowers their tendency to evaporate and consequently lead to uniform and continuous films.

Because the glycols, which are poor solvents for the latex particles, are readily soluble in water and retard its desorption from the latex particles, they are control agents for freeze thaw resistance.

Freeze Thaw Stabilizers

Freezing of emulsion-based paints causes the coagulation of the disperse phase unless the paint has been formulated to be freeze-thaw stable. Thawing results in break-down of the emulsion into a sticky oily mass and increase in viscosity in some cases. The process is generally irreversible. So anti-freeze additives are usually incorporated in latex paints to overcome this tendency during the transportation, storage and uses in cold climates having temperature under 10oC over a long time.

Glycols are usually used as freeze thaw stabilizer. Glycols do not necessarily prevent freezing but rather contribute to an orderly redistribution during the thawing of water-soluble materials upon which the dispersion of the system depends.

Sequestering Agents

Casein-based formulations may exhibit localized thickening usually found along the seam of tinplate containers, or in areas where there is direct contact with iron. Water-soluble alginates thicken in presence of polyvalent ions. The use of sequestering agents controls the thickening due to polyvalent ions. They complex with these polyvalent ions and increase their solubility in the media. Sequestering agents include potassium tri polyphosphates, tetra sodium pyrophosphate, sodium salts of ethylene diamine tetra acetic acid, barium citrate etc.

Antistatic And Conductive Additives

Antistatic agents, particularly of cationic type, are incorporated to increase the conductivity of the paint surface and assist in overcoming the nuisance of dust attraction. Antistatic agents include amine salts, quaternary ammonium compounds, oleyl polyglycols ether etc.

Paints formulated largely from nonpolar solvents have an electrical resistance that is too high for satisfactory application by electrostatic spray technique. It is necessary to reduce the paint resistance below 1MW for which very large proportion of polar solvents would be necessary. Instead certain additives such as quaternary ammonium compounds can be used as conductive additives.

Fire Retarding Additives

Fire retardancy can be achieved by incorporating additives that decompose endothermically, thus lowering the temperature at the flame front below the point at which fuel is generated. Similarly other additives on decomposition produce noncombustible gasblanket thus lowering oxygen content. Additives used for flame retardancy are antimony trioxide, organic bromine compounds like 1,2 dibromo-2, 5 dichloro ethyl benzene, 1,1,2- dibromoethane, antimony silico-oxide, barium metaborate, zinc borate, aluminium trihydrate etc.

Driers

Driers are used to accelerate the drying of curing of the oxidizable coatings. Metal soaps are used as driers. Metals used have multiple valency while the acids render the metal solubility in the vehicle. Driers are classified as Active and Auxiliary driers. They are usually supplied as liquid solutions in solvents or oils.

Drying of the unsaturated oil based films takes place by autooxidation reactions. The drying process comprises of stages such as oxygen absorption, peroxide formation and peroxide decomposition leading to subsequent free radical generation for polymerization or formation of three-dimensional network in the coating. The role of driers is to accelerate the autooxidation by enhancing the oxygen uptake.

Metals like cobalt and manganese are classified as active driers. Active driers readily undergo oxidation-reduction reactions. Cobalt driers are the most extensively used driers and are available in 6 and 18% metal concentrations. Their use level ranges from 0.02 to 0.05 % metal based on the total nonvolatile binder. For bake finishes the range is 0,005 to 0.02 % metal. When used in excess, Co driers can give rise to various problems like wrinkling, low gloss, brittle films, poor thorough drying, discoloration and skinning. Mn drier is an effective alternative to Co drier when wrinkling is a problem. Its use level is same as that of Co drier. Iron drier is a speciality drier active at higher temperature. It is used in bake coatings that require more hardness. However it imparts brownish red color to the coating.

Auxillary driers have little influence on drying when used alone. However they accelerate the drying and improve film properties when added to a coating in combination with active driers. Auxillary driers include zinc, calcium, zirconium, and bismuth metals. Lead based driers give excellent thorough dry over a wide temperature range in most alkyd-based coatings. However their used is limited due to their toxicity. Calcium drier finds use in a variety of coatings and is available at 4,5,6 & 10% based metal concentrations. It improves the drying characteristics at low temperature and high humidity. Zirconium drier is effective in both ambient and bake coating systems. It improves gloss, hardness and hardness without adversely affecting other coating properties. Its use level ranges from 0.03 to 0.2% metal based on nonvolatile vehicle.

Selection of the drier for a particular system is based on the required drying rates and interactive effects of other components in the system. For water-reducible coatings the selection of the drier is critical as these systems contain amines as neutralizing agents. Amines affect drying times due to their complexation with metals. Secondly relatively low solubility of oxygen in water as compared to organic solvents delays autooxidation reactions

There are other additives such as glossing agents, flatting agents, antisagging agents that are used to accomplish specific property in the coatings. More and more new proprietary additives are coming into the market. The quantity in which these additives are employed is very insignificant but they influence the overall performance of the coating in every stage of its life. Their correct dosage is extremely important for optimum effectiveness and also to avoid undesirable side effects like loss in adhesion if excess of silicone additives is used, slow drying in case of excessive antiskinning agent, improved freeze-thawing tendency due to the presence of coalescing agents etc., to name a few. Secondly the same compound like silicones, metallic soaps can perform multifunction in the same formulation. Sometimes their function is limited due to the nature of the system like HALS, due to its basic nature, will not be effective in acidic media. So thorough evaluation of an additive is a must before employing it for final use.

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