

ORGANIC COATINGS -- BASIC CONSIDERATIONS
OF PROTECTION OF IRON AND STEEL

P.PRABHAKARAM*

ABSTRACT:

Since iron forms the commonest structural material wide variety of coatings are used for its protection against corrosion and in the realm of organic coatings both natural and synthetic resins are used in coating formulations. With advancement of research in polymers for protection and the demands on coating performance under different environmental conditions, a variety of formulations and coating techniques are adopted to suit specific requirements and performance criteria. In this paper basic considerations of protection of iron and steel by organic coatings is dealt in detail along with the criteria of selection of specific coating materials for different end uses. The work carried at the The National Metallurgical Laboratory on Vinyl coatings and Zinc rich primers is briefly discussed.

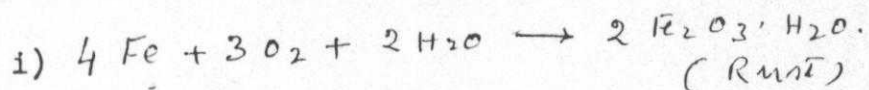
Ferrous metals which are widely used require protection of their surface against corrosion. Various special alloy steels used in industry do not require painting. Most of the steel used is the low alloy type which contains more than 98% iron and the rest is principally carbon and manganese with a little silicon, sulphur and phosphorus. When low alloy steels are molten red hot, they oxidise rapidly on the surface and forms mill scale which varies in oxygen content from FeO to Fe₂O₃. Under rolling and forging operations of hot steel, part of the mill scale flies off and part of it remains on the surface. The composition of the steel influences the appearance and adhesion of mill scale. Because of the unreliability of the adhesion of mill scale, it is usually advisable to remove it before applying of organic coatings to ordinary steels.

* Dr.P.Prabhakaram, Retd. Sct E_{II}, Ex- Head of Coatings Div. NML, Jamshedpur.

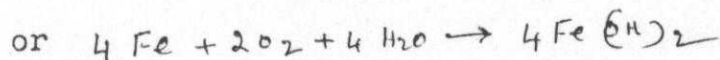
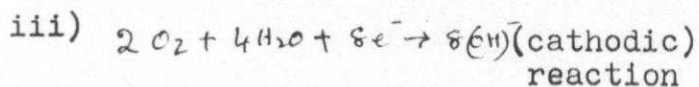
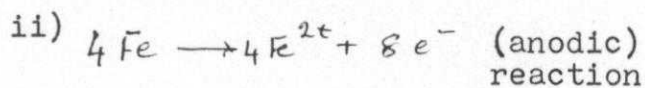
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MECHANISM OF CORROSION:

The electrochemical theory of corrosion satisfactorily explains the mechanism of the rusting of iron and steel. When Iron is in contact with water, tiny electrical cells consisting of anodes and cathodes form all over the surface. The position of the anodes and cathodes is determined by many factors such as differences in composition, crystal structure or stresses in the material and differences in film thickness or actual breaks in protective surface coatings. Areas covered with mill scale are always cathodic to pure iron. The electric currents flow from the positive anodes to the negative cathodes through the water and back to the anodes through the metal. The flow of the current is greatly increased by the presence of dissolved salts or acids which make the water greater conductor of electricity. It is known that Iron does not visibly corrode in the absence of either water or oxygen. The overall reaction in their presence may be written as:

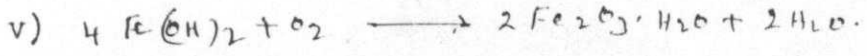


When the supply of oxygen is restricted the corrosion product contains ferrous ions. The overall reaction can be broken down into two reactions, one producing electrons and the other consuming them.



In the presence of oxygen, the ferrous hydroxide will be converted to rust, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Thus in the presence of water and oxygen alone the corrosion product may be formed in close contact with the surface and attack will consequently be stifled. In the presence of an electrolyte such as sodium chloride, the anodic and cathodic reactions are modified, ferrous chloride being formed at the anode and sodium hydroxide at the cathode. These two compounds are highly soluble and diffuse away from the surface and combine to form ferrous

hydroxide or a basic salt which then combines with oxygen to form rust with the regeneration of sodium chloride.



The rust is formed at a distance from the surface and hence attack on metal cannot be stifled. This conclusion was firmly established by Evans⁽¹⁾ and co-workers and as a result of this continuous reaction, there is a flow of electrons in the metal from anodic to cathodic regions and by movement of ions in the solution and this forms corrosion current which is equivalent to corrosion rate. In order to inhibit corrosion, it is necessary to stop the corrosion current and this is achieved by either suppressing the cathodic or anodic reactions or by inserting high resistance in the electrolytic path of corrosion current. The three methods of suppression are called cathodic, anodic and resistance inhibition respectively.

MECHANISM OF PROTECTION BY ORGANIC COATINGS:

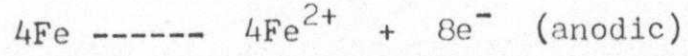
The cathodic reaction: In neutral solutions, this reaction involves oxygen, water and electrons



If a paint film is to prevent this reaction it must be impervious to electrons, otherwise the cathodic reaction is merely transferred from the metal surface to the surface of the film.

Organic polymers films do not contain free electrons except in the special case of pigmentation with metal pigments. Hence it is assumed that the conductivity of the paint film is entirely ionic. It was concluded by many researchers that the cathodic reaction cannot be stopped by paint films since water and oxygen diffuse through polymer films eventhough to different degrees depending upon the composition of the film.

The anodic reaction: The anodic reaction consists of the passage of ions of iron from the metallic lattice into the solution with the liberation of electrons which are consumed at the cathode by reaction with water and oxygen



There are two ways in which this anodic reaction can be suppressed:

a) If the electrode potential of iron is made sufficiently negative, positive ions of iron will not be able to leave the lattice i.e. cathodic protection.

b) If the surface of the iron becomes covered with a film impervious to iron ions, then the passage of iron ions into solution will be prevented i.e. anodic passivation.

In the cathodic protection by coatings, the metallic pigment used with the binder either organic or inorganic must be a metal less noble than iron so that iron is protected at the expense of the metal pigment and the pigment particles must be in electronic contact with each other and the coated surface. This is the basis for many zinc pigment based primers for protection.

In the anodic passivation by coatings, the pigments used are sufficiently basic to form soaps as in linseed oil which in the presence of water and oxygen autooxidise to form soluble inhibitive degradation product. Typical pigments in this class are basic lead carbonate, basic lead sulphate, red lead and zinc oxide. ~~In~~ the case of soluble chromates used in primers, it was established that the air formed film on iron and steel is reinforced with a more protective material in the form of a chromium containing spinel⁽²⁾. Some chromates which are basic ones may inhibit through the formation of soaps.

Resistance Inhibition: Paints films are so permeable to water and oxygen that they cannot prevent cathodic reaction and the anodic reaction may be modified by certain pigments. In case of organic coatings which do not contain inhibitive pigments, it was considered that the paint protects by virtue of its high ionic resistance which impedes the movement of ions and thereby reduces the corrosion current to a very low value. The factors which influence this resistance are 1) Electrolyte underneath the film 2) Inorganic groups in the polymer film and 3) water and electrolytes outside the film. The physical factors which affect the resistance are temperature, concentration of electrolyte, film thickness and solvents etc. If the protection of paints or varnish films are due to their high ionic resistance, then the ionic resistance measurements of different coatings should yield useful data to predict their corrosion resistance.

It was shown by Bacon et al⁽³⁾ who measured resistance of over 300 paint systems immersed in sea water using a d.c. technique that for good performance of a coating the resistance should be in excess of 10^8 ohms/cm² and those in the range of 10^6 - 10^8 ohms/cm² are unreliable and those with still lower resistance had performed poorly.

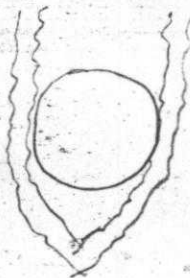
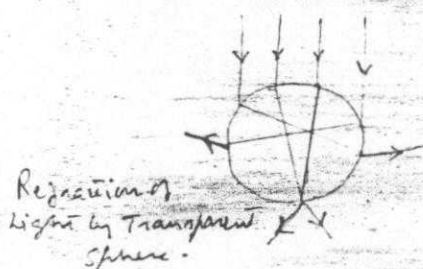
Paints: Paints consist essentially an organic binder in which pigments are dispersed to impart desired properties to the dried film which protect the base metal. The main purpose of the solvents used in paint formulation is to control the viscosity of the paint during manufacture and its subsequent application. During application the solvent evaporates and is lost. A different class of paints which are of recent origin are emulsion paints in which the binder is emulsified in water and the properly formulated paints are finding increasing use in protection due to their non-toxic nature and relatively low cost and absence of fire hazards. The variations in binders for coatings are limitless and they vary from drying oils and their modifications, natural resins and their modifications and the ever expanding range of synthetic resins to meet the increasing demand of organic coatings in different areas of applications which require to fulfil various performance criteria.

Binder: The role of the film former is to serve as a binder for the pigments besides imparting the desired physical and chemical properties to the paint. The binders consist of drying oils, oil varnishes, phenolics, alkyd resins, polythenes, amino resins, epoxy resins, poly urethanes, vinyl resins, acrylics, chlorinated rubber, nitro cellulose and other miscellaneous binders such as silicones, silicates, fluorinated polymers such as polytetrafluoroethylene etc, for special purposes. The film formers are also blended with plasticizers and other chemicals which contribute to the heat and ultraviolet resistance, flexibility of the dried films besides contributing to the adhesion of the film to the substrate.

Pigments:- Pigments provide colour to the coating besides hiding the surface on which the coating is applied. The pigments are suspended in the binder as they are insoluble in the medium. They range from natural minerals to synthetic inorganic and organic compounds.

They may be broadly divided into priming pigments, colour pigments, extenders and metal powders. Extender pigments confer special properties to the paint such as prevention of hard settlement, improvement of build (viscosity) and better intercoat adhesion. Pigments must have substantially higher refractive index than the binder in order to hide the surface by refraction and reflection. For example rutile titanium di-oxide which has the highest hiding power in white pigments has the highest refractive index - 2.76 while most of the oils and resins used as binders have refractive index around 1.5 - 1.6.

When light rays impinge on a white surface coating pigmented with a hiding pigment such as titanium di-oxide, some of the rays are reflected back into the air from the film-air interface and the rest enters the film with some refraction because of the refractive index of the binder. In the film the light rays impinge on millions of particles of pigment at angles of incidence and are reflected and refracted in all directions as they enter and leave the pigment particles. There is also large amount of light scattering by diffraction. This scattering of light rays produce hiding. The greater the difference in refractive index between the pigment particles and the binder, the greater the angles of refraction when the light rays enter particles, the more light ray scattering occurs and better the hiding.



Coloured pigments absorb a large portion of incident light and convert it to heat reflecting only certain wave lengths. For instance red pigments reflect light in red wave lengths, blue pigments reflect light in blue wave lengths etc.

Red lead, zinc chromate, calcium plumbate and zinc dust are widely used in metal primers. The first three when dispersed in raw or lightly treated linseed oil inhibit corrosion by anodic passivation as mentioned earlier in the text and zinc dust upto 93-95 per cent by weight in non-saponifiable medium provide sacrificial protection.

Additives: In a paint formulation, besides the pigments dispersed in a solution of a binder, small quantities of other materials are added which are known as additives. These are mostly organic salts of metals like cobalt, zinc, calcium, barium and manganese which are added in air drying compositions and are called driers. Anti-oxidants are added to prevent skinning of air drying paints and surface active agents are used to facilitate suspension of the pigments and to maintain homogeneity of the film while drying.

Solvents: It is the volatile component of a paint and consists of a true solvent for the binder and non-solvent or diluent which reduces cost. The diluent should be more volatile than the solvent so that the medium remains in solution during the drying process. This group consists of aliphatic or aromatic hydrocarbons, alcohols, esters, ketone etc. Flash point of the solvents and diluents is an important factor in reducing the fire hazards and are generally governed by statutory regulations.

In formulating a paint the main considerations are

- i) the appropriate pigment:Binder ratio
- ii) In the case of composite binders, the optimum proportions of each binder.
- iii) The optimum amounts of driers where necessary such as in drying oils.
- iv) The optimum amount of plasticizers used with many of the synthetic polymers.
- v) The appropriate solvent balance for proper viscosity during storage and during application and drying.

Paint Failure:+ Paint failure arises to various reasons and some of the factors are 1) Improper paint formulation 2) loss of adhesion due to inadequate surface preparation 3) Loss of adhesion between primer and top coats 4) Environment in outdoor exposure.

Frequent defect, encountered in organic coatings are chalking, checking, flaking, scaling and peeling. No paint can serve for a life time and even the best formulations have limited service life after which the structure is to be repainted.

Paint films start their gradual decomposition due to oxidation, erosion, weathering etc., from the moment of exposure onwards at a rate dependent on the constituents, the environmental conditions and conditions of application. With increasing age

of the coating, the film loses its elasticity due to continued oxidation in oil based paints and migration of plasticizers in synthetic polymers coupled with degradation due to ultraviolet light in many film formers. Expansion and contraction of the metal base caused by severe temperature changes will result in the formation of discontinuities in a relatively inelastic paint films. Excessive high temperatures cause unsuitable paints to become brittle and crack due to loss of adhesion. Due to the swelling of the film also adhesion is lost. Due to inadequate surface preparation, rust under the paint coat will also cause adhesion loss of the paint leading to its failure. Paint failure is related to climatic conditions and the weather prevailing during application and subsequent exposure will determine the life of paint system.

The majority of paint failures on metal surfaces are due to insufficient surface preparation. The most common cause of failure on steel is insufficient removal of corrosion products such as rust or mill scale. The common practice in outdoor painting after the removal of corrosion products is to paint the structure immediately with a proper primer coat and this is more important when grit blasting or any other mechanical operations involved in cleaning since the metal is sensitive to corrosion after the above operations.

Effect of environment:- In industrial atmosphere many of the oil based paints which dry by oxidation have poor performance due to the presence of fumes which act as anti-oxidants. Selected chlorinated paints or catalysed epoxies are used.

Acid Environment:- Acid conditions exist in the vicinity of coke ovens, gas works, galvanizing plants, paper mills etc and in these conditions cracking is a frequent failure. For resistant to acid conditions alone, filled and unfilled bituminous solutions, amine cured epoxies often blended with coal tar are used.

Alkaline Environment:- Oil based paints should not be used in alkaline environments since the binder deteriorates by saponification. Under these conditions polyurethanes, chlorinated rubber, epoxies, polyvinyl chloride or acrylic resin based paints are considered to be very effective.

Marine Environment:- Salt laden atmosphere is highly aggressive towards corrosion of steel and hence special paints known as marine paints is a class by itself both for protection of on shore and off shore structures, ships and other ocean going vessels and the topic is so wide and innumerable specifications are drawn for satisfactory protection of steel under different conditions. The often used film formers are coal tar epoxies, chlorinated rubber, bitumin or pitch solutions, vinyls, phenolics and others. Depending upon the area of application, the type of primers to be used, the intercoats and the finish coats and their compositions, their thickness levels and the the methods of application to achieve the desired results are specified in literature based on experience and exhaustive testing.

Zinc rich primers based on both organic and inorganic vehicles are widely used in marine applications and specially those based on inorganic vehicles such as sodium silicate and Ethyl silicate are widely used with a proven long performance. Exhaustive work was carried at the National Metallurgical Laboratory on zinc rich primers and it is discussed further in this paper.

Surface Preparation:- Slight roughness of the surface improves mechanical anchorage of many organic coatings. The tiny hills and valleys tend to hold the coating better than a perfectly smooth surface. A coating of inherently good adhesion may be retained well by smooth surfaces possessing very little mechanical anchorage. If a coating has poor adhesion, the surface is to be properly conditioned.

Thin sections of metals such as steel, aluminium, zinc etc, are subjected to various chemical treatments which improve the adhesion of organic coatings to the metal. Phosphating of steel is a common practice in automobile industry to improve the corrosion resistance of steel as well as to improve the adhesion of organic coatings in subsequent processing. Zinc phosphate is the common one used eventhough manganese and iron phosphates are also used in some cases. In automobile industry 8 to 9 tank process is used for phosphating of steel. There are number of chemical treatments for aluminium and zinc also which improve their corrosion resistance and adhesion of organic coatings.

Heavy structural steel components are cleaned by mechanical means such as blasting with sand, carborandum and other abrasives and there are specifications regarding the degree of cleaning required for specific purposes.

Paint application Techniques:- These vary from the conventional dipping, brushing, spraying processes to the more sophisticated techniques of hot spraying, airless spraying, electrostatic spraying etc. Electrodeposition of primers is carried in modern automobile industries. The object of the various improved techniques is to achieve the desired wet thickness without wasting of the paint material. In the electrodeposition of paints, the paint is water based and the solids of the paints are very low compared to the conventional paints. The work is made the cathode in a d.c. circuit and the anode can be either the tank or suitable anodes are properly placed in the tank for optimum coating conditions. In electrostatic spraying which is applied both for liquid and powder coatings, paint droplets or powders are passed through a powerful electrostatic field and become charged. They are attracted to the earthed work piece and coat not only the front surface but also the back surface to a large extent if the object is not too deep or too wide.

An automatic paint application technique to sheet steel is coil coating in which coils of different widths are coated continuously on a coil coating line which includes different metal pretreatments by passing through various processing tanks, priming and finish coats and flashing of the coatings. Since the strip moves at high speeds, all the pretreatments are carried in a few seconds and special formulations are used to meet the requirements of the coating line. The paints are applied by rolls and the wet coating thickness is controlled by ^{β-ray} -gauges. Baking is carried in continuous baking ovens. There are adoptions in some plants to collect the solvents from the baking process and utilize them for heating the pretreatment tanks in the process.

Drying Methods:- Lacquers, resin solutions and emulsions which dry largely by solvent evaporation are usually air dried or force-dried at low temperatures. Non-oxidizing materials such as vinyl plastisols or organosols which form films by heat fluxing are baked to remove the solvents and fuse the particles of the polymer into a coherent flexible film. Surface coatings containing drying oils with or without hardening resins also contain volatile solvents and they dry by a combination of solvent evaporation, oxidation and polymerization. In addition to speeding up the drying process, baking a given coating at appropriate temperature tends to give harder, tougher and more durable film than air drying.

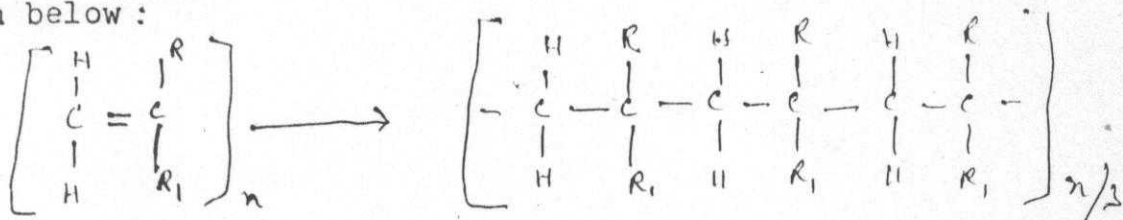
Test Methods:- There are number of methods for testing of organic coatings and they are covered by different specifications to cater to the needs of consumers and their required performance. The more important ones are drying time, hardness, abrasion resistance, adhesion, flexibility, Gloss, cold checking, water resistance, humidity resistance, vapour transmission, washability, salt spray resistance, solvent resistance, chemical resistance, bleed resistance, light fastness indoors, weathering outdoors and accelerated weathering tests etc.

WORK AT THE NATIONAL METALLURGICAL LABORATORY ON VINYL COATINGS
AND ZINC RICH PRIMERS

VINYL COATINGS:

Around 1964 there was considerable scarcity of zinc for galvanizing and M/S Tata Iron and Steel Company Ltd., Jamshedpur, ^{evinced} interest in plastic coating of steel sheets as an alternative to galvanizing since plastics have good corrosion resistance. In developed countries vinyl coated sheets and strips are used for panneling, furniture, instrument cabins, internal panneling in houses and offices, railway coaches etc, to name a few. Hence vinyl coatings on steel was carried at NML and the project completed and patents taken on some successful formulations which were exhaustively tested both in the laboratory and outdoor exposure at different places.

Vinyl-type homo polymers and co-polymers are used in surface coatings and the polymerization of vinyl monomer is shown below :



where R and R₁ represent pendant groups such as hydrogen, chlorine, acetate, benzene toluene etc.

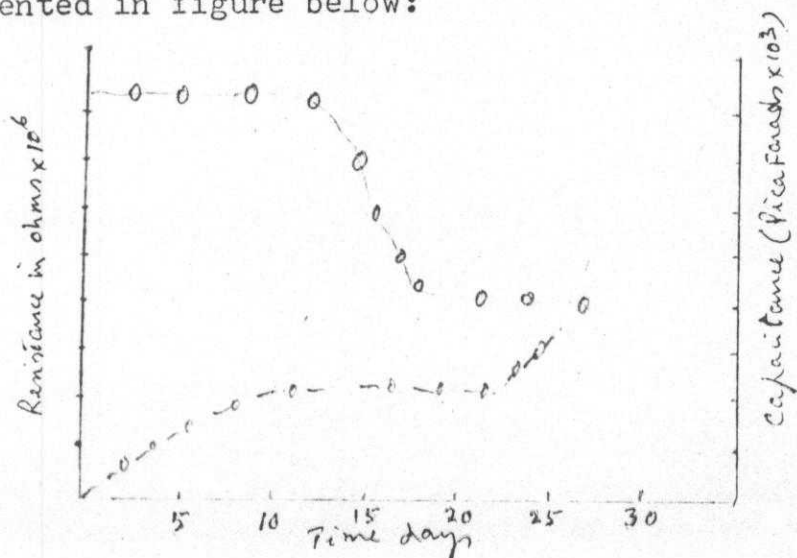
In our work we had carried formulations based upon Polyvinyl chloride-vinyl acetate co-polymer as this polymer has good solubility in ketones and flexibility of the baked film coupled with good corrosion resistance. Poly vinyl chloride homopolymer of the paste grade available indigeneously was also used as

film former. The coatings studied are of the barrier type and no inhibitive pigments were incorporated. The other materials are stabilizers, plasticizers etc, which are commonly used with vinyl resins. Two primers based on 1) Poly vinyl chloride/acetate co-polymer 2) Phenolic-Nitrile rubber were prepared and they were applied on phosphated steel either by dipping or spraying. The application of primer and finish coats was followed by baking at temperatures in the range of 160° - 190° C.

Since outside exposure tests take a long time for assessment of different compositions towards their corrosion resistance and accelerated tests are of pass or fail estimations, it was considered appropriate to measure the resistance and capacitance of coated steel panels immersed in 1% sodium chloride solution which could yield quick information on assessment of different compositions for further evaluation by accelerated salt spray and outdoor exposure tests. The work was presented and published in the proceedings of a Symposium on "Surface coatings and Printing Inks" organised by the Colour Society of India⁽⁴⁾.

From our studies it was concluded that barrier type coatings such as those based on vinyls can't be rapidly assessed from their electrochemical behaviour in 1% NaCl solution. A steady state of capacitance followed by a rapid rise in capacitance is considered the normal behaviour of coatings when the pigment concentration is below CPVC.

A steady rise in capacitance from the beginning of the ~~beginning~~ exposure indicates high macroporosity due to incorporation of pigment beyond CPVC and such films do not offer good protection due to the ease ^{with} which water and corroding medium permeates and cause blistering, peeling and subsequent corrosion from the damaged portions. The type of results obtained is represented in figure below:



Those formulations which offered long periods of steady state capacitance before rapid rise of capacitance are also found to have good ohmic resistance. These compositions were found to offer excellent corrosion resistance as further evaluated by salt spray tests and exposure ~~tests~~ ^{and} tests at NML ~~and~~ NML Corrosion research station at Digha, W.Bengal.

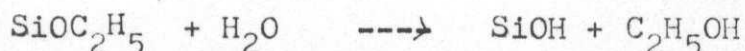
ZINC RICH PRIMERS:-

In the electrochemical explanation of corrosion of steel in the presence oxygen and water, iron goes into solution as Fe^{++} at the anode and $(OH)^{-}$ ions are produced at the cathode as mentioned earlier. If iron is made to have electrical contact with a baser metal like zinc, zinc will corrode in preference to ~~to~~ iron and it will be protected and this is the basis of galvanizing. Steel will not corrode as long as zinc is available for protection from the coating. There are many methods of zinc coating on steel such as galvanizing, electroplating, hot spraying, diffusion impregnation etc. When protection of structures, pipe lines, ship hulls etc, is concerned zinc rich paints are considered to have great advantage in application and ^{to have} the required coating thickness for protection.

Zinc rich pripers are based upon i) organic vehicles and ii) Inorganic vehicles. The primers based upon inorganic vehicles are a) Post curing soluble silicates such as alkali silicates and (b) self curing organic silicates such as Ethyl silicate-40. Work was carried at NML on primers based on both sodium silicate and ethylsilicate-40. The work with Sodium silicate was published by Prabhakaram et al ⁽⁵⁾. In this work sodium silicate of $Na_2O : SiO_2$ ratio of 1:3.5, zinc dust of 12-14 microns size and 99% purity were used. Certain additions of surface active agents and other chemicals such as Nitro compounds are added to the wet paint to increase its pot stability before application. It was found that a single cross coat with brushing will give 2-3 mils dry film thickness which gives adequate protection to steel. Coatings varying from 87-92% of zinc on solids basis in the dry film were evaluated for their galvanic protection by measurement of their ^{electro}chemical characteristics in 1% NaCl. The coated and cured panel was coupled with a polished mild steel specimen of 1/4th area of the coated panel and the current in the couple and the potential of the bare m.s with reference to S.C.E were measured against time. The reverse sides of the panels were

coated with bees wax and the couple shorted through 1 ohm resistance for measurement of current by VTVM. Successful compositions evaluated by potential measurements were exposed at NML, TISCO works and at Digha. They were found to give excellent protection over a period of three years of examination.

Zinc rich primers based on hydrolysed Ethyl silicate-40 were also extensively evaluated at NML for their pot stability and protective properties. Ethyl silicate-40 is a poly silicate with about 40% silica and it does not have any binding properties. The hydrolysed ethyl silicate will have good binding properties for zinc and the coatings self cure on exposure. The hydrolysis of ethyl silicate involves the conversion of ethoxy groups attached to the silicon atom to hydroxyl groups by reaction with water



The Si-OH polymerize to give a three dimensional net work and the Zn-atoms of the paint are incorporated in the polymer to give zinc silicate which contributes to the hardness to the cured film and the zinc is available for galvanic protection of the base steel.

Acid hydrolysis of ethyl silicate under optimum conditions results in solutions with good pot stability and they can be used as vehicle for metallic zinc powder of high purity for zinc primers. Zinc rich primers based on ethyl silicate hydrolysate were evaluated by electrochemical tests coupled with accelerated corrosion tests and outdoor exposure. The results of primers based on sodium silicate and ethyl silicate were published^(6,7,8) and patents were taken on these primers and interested parties can have NML know how on the subject for utilization.

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