

RESISTANCE

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In electromotive force (EMF) series, zinc occupies a place much lower than iron ($E_0\text{Zn} = -0.76\text{V}$ and for iron $E_0\text{Fe} = -0.44\text{V}$). Thus thermodynamically, Zn is very unstable compared to iron and in practice, it is indeed found to corrode sacrificially in contact of iron in most of the environments. In dry environment having plenty of supply of oxygen and carbon dioxide, the corrosion rate of zinc, however, is about 25 times less than iron. It is a very surprising fact and reason is attributed to the formation of passive layer on the zinc surface. Zinc surface combines with Oxygen to form ZnO. If CO_2 is also available, the upper layer is converted into zinc carbonate. These compounds provide protection to the surface in absence of moisture. However, if ingress of moisture and other gases take place to the surface, these protective films are damaged and an onset of deterioration of metal/coating takes place as a result of formation of zinc hydroxide, $\text{Zn}(\text{OH})_2$. This initial discolouration of the zinc surface is known as white rusting.

White rusting of galvanized surfaces reduce the life of coatings:

A simple ZnO/ZnCO_3 protective film formed on the zinc surface occupies more volume than the parent metal (about 500 times more) and is under compression. As the oxide film thickens, the outer layers tend to fissure and scale. Under the influence of erosion caused due to nature (wind, rain etc) or during handling of the products, the outer layer of oxide is detached from the surface. This results in a gradual loss of the coatings layer after layers. The protection of upper layer of galvanized coating against white rusting is therefore, not important only from aesthetical point of view but also plays important role in increasing the durability of the coatings. The compactness of the coating's protective upper surface and its adherence to the parent zinc metal can be increased by providing following surface treatments to the coatings

Providing Top coat based on organic coatings:

(a) **Top coat based on organic coatings:** The purpose of application of organic coating on the surface of the galvanized coating is to ensure that no active ingredients should reach to the

galvanized surface to form white rust. In some cases, the coating is also applied for decorative purposes. The greatest problem, however, associated with the galvanized coating is that the surface does not have an anchor profile to support the shrinkage stresses of the relatively heavy organic coating. Another problem associated with the galvanized surface is that the ingress of oxygen and carbon dioxide to the base surface is essential to maintain the protective properties of the surface. Thus choice of an organic coating should be such that it should transmit water vapour but must allow oxygen and carbon dioxide to reach the zinc surface so that its protective property is maintained. Before providing an organic coating on zinc surface, the following aspects should be kept in mind:

- (i) The coating should be provided after a conversion treatment such as chromating, molybdate treatment or phosphate treatment.
- (ii) The surface should not be providedd vinegar washing. The acetic acid converts the protective oxide/carbonate layer into soluble zinc acetate.
- (iii) An anodic inhibiting primer is preferred.
- (iv) Air oxidizing alkyl paints shuld not be used. They are quite alkaline in nature. Ester type of solvent if used in organic coatings, they have a detrimental effect.
- (v) The coatings that allows the ingress of moisture but inhibit the access of oxygen should not be used.
- (vi) A thin film coating which provides erosion protection and allows ready permeation of oxygen to the substrate should be used.
- (vii) A baked organic coating system should be preferred. This helps in enhancing of the film strength and driving out of solvent entrapped with the organic coating.

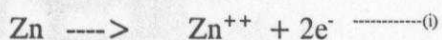
Surface conversion coatings:

As discussed earlier, the life of a galvanized coating can be substantially enhanced by providing a treatment to the surface so that the coating formed is not under compression and free of fissures. A number of attempts had been made by researchers to provide such a treatment. It has been established that chromating of the galvanized surfaces is a fool-proof technique to achieve the above goal. However, due to the basic nature of chromium in its hexavalent form, the corrosion protecting products based on low chromium, molybdate, tungstate, phosphate, oxidizers and organic chelating agents have been developed. The functioning of these formulations and their industrial applications will be discussed here one by one.

High Chromium based surface conversion coatings:

Oxygen containing oxidizing agents are reported to be good corrosion inhibitors for iron in neutral media. In recent years, considerable attention has been paid towards evaluating these

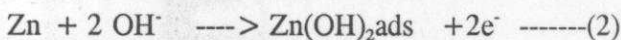
type of oxidizers as corrosion resistant film forming agents for non ferrous metals such as zinc, copper, tin , aluminium etc. The chromate ion is considered to be one of the most effective passivating species towards the metals and alloys. The superimposition of potential- pH diagram of zinc and chromium indicates that the galvanized surfaces can be protected by the formation of a passive film of $\text{Cr}(\text{OH})_3$ or Cr_2O_3 if the metal is immersed in an acidic solution (pH 4-5) of hexavalent chromium. When zinc is immersed in an acidic solution, it reacts with acid to liberate electrons;



The dissolved oxygen is cathodically reduced to produce OH^- ;



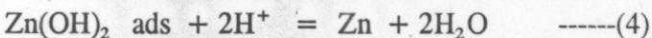
The chemisorption of hydroxyl ions takes place at the metal surface.



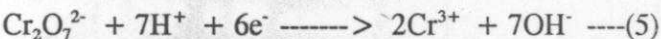
The reaction (2) has a stimulating effect on zinc reaction with the electrolyte. Due to the acidic nature of the bulk electrolyte of the passivating bath (pH 3.5), desorbed OH^- ions are neutralized by protons near the electrical double layer,



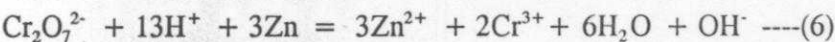
the intermediate compound $\text{Zn}(\text{OH})_2\text{ads}$ will, thus not accumulate at the surface and therefore, no polarization of the reaction will occur. The overall reaction can be written as:



As is evident from equation (2) the rate of reaction of formation of $\text{Zn}(\text{OH})_2\text{ads}$ at the corrosion potential region is controlled by the concentration of generated hydroxyl ions in the electrical double layer. This reaction is expected to be facilitated by the reduction of the dichromate ion in an acidic solution where OH^- ions are formed:

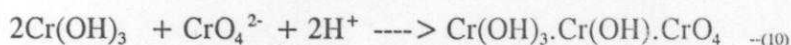
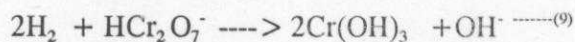
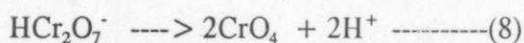
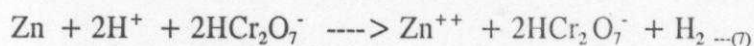


The reaction for zinc in an acidic solution having dichromate ion can be written as:



The above reaction (6) shows that the OH^- ions formed by the reduction of dichromate are not completely utilized in the anodic reaction of zinc. During the exposure of the zinc or galvanized articles in the passivating baths having $\text{Cr}_2\text{O}_7^{2-}$ ions, the excess OH^- ions (relative to the number of electrons consumed in the cathodic process) accumulate at the electrode surface. This results in localized increase in pH at the interface which results in the formation of $\text{Zn}(\text{OH})_2$ and $\text{Cr}(\text{OH})_3$ on zinc metal. It is now well established that the mixed oxide of zinc and chromium formed on the surface causes the passivation of zinc surface.

Another mechanism for the passivation reaction has been suggested as follows:



(chromium chromate film)

It is now well established that the above chromium chromate film $\{\text{Cr(OH)}_3 \cdot \text{Cr(OH)} \cdot \text{CrO}_4\}$ is mainly responsible for the formation of protective coatings. It is also evident from the above reactions that zinc cation is not associated with the passive film. It is therefore, important that the pH of the solution of passivator should be strictly maintained between 3.5-4.5 so that it can help in liberation of electrons from zinc and also could precipitate out hydroxide at the interface. A solution having very high value of acidity and also lesser acidity will not help in proper formation of the coating.

Low chromium containing passivators:

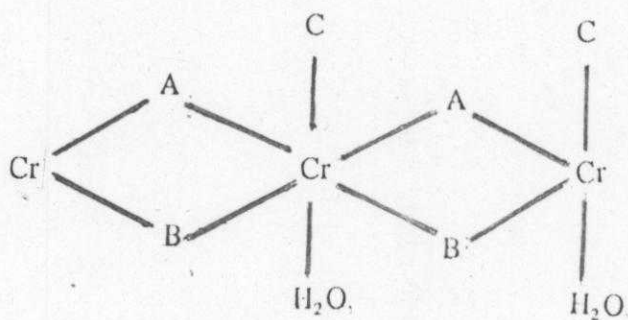
Due to stringent rules of pollution control in discharge and use of hexavalent chromium, efforts are being put allover world to reduce the use of Cr^{+6} in passivators, as low as possible. It has been reported, for example, that the chromium (vi) in the passivation baths should be of the order of 1.2% or above to achieve satisfactory protection to the galvanized surfaces. The recent studies have revealed that incorporation of certain organic and inorganic materials with Cr^{+6} enhances the performance of chromium chromate film formed on the surface. Phosphates, molybdates, nitrates and sulphates also responds positively with Cr^{+6} in improving the corrosion resistance.

It has been reported that a salt spray resistance (BS 117) of about 100 hours of coating can withstand white rusting in industrial and saline environments for quite a considerable period of time (6 months minimum) provided no water is entrapped at any part of the coating and oxygen availability is not reduced. To achieve this resistance, conjoint actions of some ingredients known to enhance the protective properties of coatings, are employed to reduce Cr^{+6} in the passivation baths. Some lab scale results are shown in figures 1 to 5. It can be seen from these figures that molebdate, nitrates, sulphate and polymeric materials improve the performance of Cr^{+6} maintained at a low concentration (0.07%) in the bath. It is also noted from figure 2 that a 100 hours corrosion resistance in the presence of Cr^{+6} alone is never achieved even if its concentration is maintained as high as 10%. The performance of a newly developed product

NML-Galvasave which is based on a very low concentration of Cr^{+6} ($<0.07\%$) vis-a-vis a best passivator available in the market and is based on a high concentration of Cr^{+6} , is shown in figures 6 and 7. The figures reveal that even at lower concentration of Cr^{+6} , a better protection than high Cr^{+6} can be achieved by the proper designing of the passivators.

Effect of ageing time after passivation on performance of coatings:

The complex reactions during the formation of passive film on galvanized surfaces, as discussed above, clearly indicate that a number of ingredients added in the passivation bath, affect the performance of the coatings. The six distinctive sites of Cr^{+6} are bound with ions and in this wet unstable gel like conversion film, some chromate solution is entrapped.



Where $A = \text{HSO}_4^-$ or HCrO_4^-

$B = \text{OH}^-, \text{NO}_2^-, \text{Cl}^-$

$C = \text{H}_2\text{O}, \text{F}^-, \text{B}$

The above schematic representations clearly indicates that the film formed on the galvanized coating in passivation bath, remains active in reacting with zinc even after its removal from the bath. A perfect film to withstand the corrosive attack of gases and moisture, develops only after the treated surface is allowed to age in a shed or under the influence of air blowing. Experiments have shown that the number of hours required for on set of white rusting increases with ageing time allowed to passivated surface (figure 7). It is therefore, important that the passivated surface should be stored in a shed at least for 100 hours to achieve a stable passive film.

Optimization of concentration of passivators in a bath:

The galvanized surface after passivation in a proper passivation bath should acquire an anodic passive film on the surface. This helps in forming a compact film having negligible fissures and also compression free. A galvanized surface, therefore, when dipped in a passivation solution bath should have an anodically controlled reaction and its potential should move towards more

nobler values. A plot of concentration vs potential of the galvanized coating will give a maxima (figure 8). This is the optimum concentration required for achieving greatest degree of protection for a coating. It is to be noted here that this technique takes hardly 2-3 hours to know the required concentration in a bath in comparison to the usual salt spray technique which requires more than 100 hours for ageing of film and another 100 hours for exposure test.

Polarization technique:

This technique also gives quicker result in optimization of the concentration and also in evaluation of comparative performance of passivators. Some examples are shown in figures 9 and 10.

Thickness of chromium layer after passivation :

This is the technique employed to determine the expected corrosion resistance with amount of Chromium present on the galvanized surface. The result of such an observation is however, redundant now, in view of the passivators who provide superior performance even though the chromium content is minimal, on the surface.

Actual exposure of galvanized sheets passivated in the presence of different types of passivators:

Some of the passivators perform well in salt spray tests but behave otherwise when exposed to actual industrial/marine environment. To confirm this, some samples were treated in different compositions of passivation baths and were exposed in marine environment of Digha (Bay of Bengal). The conditions of the treatment were the same. Both the passivators behaved equally good in salt spray tests. Two controlled specimen were also kept in dessicator after the treatment. The microphotographs are shown in figures 12-19. The results clearly demonstrate that a passivator low in chromium but having other ingredients (designated as NML-GALVASAVE) has an amorphous passive layer compared to a surface treated with a high chromium passivator (Chemidite) which produces a brittle structure. The film produced by the latter passivator is observed to be cracked probably due to high degree of compression in the film. After treatment and exposure to marine environment for 6 months, the surfaces treated with chemidite (producing brittle structure) have got more deteriorated in comparison to the surfaces treated with low chromium passivator having organics and other film forming substances (NML-GALVASAVE).

ACKNOWLEDGEMENTS

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Further readings:

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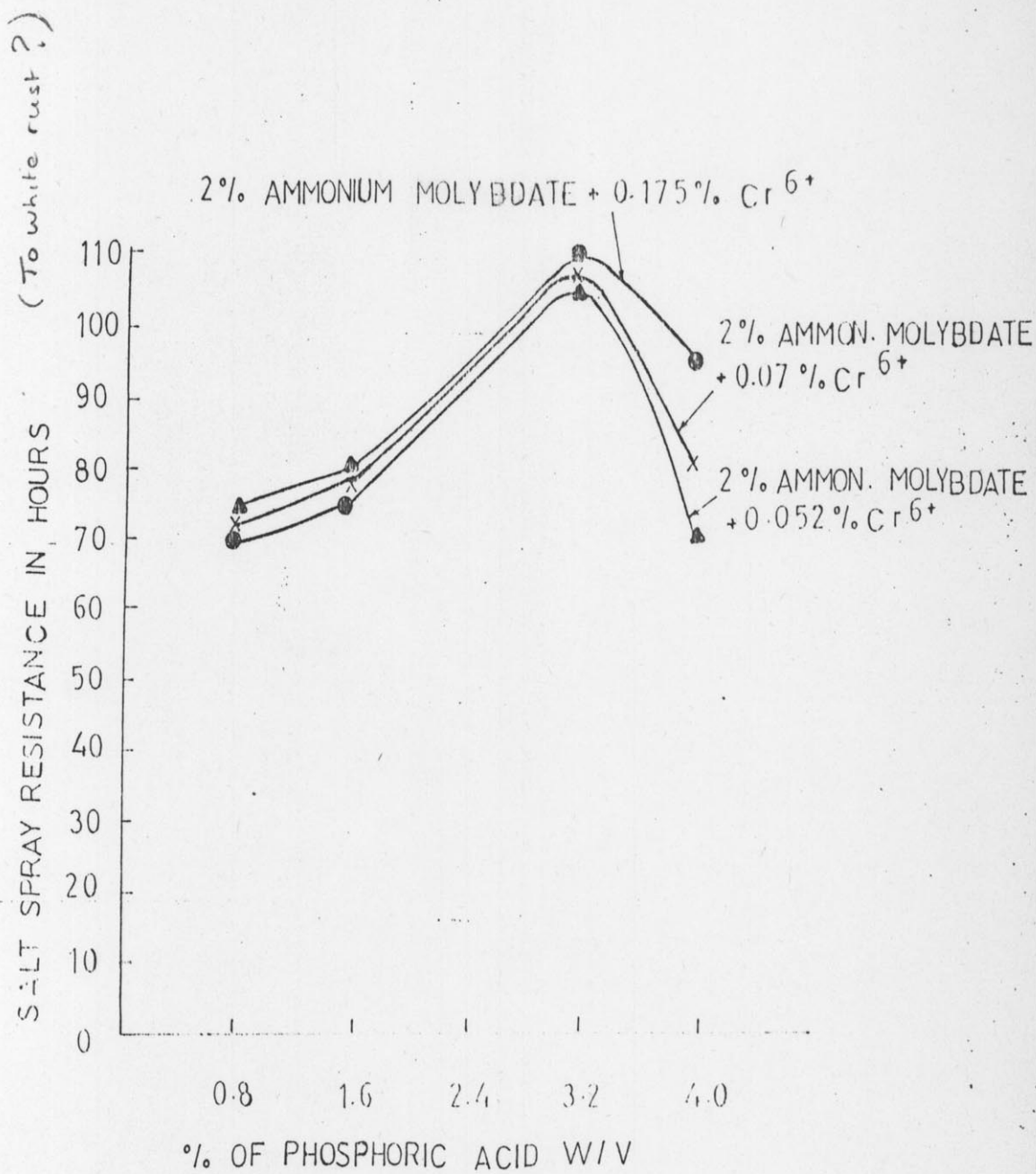


FIG. 1 EFFECT OF H₃PO₄ ON PERFORMANCE OF MOLYBDATE + CHROMATE COMPOSITION

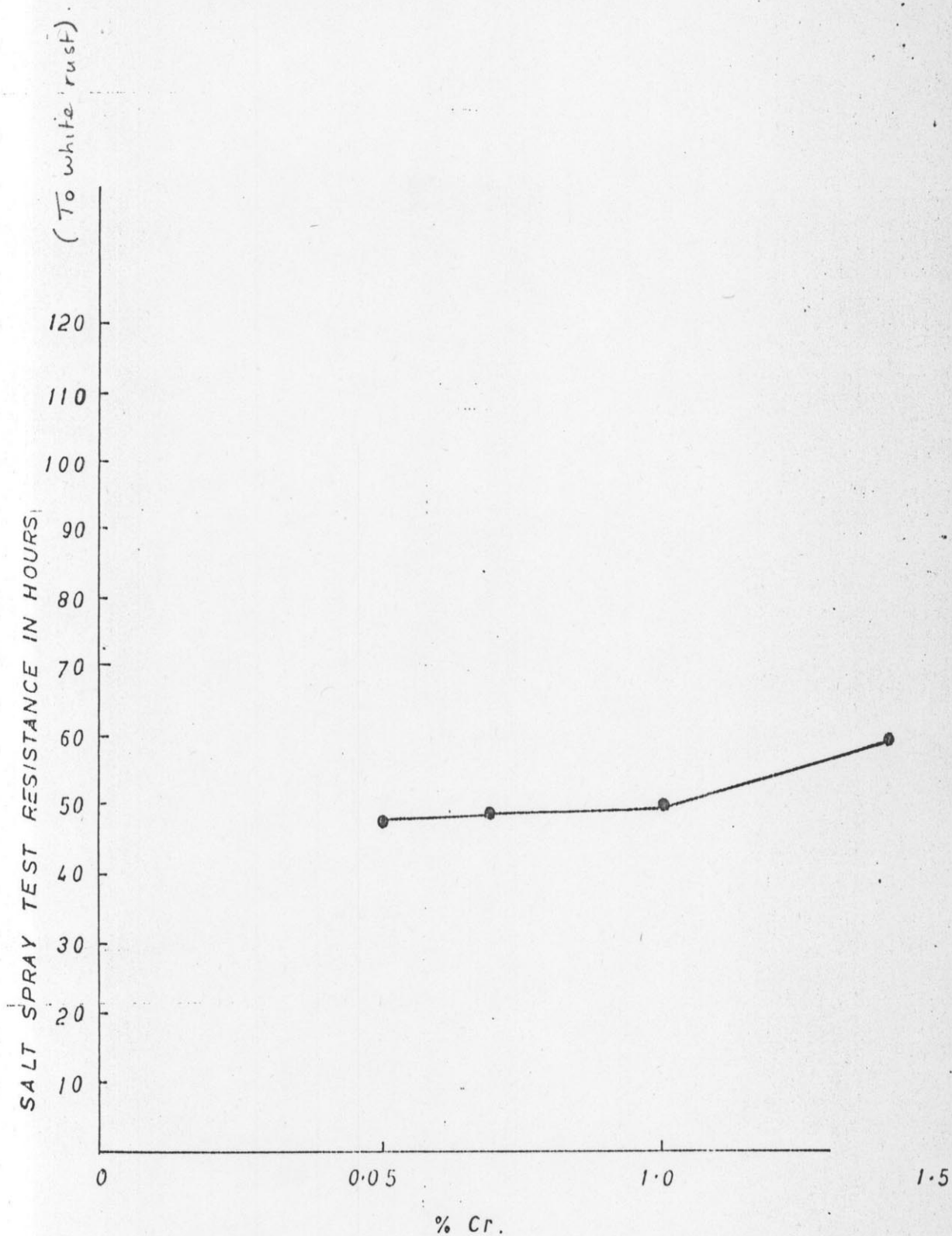


FIG.2 EFFECT OF CONCENTRATION OF CHROMIUM IN THE BATH OF PASSIVATOR

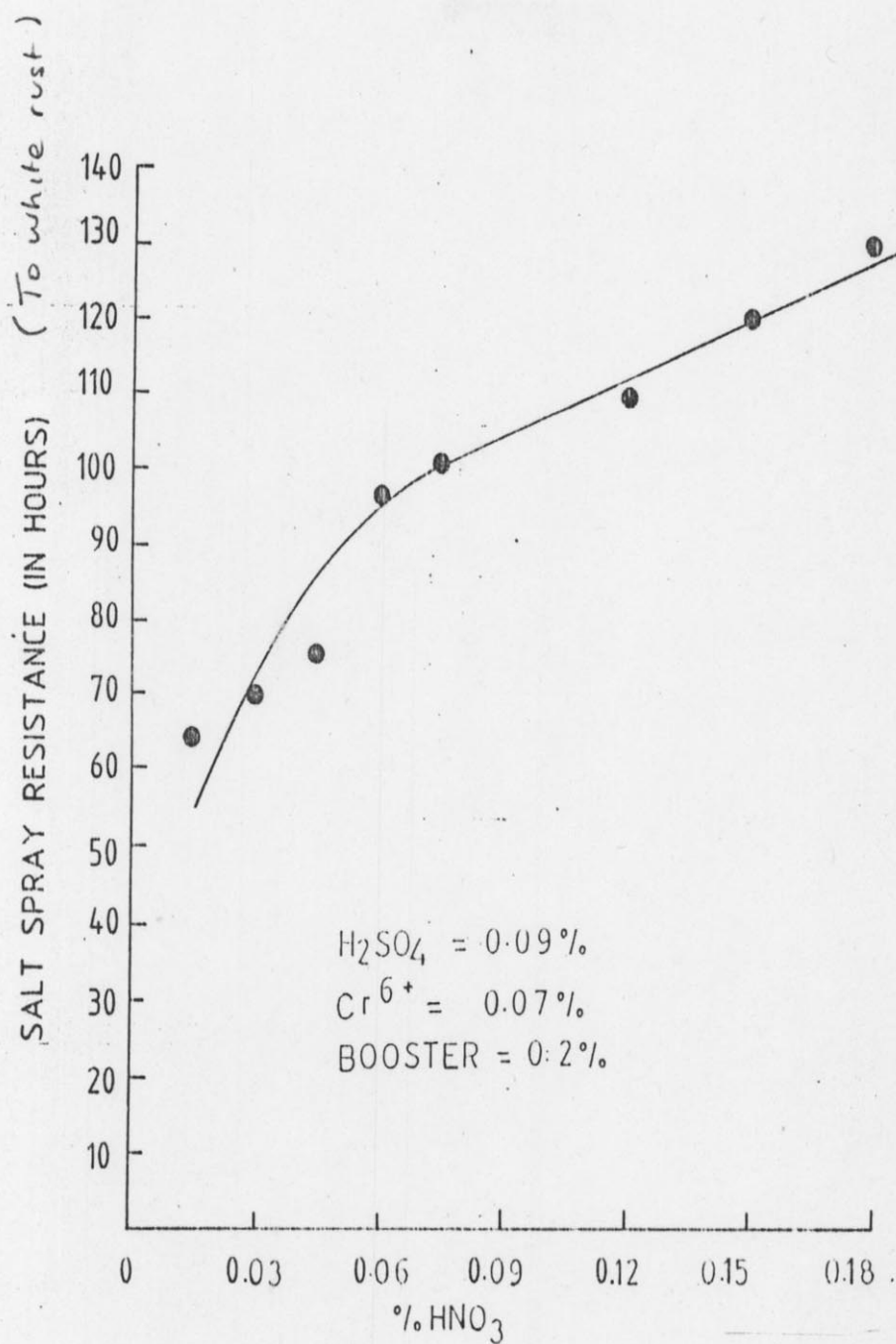


FIG.3. EFFECT OF INCREASED CONCENTRATION OF HNO_3 IN THE PASSIVATION BATH.

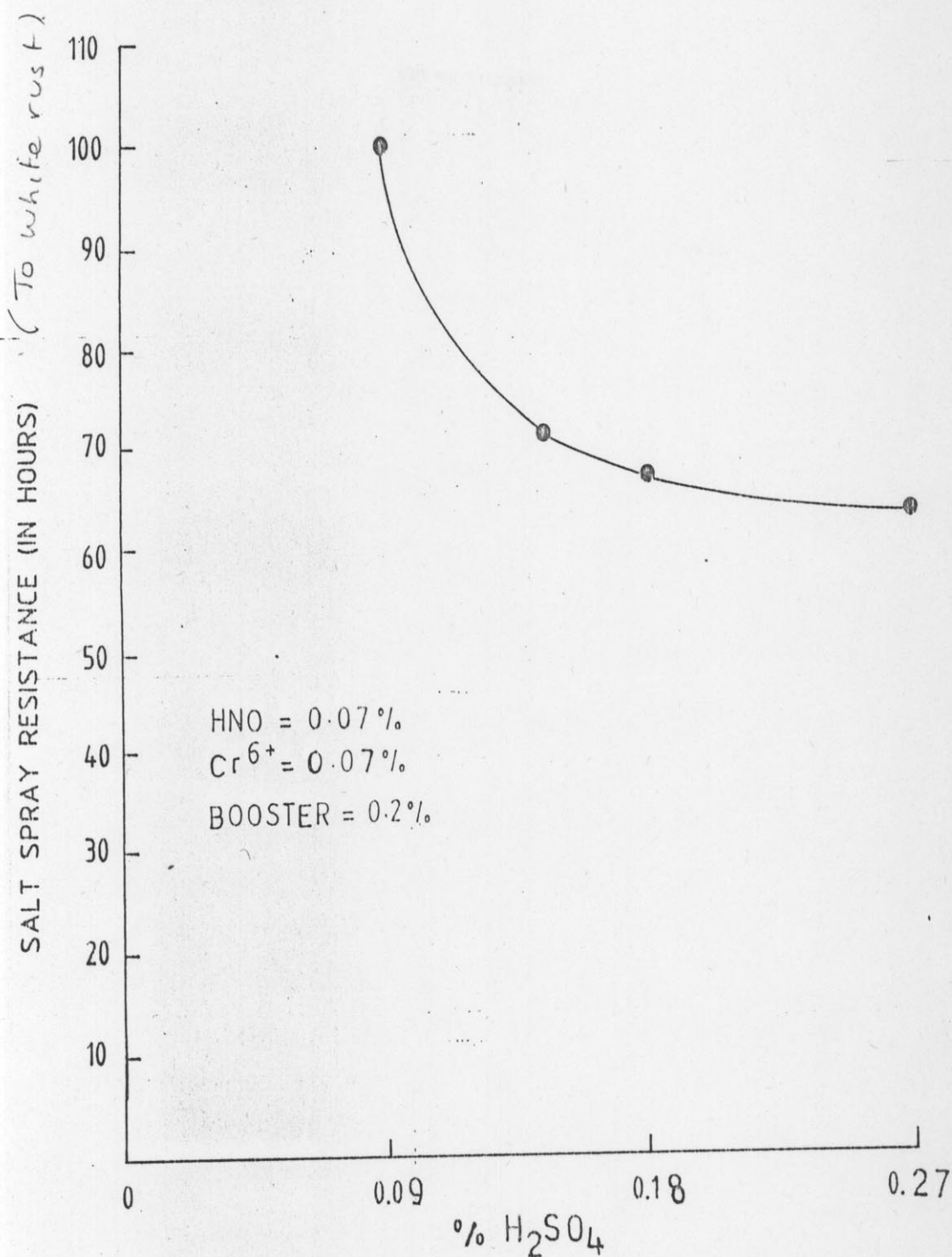
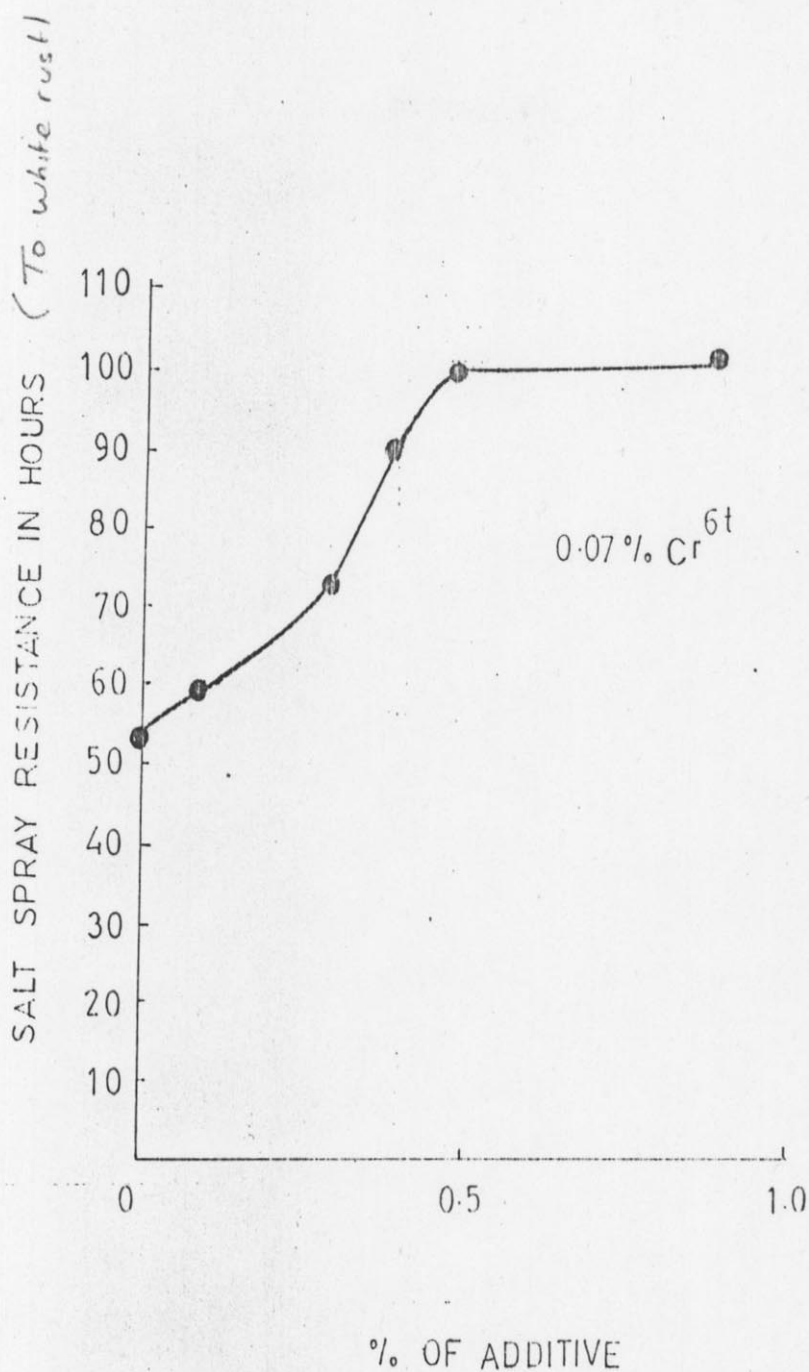


FIG. 4 EFFECT OF INCREASED CONCENTRATION OF ACTIVATOR-1 IN THE PASSIVATION BATH.



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FIG.5 EFFECT OF ADDITION OF RESIN ON SALT SPRAY
RESISTANCE IN THE PRESENCE OF Cr⁶⁺

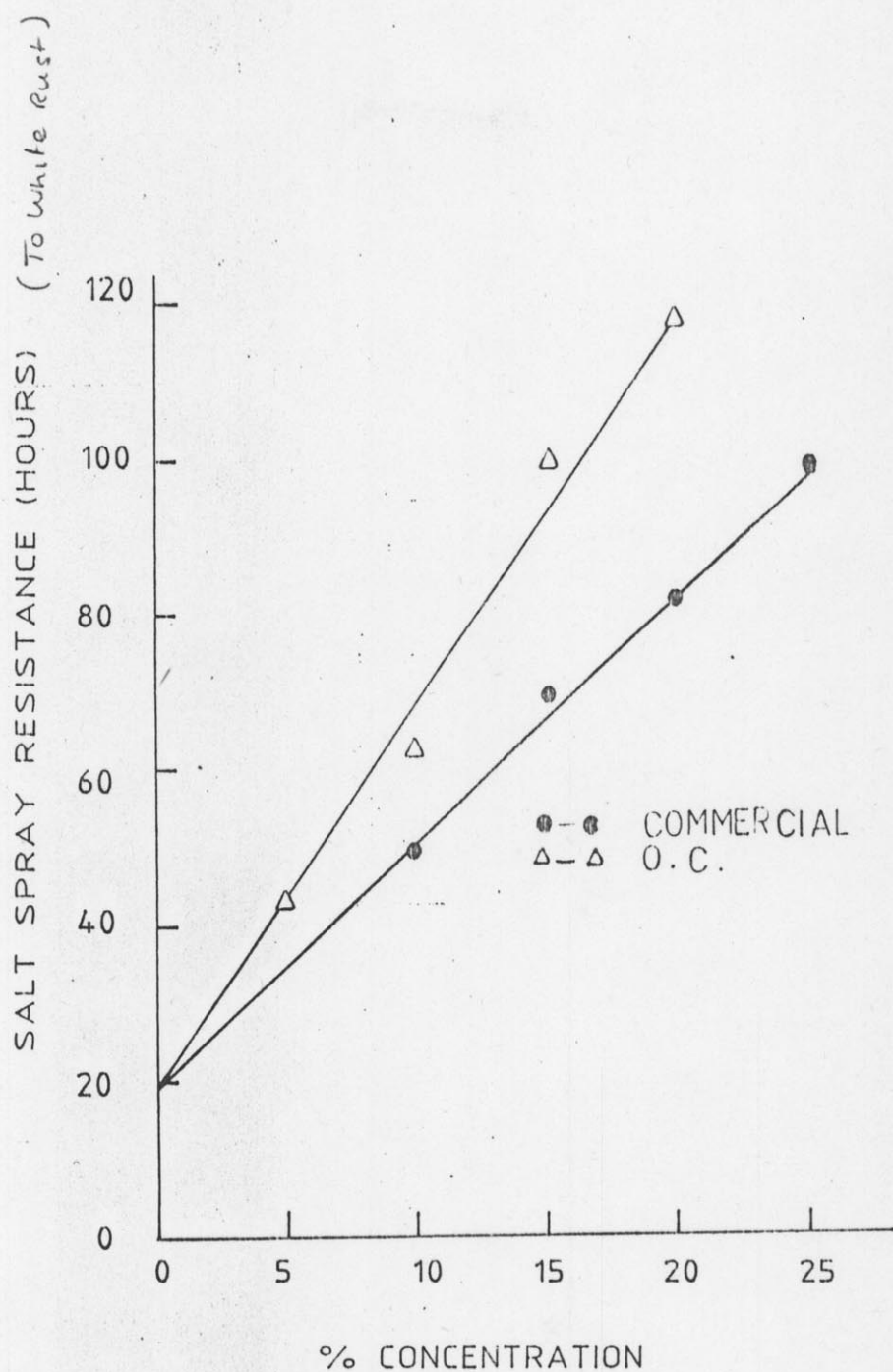


FIG. 6. Variation in salt spray resistance with concentrations of NML-galvasave and pyrobond-253.

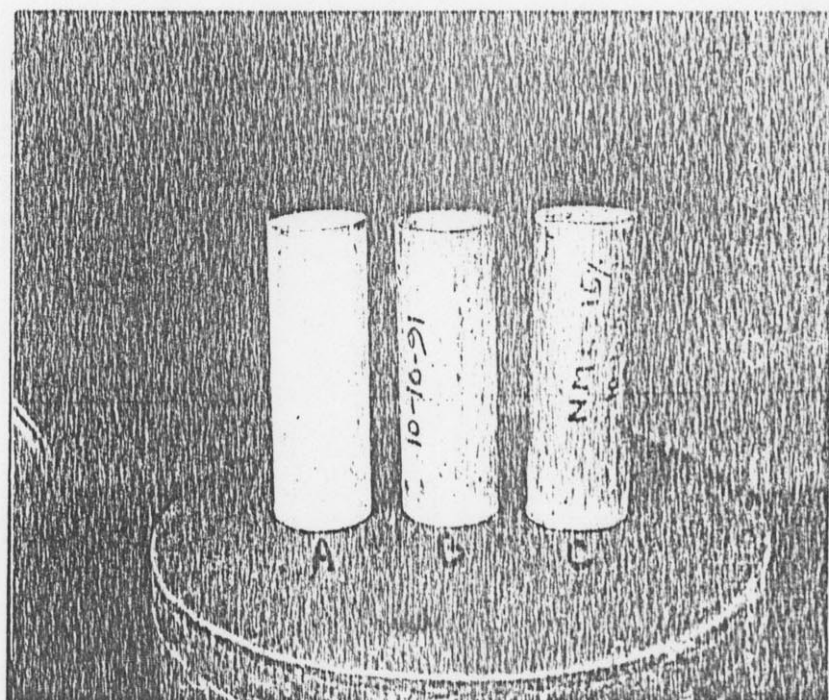


Fig.7 Surface conditions of specimens exposed to salt spray chamber

- a) Unpassivated surface
- b) Passivated with 25% solution of commercial passivator
- c) Passivated in 20% solution of o.c.

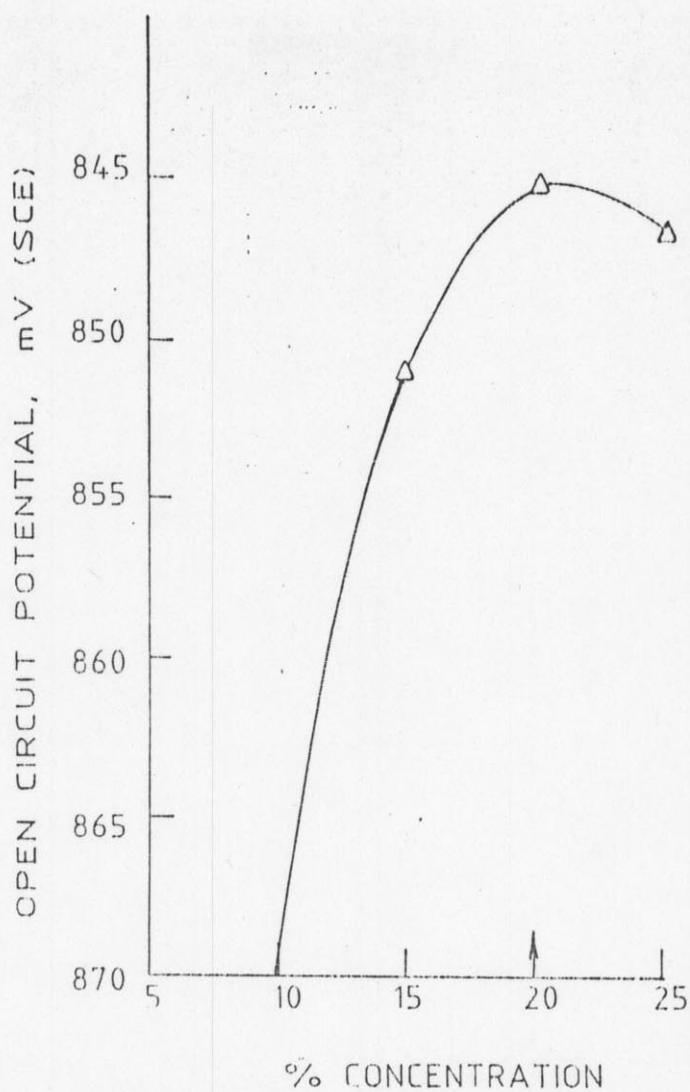


FIG. 8. VARIATION IN OPEN CIRCUIT POTENTIAL OF ZINC WITH CONCENTRATION OF PASSIVATOR.

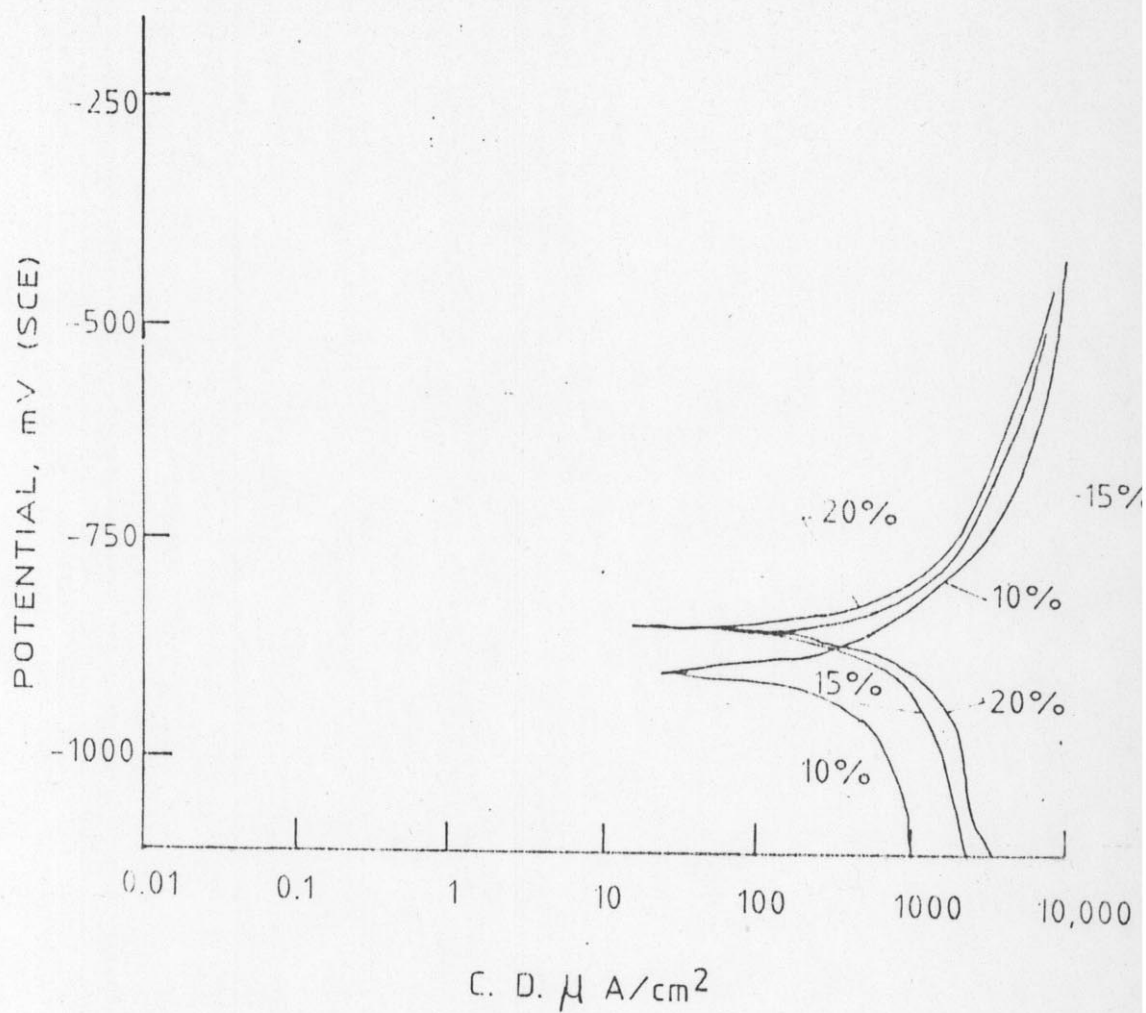


FIG. 9. passivation behaviour of zinc in 10,15 and 20% solution of passivator

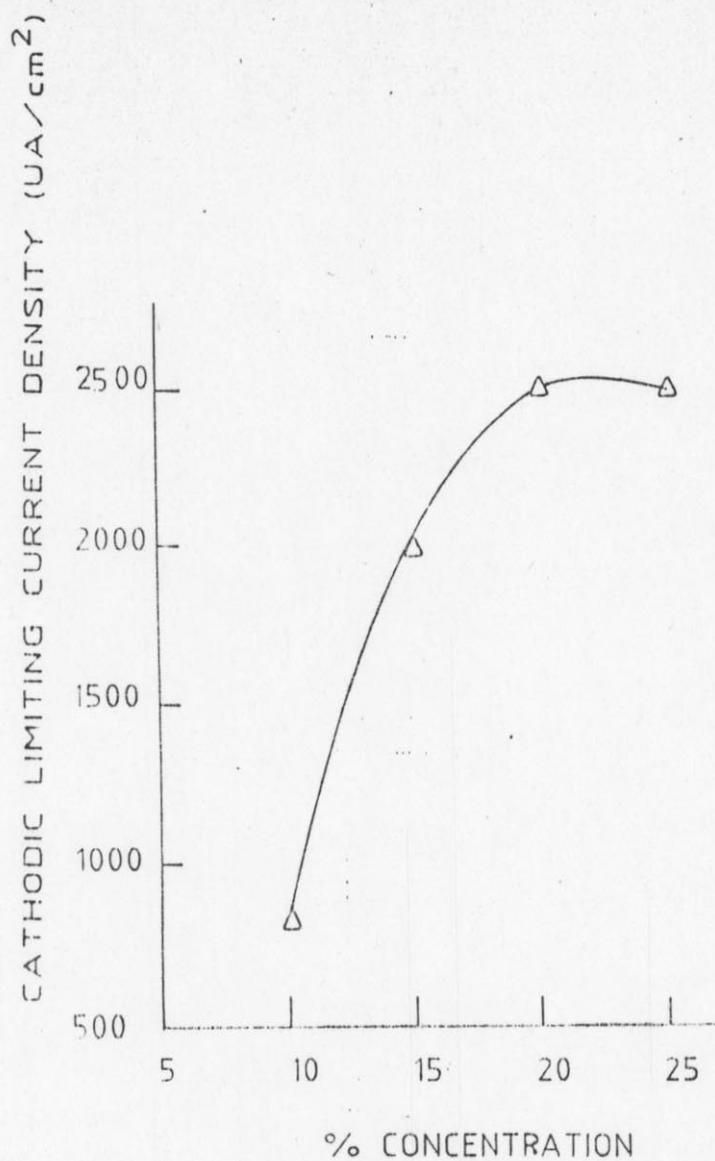


FIG. 10 Variation in limiting cathodic current density with concentration of O.C.

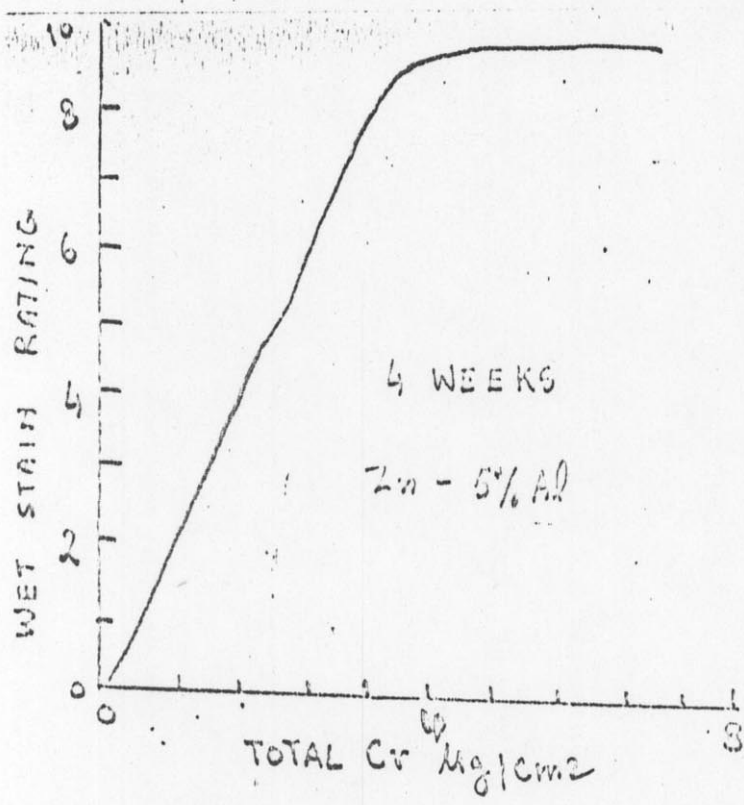


FIG. 11. EFFECT OF Cr CONCENTRATION ON GALVANIZED SURFACES ON CORROSION RESISTANCE

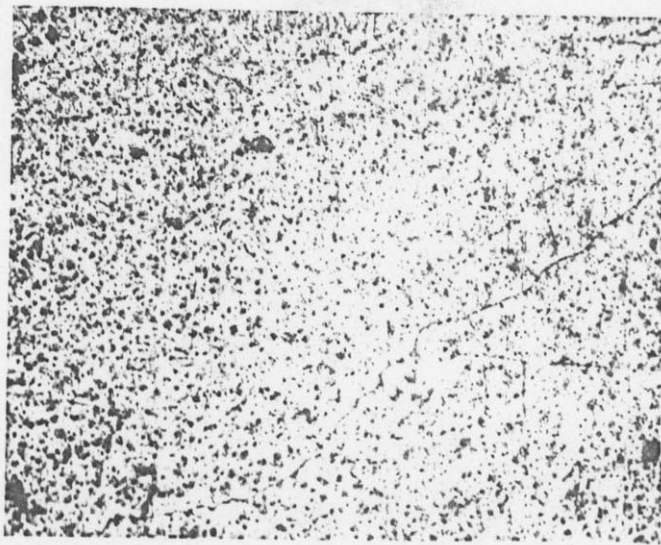


Fig.12. Optical microphotographs showing the cracks developed in a brittle passive film. (Chemidite treated, X 160, Unexposed) This type of passivators are not suitable for providing anti white rusting film on coatings to be used in marine environments



Fig.13. Optical photograph showing no crack in a film produced by the low chromium passivator having organic additives. (Galvasave treated, X 160, Unexposed).No cracking in the film is observed. This is due to the formation of amorphous type of coating which withstands compression.

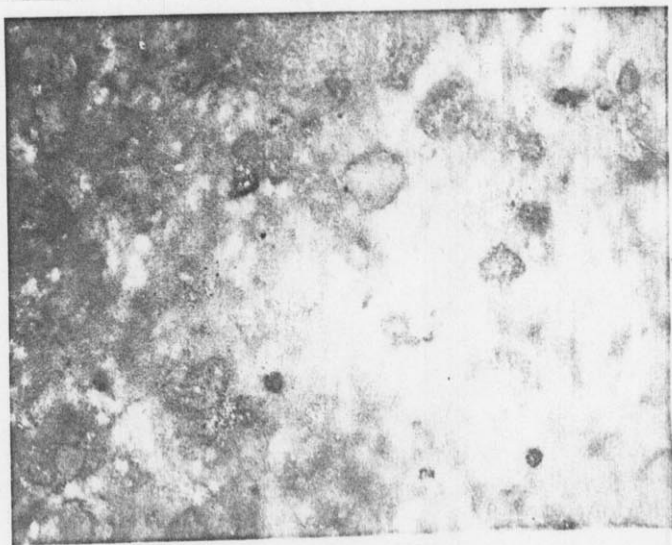


Fig.14. Sample as treated in 12, exposed in marine environment for 6 months, X 160. Surface facing sky, lot of white rust appeared. The surface was subjected to one complete period of summer and one winter season.

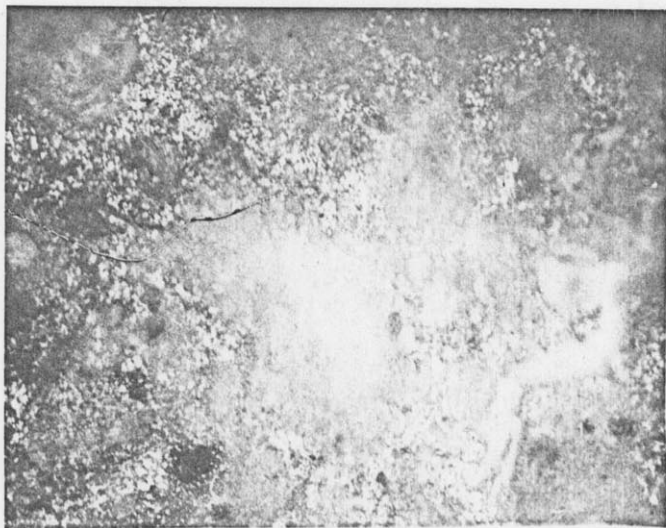


Fig.15. Same as in 14, surface facing ground, comparatively less white rusted.

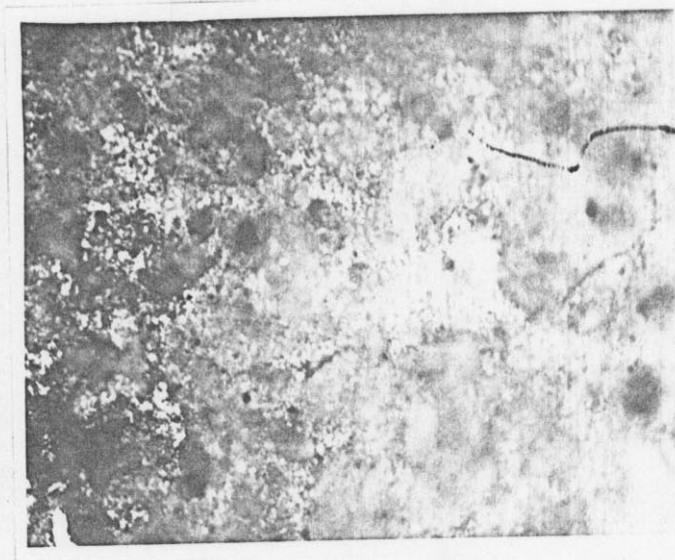


Fig.16. Sample as treated in 13, surface facing sky, comparatively less white rusted than in 14.



Fig.17 As in 16, the surface facing ground, surface almost intact.



Fig.18. Blank, no treatment provide, sky side surface, Heavy corrosion observed.



Fig.19. Same as 18, ground facing, surface white rusted.