Anti-Corrosive Pigments

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A pigment is an inorganic or organic solid in a state of fine subdivision (average particle size less than one micron), which, either alone or in conjunction with a suitable film forming composition, has the ability to hide and colour a surface when spread on it in thin layers. Pigments are mainly employed in the manufacture of paints and printing inks, though they are also used for various other purposes, e.g. reinforcing of rubber, delustering of rayon, glazing of ceramics, etc. Certain pigments, besides their characteristic colour and opacity, may also show other specific properties such as fluorescence, luminescence, toxicity and corrosion-inhibition. Also, in some cases, these secondary characteristics may be of greater usefulness, while the colour and opacity are of minor importance. Anti-corrosive pigments belong to this special category, and when used as paints with an appropriate binder, have the ability to inhibit, or at least suppress, the corrosion of metal surfaces over which they are applied in thin layers.

The term corrosion is applied for the wastage or deterioration of metals by chemical processes and may thus be distinguished from erosion which denotes a wearing away by mechanical agencies. Corrosion may occur either as a direct chemical, or as an electro-chemical attack. Mutual contact of metal with certain chemicals or exposure to humid environment affords conditions for direct chemical attack. Atmospheric corrosion is enhanced if atmosphere is fouled with gases such as carbon dioxide, sulphur dioxide, oxides of nitrogen, acidic fumes and suspended particles of electrolytes. Electro-chemical corrosion occurs when a metal, which occupies a position higher than hydrogen in the electromotive series, is immersed in water. The rate and extent of corrosion is dependent on the type and amount of other ions in solution. The corrosion can be purely chemical, as in the presence of hydrogen ions and dissolved oxygen, or galvanic, when another metal lower in electromotive series is in electrical contact with the first.

It is obvious therefore, that in order to prevent[1] or minimise corrosion, moisture and oxygen are to be excluded from the metal surface, and the best way is to have a thin layer of a protective coat. However, as such protective coats, barring a few exceptions, are still permeable to water and air, it is essential to maintain alkaline conditions at the interface. Furthermore, if a galvanic circuit is likely to be formed, then either there should be an intervening insulating layer or alternately the metal surface should be rendered cathodic.

In view of the widespread use of iron and its alloys for structural purposes, agricultural implements, industrial equipments, etc., protection of iron and steel from corrosion has acquired considerable significance. In recent years aluminium and its alloys have also become prominent, not only because of their use in air-craft construction but also because of their use in automobile parts, chemical plant, domestic ware, etc. Iron and its alloys are best protected by having a layer of metal which is electropositive to it, e.g. zinc, applied by way of dipping, spraying or electroplating. As galvanised or zinc coated iron also corrodes with the formation of zinc oxide, it is essential that either the iron, as such, or after galvanising, is given a

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protective coat which could be conveniently replaced at infrequent intervals. Unlike iron, aluminium and its alloys do not require a protective coating of metal, as a layer of aluminium oxide is formed on the surface which prevents or at least suppresses further corrosion. However, in order to maintain the decorative effect of aluminium surfaces, it is desirable that they are also given an appropriate protective coating. Obviously, by using specific iron or aluminium alloys it should be possible to have a minimum amount of corrosion ; but such special alloys are costlier than the parent metal and their usual alloys, thus making it necessary to protect these common metals and alloys against corrosion by the application of protective coats.

Of the many methods of protecting metal surfaces, painting is perhaps the most important. A paint is essentially a dispersion of a pigment, or mixture of pigments, in a suitable film forming medium, whose flow characteristics have been adjusted to meet the specific method of application. As none of the paint compositions are completely impermeable[2] to moisture and air, more than one coat of paint is necessary in order to protect metal surfaces against corrosion. The first coat of a paint to be applied should have not only good adhesion to the metal surface but should also possess anticorrosive properties, i.e. maintain alkalinity at the interface. Besides, it should offer a suitable surface to take on the next coat of paint. The second, and possibly a third coat should be non-reactive and of low permeability in order to impart maximum durability. The combined paint film, in addition, should have a coefficient of expansion which is of the same order as that of the metal substrate in order to maintain film continuity with changes in environmental temperature conditions. The elastic properties of the paint film should also be unaffected to any appreciable extent by variation in humidity. The first coat of paint applied to a metal surface is termed primer and is usually of an anticorrosive composition.

The choice of the appropriate medium[3] to give tough, elastic, adherent and durable film is of the utmost importance. Numerous film forming compositions are in use, each one having some outstanding characteristics. However, drying oils, both raw and heat treated, oil varnishes, alkyd resins, chlorinated rubber are some of the more important binders used in anti-corrosive compositions. The various film forming compositions may also contain added solvents which evaporate after application. While the importance of binder cannot be overlooked, the determining factor is the pigment, which should be so chosen as to obtain maximum performance with the particular medium.

Anticorrosive pigments can be divided into four groups namely, (i) basic pigments, (ii) chromate pigments, (iii) metallic pigments and (iv) miscellaneous pigments.

Basic Pigments :

The anticorrosive effect of basic pigments is associated with the soap formation by reaction with a saponifiable component of the medium and also with their alkaline nature, which make them mild anodic inhibitors. Among these pigments red lead deserves pride of a place. Red lead[1] is a pigment of ancient origin and it has a long record of successful application in anticorrosive formulations. It is manufactured by direct oxidation of metallic lead with air. In the older furnace process lead is oxidised first to massicot, (PbO), which is further oxidised to red lead (Pb_3O_4) in a subsequent operation. In the modern fume process vapourised lead is oxidised directly in a current of air to form red lead. Fume red lead has finer particle size and is superior to furnace red lend in keeping qualities. Red lead contains 72-95% Pb_3O_4 and 5-28% PbO. Pb_3O_4 acts as an oxidising agent and keeps the superficial oxide film in good repair, whereas PbO acts as a mild anodic inhibitor due to its alkaline nature. The formation of lead soap in a paint helps in making the film tougher and resistant to water.

Red lead is used in conjunction with raw linseed oil and boiled oil with perhaps a small quantity of turpentine to impart ease of brushing. The usual grades of red lead, however, set to a hard mass when the dispersion in oil is stored for any length of time. Non-setting grades of red lead are however available which do not suffer from such a defect. These grades contain very little free litharge. Because of the high density of red lead and also its poor spreading or covering power and difficulty of brushing, red lead is generally extended with other pigments. Preference is given to fibrous extenders like asbestine or laminar pigments like mica and talc, though ordinary pigments like barytes or iron oxide can also be employed. However, red lead should form at least 50% of the total pigments in order to maintain useful anti-corrosive properties. Also to compensate for the absence of free litharge in non-setting red lead, it is customary to employ small proportions of white lead or zinc oxide. Red lead is unique in that its performance is best with linseed oil medium, though it can also be used with phenol—formaldehyde—tung oil varnishes or plasticised chlorinated rubber; its use however, is restricted only to iron and its alloys.

Other basic lead pigments used in anti-corrosive compositions are basic carbonate white lead (BCWL), basic sulphate white lead (BSWL) and blue lead.

BCWL, [$2PbCO_3$, $Pb(OH)_2$], is prepared by the action of carbon dioxide, moisture and acetic acid on metallic lead at 50-70°C. In recent years it has been manufactured by electrolytic methods. BSWL, [$PbO.2PbSO_4$], is prepared by partial oxidation of vapourised galena in a current of air. Blue lead contains a mixture of basic sulphate, sulphite and sulphide of lead, and some carbon. It is manufactured by oxidising galena in the presence of carbonaceous materials. Its bluish-grey colour is due to lead sulphide and carbon. Among these three pigments basic carbonate and sulphate have only mild inhibitive properties, but blue lead possesses corrosion inhibitive properties and under certain conditions (water immersion) this pigment shows performance superior to that of red lead.

Of the recent developments in basic anti-corrosive pigments lead cyanamide[4], ($PbCN_2$) and orthoplumbates of alkaline earth metals are of importance. Lead cyanamide[5] is industrially prepared by leaching calcium cyanamide with water and treating the resulting extract with lead nitrate or acetate solution. The product obtained at this stage is further treated with hydrogen peroxide to oxidise other lead compounds such as lead sulphide, lead carbide, etc., which are formed due to the impurities in commercial calcium cyanamide. Lead cyanamide is yellow in colour and it has lower density, better can-stability and higher covering power than that of red lead. It reacts with free fatty acids of the medium to a greater extent and at a more rapid rate than red lead. It has been suggested that inhibition[6] of corrosion by lead cyanamide is due to the formation of $(NH_4)_2CO_3$ and $Pb(OH)_2$; the former renders the medium alkaline, while the latter is absorbed on the surface of iron. It neutralises sulphur compounds[7] which often form on metal surfaces and eliminates traces of water by reacting with it to form ammonia which in turn enhances the corrosion inhibitive properties of the coating. Even extended lead cyanamide pigment is superior to similarly extended red lead pigment. Lead cyanamide paints can be based on linseed oil, alkyd resins, chlorinated rubber and polyvinyl resins ; but maximum corrosion inhibitive effect is obtained by the use of linseed oil and boiled oil. The excellent elasticity of the paint film counterbalances its higher swelling characteristics, thus maintaining the anti-corrosive effect. Lead cyanamide paint is used for steel-frame superstructure, in mining and metallurgical industries, chemical industries and for painting cars and ships.

Red lead may be looked upon as lead salt of orthoplumbic acid. Alkaline earth orthoplumbates are prepared on the basis that replacement of plumbous radical by alkaline earth radical will help in conservation of lead, without impairing their corrosion inhibitive properties. They are more basic than red lead, but only anhydrous orthoplumbates are of pigmentary interest, as hydrated compounds are too reactive for use in paints.

Alkaline earth orthoplumbates[8] are prepared by heating alkaline earth metal oxides or carbonates with lead monoxide in air under controlled conditions. These plumbates are water insoluble and easily dispersible in oil to form a stable paint of high opacity. Among these the calcium salt is the most used because of its pale buff colour and low specific gravity. Though calcium plumbate contains the highest proportion of lead its low specific gravity always keeps the total lead in the paint at a minimum. Calcium plumbate, because of its powerful rust inhibitive properties and toughening effect on the paint film, can be used with large amounts of extenders. It can be used in tinted paints and does not affect the shade of alkali sensitive pigments. These pigments can be conveniently used with drying oils, though plasticised chlorinated rubber and long oil alkyd varnishes are to be preferred. They have the advantage over red lead from the point of view of superior can-stability, greater covering power and ease of application. Like red lead they can be employed only for iron and its alloys but not for aluminium.

Zinc oxide is sometimes used as an anti-corrosive pigment as it has got a weak anodic inhibitive power and the ability to neutralise acidity of the medium. However, its anti-corrosive properties are of a very low order and as the film in oil media lacks toughness it is rarely employed by itself.

Chromate Pigments:

Chromate pigments are powerful corrosion inhibitors as they render metal surfaces passive to further oxidation. The mechanism[9] by which corrosion inhibition occurs is not completely understood, but it has been suggested that ferrous ions formed at the surface combine with the chromate ions to give a ferric-chromic hydroxide-chromate complex which completely seals the surface from further attacks by oxygen and moisture. It is obvious that chromate pigments must be capable of ionisation under conditions of use.

Pure lead chromate ($PbCrO_4$) has very little inhibitive action, though in the presence of basic pigments like zinc oxide or white lead improved performance may be obtained. Basic lead chromates ($PbO.PbCrO_4$) on the other hand are slightly more effective but owing to their insolubility in water their corrosion inhibitive action is not of a high order. Superior performance is obtained with the chromates of group II metals of the periodic table.

Zinc chromate is perhaps the best known pigment of this group. Zinc chromate ($4ZnO.K_2O.4CrO_3.3H_2O$) is prepared by the action of potassium dichromate on zinc oxide containing small percentage of zinc sulphate. As the pigment is slightly soluble in water, it is not possible to wash it free from sulphate ions, the presence of which is undesirable in anti-corrosive compositions. Zinc chromate readily gives out chromate ions in contact with water and hence it is more effective. Its slight solubility however, is a disadvantage in that the paint film becomes weaker in corrosion inhibiting action. It is, therefore, necessary to employ a medium which gives a compact film with superior water resistance. Drying oils cannot therefore be employed but oil modified alkyd varnishes of low acid value have been found to be eminently satisfactory.

Zinc tetrahydroxy chromate, [$ZnCrO_4.4Zn(OH)_2$], as against the usual zinc chromate, overcomes some of the defects. The pigment is readily prepared from a soluble zinc salt and alkaline sodium chromate. It is much cheaper than zinc chromate and has the advantage that it can be employed with drying oils, though superior performance is obtained with alkyd varnishes. The pigmented composition also maintains its effectiveness for much longer periods.

Primers based on zinc chrome can be employed on all metal surfaces though they are particularly suited for light metals and their alloys. Furthermore, they are eminently suitable for use in mass production techniques. They are also the basis of the presently employed "wash primers" which are being employed widely not only in aircraft painting but also in other fields.

Barium-potassium-chromate [$BaK_2(CrO_4)_2$][10] is another chromate pigment which is prepared by reacting together potassium bichromate and barium carbonate in a rotary kiln at 550°C. It contains least amounts of sulphate and chloride impurities whose presence enhances corrosion. This pigment is best employed with varnishes based on synthetic resins such as phenolics, alkyds, alkyd-modified chlorinated rubber and coumarone-indene. The performance of this pigment on ferrous metals is better under atmospheric conditions. For aluminium and magnesium metals the pigment shows equal performance both for atmospheric exposure and water immersion services. The paint film has good hardness, high tensile strength, elongation, flexibility and impact resistance.

Metallic Pigments:

Though various lead compounds have been used in paints from the earliest times, the use of metallic lead[11] is of relatively recent date. Electrolytically lead is on the border line and may be slightly anodic or cathodic to iron depending upon circumstances. Lead forms a protective coat on its surface and thus becomes passive to the action of corrosive agents. Though metallic lead is very heavy it does not settle to a hard cake in the container. It is prepared by flaking selected atomised lead in a steel ball mill with stearic acid as a lubricant. Pigmentary metallic lead has low oil absorption and forms a very impervious film of high lead content. It gives satisfactory performance when used with raw linseed oil or polymerised oil. This paint is used exclusively for painting iron surfaces. The metallic lead is not used much because of its high weight and cost; but under severe conditions it surpasses most other pigments.

The use of zinc dust for corrosion prevention depends on its specific position in electromotive series with respect to iron. Zinc dust is prepared by cooling vapourised metallic zinc in an inert atmosphere. In the protection of iron, zinc[12,13,14] is sacrificed, as it is the anode in the galvanic cell formed during corrosion. Zinc is also a deoxygeating agent and thus inhibits corrosion by reacting with any dissolved oxygen. The presence of zinc oxide that is formed on the surface of zinc dust particles neutralises the acidic portion of the vehicle. The electro-chemical properties of zinc are so effective that a bare iron area in the vicinity of zinc can remain uncorroded just as that under the coat of zinc dust. Like other metals zinc liberates hydrogen by reaction with acids, and therefore, the medium used for zinc dust paints should be of low acidity. The usual binder used for zinc dust paint consists of a mixture of raw and boiled linseed oil. Plasticised polystyrene is used sometimes to obtain a higher proportion of zinc. Zinc dust paints are used mainly over iron surfaces, but recently it has been used for coating copper and its alloys to avoid staining effects.

In recent years aluminium pigment has been used for anti-corrosive purposes. It is prepared by beating small pieces of sheet aluminium in a combination of light and heavy stamp mills in the presence of stearic acid as lubricant. The protection of metal by aluminium paint is purely physical in nature. Because of its "leafing" character, flaky particles of metallic aluminium[11] tend to lie in a plane parallel to the metal surface, and thus produce smooth and compact coating, which discourages lodgement of dirt particles and provides a very intricate passage for any corrosive agent making its way to the metal surface. Aluminium possesses good reflectivity for electromagnetic waves and thus protects the binder in the paint film from ultra-violet light which is chemically active and infra-red radiations which result in a rise of temperature. In choosing a medium for aluminium paint care must be taken to preserve the leafing character of the aluminium flakes. Raw linseed oil and boiled oils do not permit "leafing." Varnish media have been found suitable for this purpose. The medium should have low acid value and should not contain lead driers which destroy "leafing." Varnishes based on ester gum, phenolics, alkyds and chlorinated rubber have been used in different types of applications, though coumarone-indene resins will be preferred. Aluminium paint is best used as a top coat because of its superior physical properties. Aluminium paint is used for iron and its alloys and also as top coat over zinc chrome primers on aluminium surfaces.

Aluminium bronzes also give good physical protection to metal but their use is restricted for top coats only because of their strongly cathodic action to iron.

Aluminium-silicon alloy[15] (87.13) has also been suggested as a rust inhibitive pigment.

Miscellaneous Pigments:

Red oxide of iron (Fe_2O_3) is used invariably in anti-corrosive paints. It is prepared by pulverising naturally occurring red ochre or synthetically by calcination of by-product ferrous sulphate in a rotary kiln. It can be obtained in varying shades by co-precipitating ferrous hydroxide and calcium sulphate and calcining the precipitate so obtained. It neither inhibits nor promotes corrosion, but is used in anti-corrosive paints because of its ability to degrade actinic light which is the main and potent cause for paint destruction. Red oxide is added to anti-corrosive pigments to cheapen them and to improve some of their physical properties. The micaceous oxide of iron occurs in the form of fine flakes and is used to improve brushability and covering power of the usual anti-corrosive pigments.

Graphite[16] is also used in anti-corrosive paints. Many controversial statements have been made over the use of graphite. Natural graphite, either coarse or finely ground, always promotes corrosion. On the other hand, it has been proved that graphite in colloidal form does reduce corrosion. Graphite particles have hexagonal plate—like structure and they tend to be parallel to the painted surface and constitute a sheath more like true plating which helps in "running off" rain water. The colloidal nature of graphite improves the brushing qualities of red lead paints. Other pigments having leaf-like structure are mica and aluminium; but graphite has an advantage over aluminium in being chemically unreactive and over mica in being opaque to light. Since graphite is unreactive it can be used in a variety of media. The red lead primer and graphite top coat gives an excellent protection against corrosion.

"Silear,"[17] a pure silicon carbide, quartz-like material, has been used in anti-corrosive compositions. It is chemically inert and has got good covering power. The paint containing 60 parts of Silear and 40 parts of red lead gives 35% more covering than a composition containing 60 parts of barytes and 40 parts of red lead.

Carbon[18] activated with ammonia has been tried as a corrosion inhibiting pigment. Ammonia adsorbed on the carbon particles makes penetrating water alkaline, thereby suppressing corrosion. Full details, however, are not available.

Surface preparation:

It is not generally realised that even the best anti-corrosive primer can show poor performance if it is applied on a surface that has not been made receptive to it; also the primer should be correctly applied under favourable environmental condition. Both chemical and mechanical methods are employed for getting surface ready for painting, the choice being determined by the nature of the article, its location and whether post-baking is employed or not. For structural steel work only the mechanical methods are applicable.

As it is essential to get a compact and adherent film of a primer, the method of application is of considerable importance. In air-drying compositions, brushing by a skilled painter employing a paint containing little or no volatiles give by far the most compact film. However, care must be taken to see that paint is applied under conditions of fairly low humidity or else the surface layer of moisture may be entrapped underneath the paint film, thereby enhancing corrosion.

In view of the large amount of constructional work going on in the country at present, anti-corrosive pigments and paints have acquired considerable significance. For structural steel work red lead in linseed oil primer, followed by two coats of micaceous oxide of iron in oil, is the preferred method of protection. However, in view of the fact that the availability of red lead is dependent on imported lead the use of alternate pigments should be investigated. Of the many pigments which could be manufactured from indigenous raw materials potassium-barium-chromate appears to be the most promising. In view of the insufficient amount of information on the use of potassium-barium-chromate as a primer under tropical conditions, it is necessary to carry out large-scale field experiments to evaluate its performance. As the country is more than self-sufficient in linseed oil, actually exporting a large surplus, the use of other binders need only be considered if it is necessary in the national interest.

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