Chromate Conversion Coatings on Zinc Plating

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IT is almost an universal Procedure irrespective of the types of zinc plating on steel for corrosion resistance, appearance or other qualities to chromate it. Such chromate conversion coatings are reaction products of the zinc metal deposit and the solution containing hexavalent chromium and other active radicals. Such a protective film inhibits corrosion by releasing chromate ions in contact in water(1,3). Known by variety of names-chromating, bright dripping, passivating etc. this is applicable to other metals also *viz.* Al. Cd, Mg. Cu and brass. Originally patented as the cronak process(4) for zinc base die castings, the process was later modified to include active radicals like chlorides, fluorides, biflourides, acetates, sulphamates among others in addition to the sulphate radical.

IN the telecommunication industry bright zinc plated components from cynide bath are passivated according to DEF 130 specification (U.K.). However sweat due to finger prints on these formed corrosion sites and even in the absence of these some-times corrosion spots developed in storage. Nitrocellulose lacquered components however did not corrode in storage.

An alternative to the conventional process of chromating and ageing for 24 hours without impairment of the protective quality of the film is presented in this paper.

MECHANISM OF FILM FORMATION

The coating obtained by chemical or electrochemical treatment results in the formation of a compound of the general formula Cr_2O_3-$CrO_3 \times H_2O$ due to the reduction of hexavalent chromium, the surface metal being converted into a non-metallic form in the film forming reaction. A typical film dried at 110° C has been analyzed.

TABLE 1

Analysis of chromate film

Sl. No.	Element	Coloured (5) film	Clear (5) film
i.	Hexavalent Chromium	8.68%	6-12%
ii.	Trivalent Chromium	28.2%	25-30%
iii.	Sulphate	3.27%	2-3%
iv.	Zinc	2.12%	2-3%
v.	Sodium	0.32%	—
vi.	Water	19.3%	15-20%

The thickness of the film is about .0005 mm (coating wt. 0.5 to 2.0 g/sq. m). The colour and other characteristics vary with several of the parameters used in the process and the film is susceptible to damage from abrasion immediately following film formation and hence has to be aged for 12 to 24 hours before handling. Electrolytically applied coatings are not subject to this limitation(5).

The quality and thickness of the zinc deposit decide the quality of the corrosion coating and though 5 to 7.5 μ m are normally adequate, salt spray tests indicate that a 18μ thickness is desirable for Indian climate. The effect of brightness and impurites in the plating bath have been reported[3]. Electron microscope studies by Furr and Kulkarni[6] indicate that the films contain Cr (III) and Cr (VI) zinc chromate and water. Williams[7] reports from a study of various solutions that maximum film weight is obtained from a sulphate solution and has elucidated the mechanism[8]. Recent evidence[10] supports the proposal of McLaren *et al.*[9] that chromate conversion coatings are hydrated Cr (III) hydroxide films, with adsorbed anions such as chromate and sulphate though the theory of Anderson[11] that it is a basic chromium chromate is still quoted in literature. Thus there is a divergences of opinion as to the nature of the coating.

Types of chromate coating : Three major classes based on the appearance and the pH of the chromating bath are in vogue. The first is a simple dip chemical polishing solution operating at a pH 0 to 1.5, giving a lustrous clear to light iridescent yellow coating of medium corrosion resistance. The second type is a one dip non polishing type operated in the pH range 1.0 to 3.5 producing medium to heavy films from iridesent yellow to bronze, olive drab and black with maximum corrosion protection. The third is anodically produced films from solutions operating at a pH of 2.5 to 6.0 and a CD of 5 to 50 amp/ft^2 and producing yellow to black films[12]. The ISO has published

a draft proposal for chromate treatment of electroplated coatings of Zn and Cd[13] and classified them on the basis of colour and coating weight.

Film properties : As mentioned earlier the chromate conversion coating results from a transformation of the outer atomic layers of the zinc surface into a new non-metallic layer as a result of precipitation of an insoluble compound containing the metal itself and other constituents from the solution *viz.* chromates. The insoluble trivalent chromium in the dip type of coating provides the mechanical exclusive type of protection while the soluble hexavalent chromium acts as an inhibitor in the environment. The solubility of the film decreases on dehydration either by heating, dry ing or dessicating. Heavy coatings tend to powder on drying, decreasing their protective quality. While protection is directly proportional to thickness, salt spray tests indicate that thinner coatings are better perhaps due to the higher proportion of trivalent chromium in the thinner coating rendering it less soluble and more resistant on washing[1].

Conversion coatings are porous when freshly formed when still wet and can be dyed. Once dried they are nonporous but somewhat repellent to liquids. After drying they withstand handling stamping, and cold forming but cannot resist sharp scratching or abrasion. Because of the low electrical conductivity, they can be used in electrical contacts and high frequency applications. For paints having good molecular adhesion conversion coatings not only provide surface for good bonding, but also interpose a nonporous protective barrier between the paint and the metal.

Evaluation of chromate coatings : Though a number of investigatious have been made no reliable repetitive type of test has been evolved. The coatings are to be aged for at least 12-24 hours before submitting to any acalerated test, to obtain consistent and siginificant results. Accelerated tests include salt spray (ASTM-B-117-49T), immersion in hot water and exposure to alternate wetting and drying in 90% RH, in a temperature cycle of 26-49°C. Williams (8) concludes that the salt spray test is not reliable. The humidity tests include constant and cyclic exposure conditions. However this is not a accepted as a standard. The Australian Standard 1791-1976 defines 16 hours at 55°C and a minimum of 5 hours at 35°C, while ISO/DIS 3613 (1S : 8602-1977) restricts the time of storage to 24-72 hours, before testing. The hexavalent chromium content has not been found to be a good measure of the corrosion resistance. When panels were exposed out doors, it was not possible to make any correlation between chromate content and corrosion resistance even with panels plated under identical conditions.[14] Though not accepted as a standard Patch [16] has proposed a fast electrochemical method suitable for production control. There are a number of U. S. Government and A. S. T. M. specifications on chromate conversion coatings.[1]

Aging of Chromate Conversion Films : From a literature survey as well as industrial practice in a large telecommunication factory, it is found that aging of the chromate conversion film, which is a gel like precipitate is imperative. Hence earlier workers have all uniformly suggested air drying for 24 hours. Such a step, in a large organisation with 4 to 5 tons of zinc plated ware chromated daily, would not be possible without damaging the chromate film. Observation of corroded metal wares in telephone exchanges in coastal towns as also in the interior indicated severe finger prints at corroded chromate films. Condensation due to a wide variation in diurnal temperature and humidity was also observed. This was especially so when no air conditioning was provided at the time of installation and maintained there after.

As early as 1954 in zinc plating and chromating STROWGER type of telephone exchange equipments efforts were made to dry passivated ware in racks away from the shop atmosphere by drying at room temperature (15 to 36°C depending upon season). After drying a P. V. C. lacquer dip (about 16 seconds (25°C) in No. 4 Ford cup) was given and air dried. Salt spray tests were satisfactory on these. Though successful the type of lacquer was changed to a nitrocellulose lacquer due to non availability of P. V. C. resin. The components after drying in air for about 3-4 hours were dipped in nitrocellulose lacquer (16-18 seconds (25°C) No. 4 Ford cup) and allowed to dry overnight before assembling. Because of the good performance this practice was introduced as a Company Standard in 1955. Consequently this system was gradually adopted in many of the electronic and telecommunication factories, where lacquering would not hamper functioning of the

equipment. Underwood et al [15] from a study of several installations in tropical environments in South America corroborated the effects of finger prints on corrosion. They claim that out of the two lacquers, nitrocellulose type and acrylic water displacing type, the former is superior in protection. In 1972 zinc plated and chromated items of hardware were found corroding in the packages themselves. The equipment was originally packed in an alkathene film bag, evacuated and kept dry by silica gel. This was packed in a thick carton covered with a water proof brown paper packing and finally packed in wooded cases While red rust spots appeared in some after 8 to 12 weeks storage, white rust appeared, typical of attack on zinc, appeared on others. This was traced as due to release of acidic vapour from the slightly, wet packing wood and this environment in a closed humid system had punctured the weak spots in the chromate film.

The components of the type referred to above were plated μm on automatic lines with 10 to 12.5 μm of zinc coating. the coatings allowed to age before removing from jigs and later lacquered. This procedure was difficult because of large storage volume on jigs required. Under similar circumstances the practice in foreign countries is to force drying of components at 60°C for 30 minutes and taking to assembly. However such a procedure was not acceptable to the purchaser as salt spray test (ASIM B-117), though not reliable, was found to affect the performance of the components under test. A compromise accelerated ageing procedure was suggested.

Water Soluble Lacquer for Protection : The role of hexavalent chromium and the nonporous nature of the chromate film in corrosion protection has been already referred to. White corrosion product is inhibited as long as a minimum amount of hexavalent chromium remains in the film. Keeping the mechanism of protection in mind, the behaviour of water soluble lacquer in protecting a freshly formed chromated film was investigated. Components were plated in the usual bright zinc cyanide solution, using a proprietary brightner and a proprietary passivating solution in automatic plant. The films contained significant amount of hexavalent chromium. The approximate film weight of the yellow iridescent film was 0.5 to 1 g/m^2. After passivating and rinsing, the components were dipped in an acrylic type water thinned lacquer, using acrylic acid and other additives (formulated by a paint manufacturer). The lacquer was thinned to give a viscosity of 16 secs (25°C) in No. 4 Ford cup. After dipping the components were drained and stoved in an oven at 55° ±5°C for 30 minutes, leaving a thin layer of lacquer on the chromate film, Initial tackiness of the lacquer film disappeared after about 3 hours storage at room temperature. These components could be handled without damage to the chromate film, the stoving partially hardening the film and the lacquering sealing the chromate film permanently. The components stood the salt spray test for 72 hours, with out any deterioration.

DISCUSSION

From several years experience it was clear that nitrocellulose lacquer coating on passivated film is adequate to prevent finger print corrosion. In this there was an element of doubt whether chromate film would have aged sufficiently to prevent corrosion whenever lacquer film was damaged. The salt spray test on the lacquered film was satisfactory. Water thinnable types of lacquer applied immediately after chromating, in place of nitrocellulose lacquer wetted the chromate film and protected the film. In the process of drying at 55° ±5 C for 30 minutes, the chromate film gets slightly dehydrated (ages) and hardens. Incidentally the acrylic layer cures to be hard film to withstand handling from the jigs. The chromate film aged for 12-24 hours and that aged for 30 minutes at 55° ±5°C with the water thinned acrylic lacquer both withstood the salt spray test for 72 hours. Thus the chromate film is protected from physical damage, about 1-2 hours after chromate passivation by the modified process.

In addition to the nonporous nature of the chromate film the water thinnable acrylic coating further aids in protecting and sealing the basis metallic layer from exposure to moisture. In the event of puncture of the acrylic film the hexavalent chromium being slightly soluble in water exerts the inhibiting action as long as the minimum amount is present in the film. The coversion of hexavalent chromium to trivent chromium at the baking temperature, is minimum. According to

Williams[17] S.E.M. studies have shown that corrosion resistance of chromated zinc film cannot be simply related to the chromate content because, the ageing or heating of the film affects the leaching rate of the chromate. Exposure tests in a temperate urban environment and salt spray tests have confirmed this. The effect of heating on the chromate content and corrosion behaviour is given in Table[17].

TABLE II

The effect of heating on the chromate content and the time to failure in the salt-spray cabinet, for 13 μm zinc plate chromated for 10s

Treatment after chromating	Chromate content of film (μg/cm2)			Average time to failure in salt spray (h)	
	Initial	After salt spray	After a 3 months exposure	Black spots	White corrosion
i) Airdried at 20°C	11.1	0.5	11.0	107	147
ii) Heated at 40°C for 2h	11.7	0.6	11.7	129	163
iii) Heated at 60°C for 2h	12.7	5.1	11.5	91	121
iv) Heated at 80°C for 2h	11.3	9.3	10.6	30	31

It is seen that specimen heated at 60°C for 2 hours has intially a chromate content of 12.7 $\mu g/m^2$ and after salt spray test 5.1 $\mu g/m^2$ and after 3 months exposure 11.5 and has stood accelerated corrosion test for 91 days with black spots and 121 days without white spots. After exposure it was found difficult to extract Cr (VI). In contrast panels stored at 20°C Cr (VI) was readily extracted after the same period of time. This indicated that outdoor exposure produces changes similar to heated specimens, reducing the rate of desorption of Cr (VI) from the film, This will affect the performance in a very corrosive environment which involves rapid leaching.

From these investigations of Williams[17] it is clear that in a less corrosive atmosphere (like that obtaining in a telephone exchange which is generally air conditioned) no relative loss of performance can be observed with films heated up to 80°C for 2 hours. In the proposed system chromated and lacqured (water thinned) components heated 55°±5°C for 30 minutes may show a fall in desorption of Cr (VI) but this may not adversely affect its performance.

The proposed system of dip lacquering in a water thinnable acrylic lacquer is similar to the use of wash primer system applied on steel surface. Wash primer or etch primer essentially consists of polyvinyl butyral base. pigmented with zinc chromate. The metal surface is mildly etched as the metal oxide film is formed, the presence of the chromate ions assuring continuity and repair of this film. The super imposed polyvinyl butyral films protects the underlying film. The action is similar in this case. Poly acrylate resins comparatively inbibe considerably more water than nitrocellulose. The chemical composition of the base unit of the polymer making up the chain plays an important part on its sensitivity of moisture which is provided by the acrylic film. The adhesion between the chromate film and the acrylic layer is said to be outstanding. Further acrylic lacquers are superior to other types in resistance to chemical fumes acids and alkalies.

By the adoption of this new process and baking at about 60°C for 30 minutes the finger print marking and condensation induced type of corrosion has been eliminated, in addition to aiding production. Since the acrylic film also absorbs comparatively more moisture than nitrocellulose film and allows desorption of the chromate when the film is punctured the acrylic film gives better protection.

CONCLUSIONS

The conventional ageing of chromate conversion film for 24 hours is time consuming and not conducive to commercial production.

To prevent finger print type of corrosion as early as 1954 a nitrocellulose type of barrier layer protection of the conversion coating was introduced. With a view to aiding production and at the same time retaining the qualities of a protective coating, a process of lacquering the freshly formed chromate film with a water thinned acrylic lacquer and baking the coating for 3 hours at 55°±5°C was considered and tested. Preliminary tests indicated that such coatings give the same amount

of protection as the earlier type of coatings while shortening the time schedule thus aiding increased production.

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