

## CHAPTER - II

METALLIC POWDER AS PIGMENT USED IN PROTECTIVE COATINGS -  
A REVIEW

Extensive electrochemical investigations have been carried out on the mechanism of corrosion prevention by zinc rich coatings on steel substrate in sodium chloride solution. This is being reviewed in this chapter. The literature on the protective behaviour of Manganese, Nickel and Stainless steel pigmented coatings are also discussed.

2.1. MECHANISM OF PROTECTION BY ZINC RICH COATINGS IN  
CHLORIDE MEDIUM

## 2.1.(a) Development of inorganic zinc rich coatings

The corrosion of an iron surface involves the transfer of electrons from anodic area within that surface towards electrically connected cathodic area. This transfer is accompanied by the dissolution of the iron into the electrolyte as iron ions from the anodic area. If the electrode potential of the anode area could be made negative enough, then the flow of electrons towards the cathode would cease, and the positively charged iron ions would not leave the metal. This change in potential of the metal can be made by means of an impressed current or as a result of connecting electrically more positive

metal directly to the iron. This is called cathodic protection and it is achieved in the coating technology by means of galvanizing, zinc metallizing, zinc rich primer and zinc plating [1].

Zinc dust is a blue-gray powder in a finely divided state. The appearance of this powder depends on the degree of zinc oxide contamination and the size of the zinc pigment particles. The powders are normally available in spherical shape with the particle size ranging from 3 - 8  $\mu\text{m}$ . Zinc dust is one of the metallic pigments used in the paint industry to formulate corrosion inhibitive coatings for the protection of metallic substrates.

The original method of applying inorganic zinc rich coatings was by means of hot dip galvanizing and it was first developed in the 1840's in France. The real revolution in the protection of steel started in the 1940s in Australia and in the 1950's in United States [2]. Victor Nightingale, the Australian originator of the inorganic zinc coatings in the 1930s, modified his product and was used in 1942 on the 250 mile Morgah - Wyalla pipe line in South Australia. This marked the first large, full scale application of inorganic zinc coatings. Shortly following the original application, the effective use

of the coating required easy application to large fabrications and structures [3].

The basic chemistry of silica was known and well described by E.G.Rochow [4]. Rochow explains that despite the different starting point, the ultimate reaction product on the steel surface is very similar for each one of sodium silicate coatings. When zinc is added to the system, a silicon - oxygen - zinc polymer is created. This combination is very insoluble and forms the strong matrix surrounding the zinc powder to produce the coating.

In 1950s, several products were developed from silicates. One product based on lithium silicate and colloidal silica was successfully applied over petroleum tanks, bridges and industrial structures [5] and another formulation was developed based on potassium silicate and colloidal silica [6]. A third type of coating also developed was based on zinc phosphate with the chemistry quite different from the silicate. This product was proved to have excellent durability and protection, but it was not in the field because of the greater application difficulties.

In 1960s, the self-cured water based silicate coatings were being developed and used. A different approach was also being studied. This approach involved using ethyl

silicate as a binder for the zinc and applying it from an organic solvent in place of water. The first patented [7] ethyl silicate zinc coating was based on the partial acid hydrolyzation of ethyl silicate to make a stable solution of an ethyl silicate - silicic acid mixture. This solution when combined with zinc, further hydrolyzed from moisture in the air to form the inorganic zinc coating. One difference between the organic silicate and the alkali silicate is that the removal of the hydrolysed product of ethyl groups from the silicate polymer proceeds slowly and it may take weeks or months [8].

The inorganic zinc rich coatings are not only cohesively strong but are extremely adhesively secure on well prepared surfaces. The adhesive strength is due to the formation of primary valency - bonded matrix involving iron ions from the steel surface as well as zinc ions from the pigmentary surface [9]. Unlike organic systems the zinc silicate matrix is electrically conductive [10]. The protective life of the coating is also dependent upon the amount of zinc metal employed in the coating formulation [11]. Marcel Leclercq [12], Del Amo [13] had optimised the zinc content, particle size and the minimum thickness of the coating required for maximum protection life of the coatings on mild steel substrate and concluded

that the protection achieved at 80 - 90% Zn content and the thickness of the coatings must be 80 - 95 microns. Similar type of work was done by G.W.Kapse and K.M.Bela Rani [14] for organic and inorganic zinc rich coatings. They arrived at same conclusions but they found that in the case of organic coatings the amount of zinc to be used depends upon the binder.

As the cured inorganic zinc rich primer ages, the zinc continues to react with the environment, producing a variety of zinc corrosion products depending on the environment [15,16]. As this happens, the resultant corrosion current continues to render the steel totally cathodic and protected. After that, the zinc corrosion product occupies the interstitial areas between the zinc particles, thereby sealing the primer film completely and producing a dense, hard, abrasion resistant film. This behaviour of commercially available zinc coatings in different binder has been investigated by electrochemical methods. The duration of the cathodic protection given by the coatings are of shorter duration than the barrier protection period [17,18]. The mechanism of galvanic protection [19] and the barrier protection [20] period of the coatings are explained by S.Felin et.al.

For cathodic protection to be viable, a continuous

film of electrolyte is needed across both anodic and cathodic areas. Only a thin surface film is necessary for dry atmospheric environment [21]. Similarly the organic and inorganic zinc rich coatings suitable for different environmental conditions are reviewed [22-24] and the effect of atmospheric pollution on deterioration of the coatings have been given by Smieszek [25], Pereira et.al [26].

In most cases, films are recoated fairly quickly after application and long before the primer films are sealed by corrosion products. This problem is reduced as the inorganic system ages and becomes sealed, and it does not occur in post cured alkali silicates in which sealing is artificially induced during post curing. Compositions preventing cracking of thick films of high build zinc silicate coatings comprise mainly alkyl silicates hydrolysate of trialkyl borate and zinc powder [27]. In some compositions part of the zinc content is replaced by di-iron phosphide without affecting the properties of the coating [28].

The physical and chemical information on the formation of zinc corrosion layer and their evaluation are studied by T.C.Graedel [29]. The surface morphology of the organic and inorganic zinc rich coatings are evaluated

by Scanning Electron Micrographic (SEM) and energy dispersive x-ray spectroscopic methods [30,31]. The surface morphology and the kinetics of formation of the corrosion product layers were seen to differ depending upon the environments.

Single coat of inorganic zinc can effectively and economically prevent corrosion of carbon steel structures in marine environments [32-34]. New coatings are continually appearing on the market, but none can match the inorganic zinc in long term atmospheric marine exposures.

#### 2.1.(b) Butyl titanate zinc rich coatings

The development of titanium esters for use in surface coatings and related field is analogous to that of the silicon esters. In course of time, investigations for the preparation of various esters of titanium of general formula  $(RO)_4 Ti$ , Ti-acrylates, chelate of titanium and compounds of titanium with direct Ti-carbon linkage have been reported [35,36]. Among these esters, butyl titanate is the commonly used carrier vehicle in the anti-corrosive primers of industrial, high temperature and marine environments [37]. The reaction mechanism of the titanate ester with triethanolamine and then the formation of water immiscible resin with phenolic compound is explained by

R.Sidlow [38]. The structure of these compounds are confirmed by I.R. spectroscopic analysis [39].

The titanate is mixed with modified phenolic resin and pigmented with zinc which possesses heat resistant as well as anti-corrosive properties [40] but when pigmented with aluminium powders the coating possesses heat resistance at high temperatures [41]. A comparative study of galvanic protection and the impedance behaviour of the titanate zinc rich coatings with the organic zinc rich coatings shows that the titanate based coatings protect the carbon steel substrate for longer duration by galvanic protection mechanism [42].

The performance of inorganic zinc rich coatings depends upon the formulations and to a certain extent on the metallic zinc content. A comparison of performance of inorganic zinc silicate primers in marine atmosphere is in the following order, Post cured > Water base > Solvent base - 2 component > solvent base - one component systems.

### 2.1.(c) Development of organic zinc rich coatings

The development of organic zinc rich coatings in Europe preceded that in Australia. Drying oils were the first type of materials used which, were not entirely successful. But some formulations based on linseed oil



is used for a primer or a finish coat for galvanised steel. During 1930s, many other resins and oil types were used with zinc dust. These included, polystyrene, chlorinated rubber, vinyl resins and similar products. The degree of variation in the performance of coatings depended primarily on the vehicle. In general, the performance was indirectly proportional to the resistance of the vehicle to corrosive conditions.

During later 1940s, epoxy resins become available and were soon found to provide a good vehicle for zinc rich coatings. Today, three types of organic vehicles namely epoxy, chlorinated rubber and phenoxy make up the majority of the organic zinc rich products. All the three coatings have good dielectric properties provided that sufficient quantity of zinc is present in the dry coatings for particle-to-particle contact throughout the film. Various attempts have been made to specify optimum weight of zinc to be present in the coating and it is found to be between 80% to 95% by weight of the dry film [43-45]. The zinc particles must be in contact with the base metal in order for the coating to be conductive and to prevent corrosion by cathodic protection.

There is little chemistry involved in the formulation of organic zinc rich coatings other than to provide

a resistant vehicle which does not react with the zinc metal. The chemistry consists of dielectric constant of the vehicle, the presence of wetting agents, thixotropes, auxillary pigments, particle size and its proper distribution. This physiochemical factors has been discussed by several authors [46-48].

Zinc is a heavy pigment and tends to settle rapidly in paints despite the use of thixotropes. Improperly homogenized material may result in widespread variation in the zinc content of an organic zinc rich film [49]. For this reason that manufacturers recommend continuous agitation of zinc rich materials both prior to and throughout the application process [50].

Epoxy zinc rich coating has its own advantages and disadvantages. Medium molecular weight epoxy - polyamides have achieved the widest use in organic zinc rich primers. They exhibit a property similar to a chemically curing epoxy thermoset and provide strong adhesive films [51-53]. They are two component materials and require the complete mixing of two before application. Phenox systems, usually single pack ready mixed zinc primers, may be too solvent resistant for good inter coat adhesion with certain top coats such as vinyls [54]. James A. Ellor

et.al [55] studied the performance of zinc rich coatings based on epoxy, polyurethane and chlorinated rubber vehicles for ship board maintenance in marine environment and reported that the epoxy systems appear to out-perform other systems. Other reports also showed that the zinc rich epoxy coatings followed by chlorinated rubber based top coat provide excellent protection for the carbon steel structures in marine environments [56,57]. A typical composition of the coating system, which gives longer duration of protection is epoxy zinc rich primer followed by a tie coat based on vinyl - MIO and with a top coat of epoxy/vinyl/chlorinated rubber/polyurethane coating systems [58]. In Japan [59] zinc rich coatings based on epoxy ester have not often been used on steel bridge structures but extensively used in the automobile industry in U.S. [60]. Epoxy ester based zinc rich paints have better adhesion to poorly prepared substrates than do other zinc rich systems. But the evolution of alkali at the steel cathode with this system would attack the ester groups of the epoxy vehicle.

The effect of partial replacement of the zinc by di-iron phosphide extender on the anti-corrosive properties of zinc rich coatings were studied by several authors [61,62] in epoxy polyamide medium. S.Feliu et.al [63]

studied this character through impedance method and concluded that the di-iron phosphide in ethyl silicate medium does not impose the barrier effect, on the other hand the partial replacement of zinc by di-iron phosphide in epoxy polyamide media reinforce their barrier effect. In the case of galvanic effect reverse is true.

#### 2.1.(d) Cashew nut shell liquid (CNSL) primer coatings

CNSL is available as a by-product from the cashew industry in India. It lends itself to polymerisation by physical and chemical methods and the resin obtained could be used for the production of surface coatings [64]. The utilisation of CNSL in surface coating has been studied by Harvey and Caplan [65,66] in U.S.A. In India, some work on the preparation of surface coatings from CNSL has been published in 1960s [67,68]. The drying property of CNSL resin is improved by condensation with hexamine and aldehydes or treatment with drying oils. The extraction, properties and the application of the polymers obtained from the CNSL has been reviewed by L.C.Anand [69] and P.H.Gedom et.al [70], in recent years. The inhibitive primers formulated from CNSL resin is comparable in properties with other inhibitive primers [71-75]. Anti-corrosive paints based on linseed oil or DCO alkyd modified with 20-50% CNSL resin are found to give better protection

to metals from atmospheric corrosion [76]. In recent years, electrophoretic deposition is dominating in the automobile painting work. The CNSL resin is water solubilised and pigmented with inhibitive pigments and the anti-corrosive properties of the coatings are studied by M.Selvaraj and S.Guruviah [77.78].

Paints formulated using the CNSL based epoxy resin and bitumen as binders with aluminium powder, mica and zinc chromate as pigments are found to be very effective anti-corrosive coating for steel structures in marine atmosphere [79]. Similarly the primer formulated from salicylic acid CNSL-formaldehyde resin pigmented with red lead, iron oxide and talc is comparable with zinc rich epoxy primer coatings. This is due to the formation of the CNSL resin complexes with iron ions, which have a coordination number 6 [80]. Earlier S.Ramānujan has taken Indian Patent for the preparation of zinc rich paints based on CNSL polymers [81]. This zinc rich coating is also equally comparable with other organic zinc rich primer formulations.

In the organic zinc rich primers, polyamide epoxies, chlorinated rubbers and phenoxy resins are commonly used. Vinyls and styrene-butadiene resins have also been used for zinc rich coatings. The vinyl ZRP coatings are still available, whereas the styrene-butadiene is no longer

used. Alkyds and epoxy ester based zinc rich primers are widely used in automobile industries, but are not recommended as suitable vehicles for field application as industrial and maintenance primers.

## 2.2. DEVELOPMENT OF MANGANESE POWDER PIGMENTED COATINGS

In recent years manganese powder has been incorporated in zinc pigmented coatings and the corrosion protective behaviour was studied by Roland et.al [82] and found that the coatings got greater compactness and higher alkali resistance. The manganese powder is a greyish black coloured powder, hard and brittle as well as acid and alkali resistance. The properties of the partial replacement of manganese powder to ZRP coatings are explained by Tadeusz Szauer et.al [83]. This study indicated that upto 60% of the zinc is replaced by manganese and other extender without affecting the properties of the ZRP coating. The manganese ore has been used as a pigment in non-aqueous medium, but the stability of the ore is poorer in this medium. The stability of the particles in the medium is determined by the particle to particle and the particle to medium interactions [84,85]. The stability of the Egyptian manganese ore in the medium and the effect of surface treatment of the ore particles on painted films are investigated by A.A.Add El. Hakim et.al [86,87]. They

have also studied the character of the primers formulated with treated and untreated manganese ore with alkyd and epoxy resins. The results showed that the mechanical and corrosion properties of painted films improved very well with the arrangement of the ore particles in the coating formulation. The cathodic protective behaviour of the manganese pigmented inorganic coatings is reported by V.M.Kelker in 1964 [88]. But afterwards no major work has been done using the manganese pigments. In 1989, M.Selvaraj and S.Guruviah [89] carried out the electrochemical behaviour of the pigment in organic and inorganic binders and concluded that this pigment in organic binder medium gave better protection than in inorganic medium. Similarly the protective behaviour of the manganese filled organic coating was studied by A.V.Kyazimov et.al [90] and reported the performance of the coatings.

### 2.3. DEVELOPMENT OF NICKEL POWDER PIGMENTED COATINGS

Recently a new branch of surface coating technology has grown up based upon the capability of the coatings to provide effective shielding for electronic equipment against radio frequency and electromagnetic interference (R.F.I/E.M.I). Organic based coatings provide a very attractive method of applying this type of shielding. These systems are not, however, inherently electrically conducting and therefore can only provide effective shield-

ing if suitable conductive pigments are incorporated. Nickel has a combination of properties which make it a very attractive material for this application [91]. The effect of nickel particle morphology on the electrical conductivity of organic coating is quite considered. Nickel flakes produced by ball milling process [92] are useful for conductive paint applications. Nickel having regular spherical shape also could be used in conducting coatings. The flake material shows a small advantage at pigment loading in excess of about 40%, whereas the spherical pigment requires a much higher loading to exhibit the real conductivity to achieve point to point contact of the particles [93]. An electrically conductive coating is obtained from the mixing of nickel, copper and chromium powders with an acrylic resin [94].

The nickel flakes manufactured from high purity carbonyl powder has good corrosion resistance, particularly in alkaline environment. The resistivities of the nickel flake pigmented acrylic, polyurethane and polyester based paints were measured. Depending upon the resin system, the nickel pigmented coatings perform well in different environmental condition [95]. Further S.Guruviah et.al [96] had studied the properties of nickel pigment having spherical structure incorporated in epoxy resin in alkaline



medium and concluded that the corrosion resistance performance were better than that of zinc rich coatings.

#### 2.4. DEVELOPMENT OF STAINLESS STEEL POWDER PIGMENTED COATINGS

In recent years a new metallic pigment was brought to the attention of paint formulators namely stainless steel. This metal composed of iron, nickel and chromium is known to resist most types of staining, tarnishing, oxidation and chemical attack. The stainless steel flake pigment can be produced from any type of stainless steel. The shape of the particles are in irregular flake. The stainless steel flake pigment is supplied in either a dry or paste (85% solid in mineral spirit) form. The use of stainless steel pigment in the coating industry is mainly due to its inertness [97].

The stainless steel pigmented coatings show much greater resistance to abrasion than the other metallic pigmented coatings [95]. The chemical inertness of the stainless steel pigmented coating suggests its use in high temperature applications and in highly corrosive environments [98.99]. Unlike other metallic pigments, stainless steel pigment could be used in alkyd, epoxy, vinyl, phenolic, acrylic, fluoro carbons, polyurethane, chlorinated rubbers and other systems. This pigment is

used as a primer pigment as well as a component of any multipigment systems for both protective and decorative coatings [100].

Norman [101] studied the properties of the stainless steel pigmented coatings and concluded that the stainless steel is not considered as a corrosion inhibitive pigment by itself, unless used at extremely high concentration. However, stainless steel flakes offers a reinforcement property to most pigment combination. It is possible to combine with the anti-corrosive pigments so as to get a complete coating systems. The optimum results are obtained with a primer coat of iron oxide and zinc chromate applied to a dry film thickness of 1.5 mils and the similar thickness of top coat with stainless steel pigment.

Tim Race et.al [102] used the stainless steel pigment as a sealant in vinyl and epoxy polyamide coating and studied the performance in dam applications and concluded that since pin-point rusting was noticed after 10 months duration, the performance as sealant was not good. But increase in the thickness of the coating would prevent the penetration of the corrosive ions into the continuous coating. The properties of the stainless steel flake pigments in different binder system is also explained by Hiroshi Ito [103].

Nowadays the metallic pigments are incorporated with fluoro polymers and used as top coats. The fluoro polymer based metallic pigmented coating consists of a wide range of pigment percentage (5-70%), and it depends upon the end use [104]. A composition of a primer with top coat which remains weldable consists of an anti-corrosive pigment with graphite powder as primer and a top coat containing stainless steel powder in a fluoro polymer [105].

Stainless steel as a pigment offers exceptional inhibitive action in organic coatings to protect metal surfaces from corrosive environments. Once the initial cost factor has been overcome, it could prove in the long term a more economical product.

## 2.5. SCOPE OF THE PRESENT WORK

The literature relating to the metal powder pigmented coatings have been extensively reviewed. The protective mechanism of zinc dust pigmented coatings have been extensively studied from early 1920s onwards but the study of protective mechanism of other metallic pigments like nickel, manganese and stainless steel are in the developing stage. The survey of literature leads one to the conclusion that some work has been done in the field of other metallic pigmented coatings. So there is a need to do lot of work in this field.

The present study consists of preparation of metal pigmented paints based on inorganic, organic and naturally available binders incorporating zinc, nickel, manganese and stainless steel powder as pigments, and their protective mechanism is evaluated by electrochemical methods. The study relates to :

- (i) Preparation of resins based on butyl titanate, CNSL, epoxy and chlorinated rubber.
- (ii) Preparation of primers using the metallic pigments and the top coats using MIO and  $\text{TiO}_2$  pigments.
- (iii) Choosing the correct pigment weight concentration of the primers by potentiodynamic method.
- (iv) Characterisation of the physical, accelerated and electrochemical properties of the primers based on the above results and the surface morphology of the primers by SEM method.
- (v) The primers are top coated with MIO and  $\text{TiO}_2$  pigmented chlorinated rubber based formulations and protective mechanism of these top coats on the metal powder pigmented coatings by electrochemical measurements have been compared.

## References

1. Clive H.Hare. 1990. J. of protective coatings and linings, 7 (9) : 61
2. Charles G.Munger. 1987. J. of protective coatings and linings, 6 (6) : 187.
3. Zinc - Its corrosion resistance, 2nd edition, International Lead Zinc Research Organisation, Research Triangle Park, NC, 1983.
4. Rochow.E.G. 1975. 'Comprehensive Inorganic Chemistry' Ch.XV, Chemistry of Silica, Pergamon, Elmsford, N.Y.
5. Mc Mahon.W and Abda.C. U.S.Patent 3,130,061, April 21, 1964.
6. Mc Mahon.W and Abda.C. U.S.Patent, 3,142,583, July 28, 1964.
7. Lopata.S and Keithler.W. U.S.Patent, 3,056,684, Oct 2, 1962.
8. Starr.T.L. Improving the Reliability of Zinc Rich Paint Systems, JPCL, March 1986, PP.22-31.
9. Munger.C.G. 1982. S.S.P.C. Manual, Vol.1. Chapter 4.2, 125-37, Pittsburgh, PA Steel Structures Painting Council.
10. Munger.C.G. 1975. Materials Performance, 14 (5): 25-29.
11. Hendry.M.C. 1978. Materials performance, 17 (5): 19.

12. Marcel Leclercq. 1990. J. of Protective Coatings and Linings, 7 (3) : 57.
13. Del Amo.B and Gindice.C.A. 1990. World Surface Coatings Abstracts 63 (582) : 2259.
14. Kapse.G.W and Bela Rani.KM. 1980. J. of Oil and Colour Chemists Association, 63: 70-76.
15. Tator.K.B. 1976. Materials performance, 15 (3): 9-16.
16. Munger.C.G. 1977. Materials performance, 16 (3): 33-36.
17. Lindquist.S.A, Meszaros.L and Svenson.L. 1985. J. of Oil and Colour Chemists Association, 68 (1):10.
18. Lindquist.S.A, Meszaros.L and Svenson.L. 1985. J. of Oil and Colour Chemists Association, 68 (2): 34.
19. Feliu.S, Barajas.R, Bastidas.J.M and Morcillo.M. 1989. J. of Coatings Technology, 61 (776) : 63.
20. Feliu.S, Barajas.R, Bastidas.J.M and Morcillo.M. 1989. J. of Coatings Technology, 61 (776) : 71.
21. Clive H.Hare. 1990. Painting of Steel Bridges and Other Structures, Van Nostrand Reinhold Publication, New York : 19.
22. Saldutt.J. 1985. 25th Marine and Offshore Coatings Conference, Norfolk, VA : 28.
23. Cook.M. 1989. Corrosion Prevention and Control. 36 (5) : 121.
24. Moran.D.F. 1989. Ingenieria, 57 : 518 (Spanish).
25. Smieszek.E and Hamela.D. 1990. World Surface Coatings Abstracts, 63 (526) : 1092.

26. Pereira.D, Maia.A and Padinha. 1989. Rev. Iberoamericana Corrosion Protection, 20 (4) : 185.
27. Kansai Paint Co, 1987. Japanese Patent Gaz. 87(9): 7.
28. Feliu.S.Jr, Morcillo.M, Bastidas,J.M and Feliu.S. 1991. J. of Coatings Technology, 63 (793): 31.
29. Graedel.T.C. 1989. Electrochemical Society, 136(4):193.
30. Elisabeta Almeida.M, Pereira.D, Cabrel.A.M and Morcillo.M. 1991. J. of Oil and Colour Chemists Association, 74 (1): 21.
31. Al Meida.E, Pereira.D and Figuerado.D. 1989. Progress in organic coatings, 17: 175-189.
32. Tator.K.B. 1971. 9th Annual Liberty Bell Corrosion Course, Philadelphia, PA.
33. Delahunt.J.F and Nakachi.N. 1989. J. of Protective Coatings and Linings, 6 (2): 48.
34. Pepin.B. 1987. World Surface Coatings Abstracts, 60 (542): 1286.
35. Taylor.J. 1960. J. of Oil and Colour Chemists Association, 43 (8): 555.
36. Sidlow.R. 1956. J. of Oil and Colour Chemists Association, 39 (6): 415.
37. Bhatia.K.L. 1966. Paint India, 16 (4): 114.
38. Sidlow.R. 1958. J. of Oil and Colour Chemists Association, 41 (8): 577.
39. Hall.J.E. 1987. J. of Coatings Technology, 59 (749):51.

40. Selvaraj.M and Guruviah.S. 1987. Bulletin of Electro-chemistry, 3 (4): 301.
41. Miyako Co Ltd., Japan. 1984. Chemical Abstract, 93: 97003j.
42. Selvaraj.M and Guruviah.S. 1989. Trans. of SAEST, India, 24 (1): 125.
43. Evans.U.R. 1944. J. of Iron and Steel, 149 (1):67.
44. Pass.A. 1952. JOCCA, 35 (6): 241.
45. Elm.A.C. 1956. Paint and Varnish Production, 46 (8):27.
46. Hare.C.H, Leary.M.J.O and Wright.S.J. June 1983. Modern Paint and Coatings.
47. Mason.D.G. 1967. Material Protection and Performance, 6 (5): 43.
48. Castelli.R, Meda.J, Caprain.J and Damia.M. 1983. J. of Coatings Technology, 55 (70): 753.
49. Tator.K.B. 1976. Materials Performance, 15 (3): 9.
50. NACE Publication, 6B173.
51. Young.C.I. "U.K. Experience with zinc dust paints-I", In Protecting steel with zinc dust paints, Vol.2, London: Zinc Development Association.
52. Lithgow.O. "U.K. Experience with zinc dust paints-2", In protecting steel with zinc dust paints, Vol.2, London: Zinc Development Association.
53. U.S. Army Corps of Engineers, Epoxy Polyamide Zinc Rich Primers Specification, CE 1409E, 303a.
54. Berger.D.M. 1975. Modern paint and coatings, 65 (6):19.



55. James A.Ellor, Robert A.Kogler and Parks.A.P. 1990. J. of Protective Coatings and Linings, 7 (12): 47.
56. Berger.D.M. 1986. Corrosion Abstract, 25 (6): 460.
57. Jaganath.J.M and Nirvan.Y.P.S. 1987. Paint India, 37 (4): 32.
58. Visioli.F. 1987. World Surface Coatings Abstracts, 60 (541): 1128.
59. Jitsufuji.M. Zinc rich coatings in Japan. In protecting steel with zinc dust paints, Vol.2, London.: Zinc Development Association.
60. Metil.I. 1979. Modern paints and coatings, 69 (12):39.
61. Fewcett.N.C, Stearns.C.E and Bufkin.B.G. 1984. J. of coatingstechnology, 56 (709): 31.
62. Simpson.V.P and Simko.F.A. 1973. J. of oil and colour chemists association, 56 : 491.
63. Feliu.S.Jr, Bastedas.J.M, Morcillo.M and Feliu.S. 1991. J. of CoatingsTechnology, 63 (794): 67.
64. Rosswell.C and Parnn.K. 1945. Paint Technology, 10 (118): 245.
65. Harvey.M.T. 1945. Paint Technology, 10 (120): 1.
66. Caplan.S. (to Harvel Corpn), 1956. U.S.Patent. 27,54,283.
67. Ramanujan.S. 1962. Paint India, 12 (5): 22.
68. Thaker.K.R and Gupta.J. 1957. Indian Patent Specifications, 55171.

69. Lalit C.Anand. 1978. Paint India, 27 (6): 13.
70. Gedam.P.H and Sampath Kumaran.P.S. 1986. Progress in organic coatings, 14 : 15.
71. Guruviah.S and Rajagopalan.K.S. 1971. Paint India, 21 (7): 15.
72. Shirsalkar.M.M and Sivasampan.M.A. 1975. Paint India, 25 (12): 17.
73. Ramanujan.S. and Saluja.R.V. 1964. Indian Pat. 81,483.
74. Ray.S.B and Sircar.H.D. 1963. Paint India, 12:18.
75. Selvaraj.M and Guruviah.S. 1987. Paint India. 37 (8): 27.
76. Shirsalkar.M.M and Sivasampan.M.A. 1976. J. of Colour Society, 16 (2): 13.
77. Selvaraj.M and Guruviah.S. 1986. Bulletin of Electro-chemistry, 2 (4): 363.
78. Selvaraj.M and Guruviah.S. 1987. Paint India, 37(7):19.
79. Choudhuri.K.C, Ramamurthy.R, Laha.B.N and Skukla.K.K. 1972. Indian Patent 127126.
80. Mihara.K, Kobiyama.K and Yoshida.Y. 1969. Cashew Co Ltd., Ger. Offen. 1813794.
81. Ramanujan.S and Ramamurthy.A. 1958. Indian Patent Specification: 60613.
82. Roland Wolf.A and Gottwald.K.H. 1988. Metalloberflacke (Ger), 42 (6): 301.

83. Tadeusz Szauer and Andrzej Miszczyk. 1987. *Bulletin of Electrochemistry*, 3 (6): 541.
84. Moussa.M.N.H, Taha.F.I.M, Gouda.M.M.A and Singab,G.M. 1976. *Corrosion science*, 16: 379.
85. Aflaton Singab.G.M. 1975. Master Degree Thesis, Mansoura University.
86. Abd El.Hakim.A.A, Abd EI-Ghaffar.M.A, Abd EI Malek.M.M and Youssef.E.A.M. 1990. *Anticorrosion methods and materials*, 37 (1): 6.
87. Abd EI.Hakim.A.A, Abd EI.Ghaffar.M.A, Abd EI.Malek.M.M and Youssef. E.A.M. 1990. *Anticorrosion methods and materials*, 37 (2): 4.
88. Kelkar.V.M and Puntambekar.S.V. 1964. *Chemistry and Industry*, July 18: 1315.
89. Selvaraj.M and Guruviah.S. 1989. *Bulletin of Electrochemistry*, 5 (7): 528.
90. Kyazimov.A.V and Abdulayev.M.M. 1990. *World surface coatingsabstracts*, 63 (571): 94.
91. Hart.A.C. 1989. *J. of Oil and Colour Chemists Association*, 72: 95.
92. Antonsen.D.H. 'Pigment Hand Book', Vol.1, John Wiley and Sons Inc, 823.
93. Antony C.Hart. 1989. *Metal Finishing*, 87 (6): 67.
94. Asahi Pen Co, 1985. *Jap. Pat. Gaz.* 85 (43): GPG.3.

95. Hart.A.C. 1983. Trans. of Ins. of Metal Finishing, 61: 150.
96. Guruviah.S, Sundaram.M and Ganesa Sharma.V. 1989. Bulletin of Electrochemistry, 5 (7): 516.
97. Temple C.Patton. 1973. 'Pigment Hand Book', Vol.1, John Wiley and Sons, New York: 833.
98. Ellinger.M.L. 1966. Paint Technology, 51: 52.
99. Higgins.E.J. 1959. American Paint Journal, 44 (1):27.
100. Higgins.E.J. 1965. Electrical World, 163 (26):108.
101. Norman.I.G. 1967. Metal Finishing, 65: 62.
102. Tim Race, Vince Hock and Al Beitelman. 1989. J. of Protective Coatings and Linings, 6 (8): 37.
103. Hiroshi Ito. 1982. Kogyozairoyo (Japan), 30 (4):73.
104. Jap. Pat. Gaz. 1990. 90 (21): GPG 40.
105. Jap. Pat. Gaz. 1988. 88 (35): GPM 21.