New Non-Chrome Black Conversion Coating for Zinc Electroplated Steel

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Environmental and price concerns in the metal finishing industry are the drivers for new products which are also stable and easy to use. In this paper, we introduce a new conversion coating system for producing black films on Zn plate. This coating contains no chromium, nickel, molybdenum, silver or harmful organic compounds. Further, this system is stable over long periods of time under tank use and storage conditions. Both alkaline and chloride Zn deposited electroplate can be blackened. We present the results of SEM/TEM and analytical data to explore the morphology and composition. The findings present evidence that the conversion coating is thicker and more dilute in optically black centers than expected. The SEM photos of porosity of the underlying black layer and secondary layer support the observations that salt spray protection is provided primarily by the secondary layer.

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1. Introduction:

The study of passivation of active metal surfaces against corrosion has been ongoing for over 100 years [1]. Additionally, modern commercial tastes dictate that finished metal pieces be aesthetically pleasing from a color or hue standpoint. Deep coloration of protective films implies centers or clusters which can absorb photonic energy. Such absorbing clusters could provide physical pathways for which there may be a decrease in corrosion resistance for structural or morphological reasons. It is common knowledge that the industry is moving away from Cr^{6+} and heavy metals such as Ag, as a means of providing protection and color. In their place, the metal finishing industry must provide alternatives which have relatively higher performance at modest cost. The cost to be paid for the highest performance and continued ease of use is an increase in the complexity of the chemical systems and growth dynamics. Several components must precisely perform the function of the former simple chemistries and be stable for long periods of time as both a shippable concentrate and in working tanks.

We describe a new black film system which does not contain Cr, Mo or Ag. Combined with a secondary passivate, this system is capable of supplying a stable rich deep black color, without iridescence and salt spray resistance of 100 hours. It has been commercially beta tested with loads exceeding 10,000 lbs through an 85 gallon tank made up using 15% product. This system works with electroplate produced from acid/ chloride or alkaline Zn baths. Much of the initial work was heuristic in nature but one finds that it becomes difficult to fully optimize this very promising process without a solid practical understanding the solution chemistry and the physical morphology /composition of the growth.

The new system is water based and composed of a primary dip tank to produce black inorganic film plus a secondary passivate tank which increases salt spray resistance. By developing our materials to allow most of the salt spray resistance to be provided by the secondary passivate, we have avoided reactions in operation which limit the length of useful tank life. Tests have demonstrated that the working solution can be stored for, a minimum of three months, and is immediately usable only with a simple pH adjustment. The concentrate will not freeze at 20F and does not precipitate in storage over significant times.

In this paper we will describe some of the chemical approach which was used to tune the system for replenishment and SEM/TEM photographs which lend insight into areas where improvement might be made, especially in the area of salt spray protection.

2. Chemistry of the Solution and Black Film:

Although we started with water and a considerable amount trivalent iron salt, assumed to impart the black color, the question immediately arose as to whether the observed color was the result of Fe $^{3+}$ or Fe $^{2+}$. With the addition of small quantities of weakly reducing organics, an organic acid and a simple salt for Zn oxidation and film formation, the chemistry of the solution quickly became complicated. The first films were weakly black colored and powdery. The pH of the system under study was restrained to 4.5-5.0 which then made possible combinations of redox reactions which could enhance the color. Use of Pourbaix diagrams for the first row transition metals, lead to a matrix to stabilize the iron in the +3 state and add to the total blackening ability of the solution within the chosen pH range of the solution. In fact, the matrix led to a considerable increase in darkening and a strong decrease in iridescence. The margin of operation for blackening was increased by adding other metallic salts.

The solution color is red/brown and is somewhat related in looks to the mineral Lepidocrocite (γ-FeOOH), a trivalent iron compound [2]. There is however, no precipitate in solution. Stability of these types of complexes is predicted by the Pourbaix diagram at the restrained pH conditions.

Chloride and alkaline zinc electrodeposits respond differently to the blackening solution. The optimum parameters for chloride zinc were quickly determined. With increase of an oxidizing material, the identical dark blackening was reached at the same pH as with alkaline Zn. This is believed to be related to oxidation of the surface Zn required for the conversion coating. Use of higher amounts of an oxidizing material with alkaline Zn plated parts resulted in a loss of aesthetics. Using pre-dip of nitric acid also caused the parts to strip after some solution usage for both alkaline and chloride zinc. Hence, this product line has been developed with no need to acid activate zinc electrodeposits.

Several schemes were employed to eliminate powdery deposits, all aimed at controlling the kinetics of growth. Manipulation of the many moieties involved lead to a controlled, repeatable film growth. Now, when this film was coupled with the secondary passivate, the resultant black coating became aesthetically pleasing. By using a proprietary mix and control of the pH, the dwell time in the black dip has been optimized to between 40 and 100 seconds.

A complete replenishment system was developed by measuring the depletion of all components in solution using atomic absorption for the cations and chromatographic techniques for the anions. We also observed Zn and Fe levels in the residual solutions. With iron as a component of the film, the replenishment scheme is able to hold the iron concentration approximately constant. The Zn concentration has been measured above 1 ounce per gallon with no measureable effect on the blackening ability of the solution. The coverage capability of the solution in the laboratory was 10ft^2 per liter of working solution between replenishments. Coverage capacity varied slightly in the field as a function of the porosity of the Zn electroplate.

3. Morphology and Film Composition:

A: Morphology - For this study a Hitachi N3400 SEM was used with an XPS/EDX attachment for elemental analysis. High magnification images were performed with a S4800 Hitachi Field Emission SEM. A H7600 Hitachi TEM was used for cross sections. While the chemistry development and field trials were performed on electroplated bolts and irregularly shaped parts, the electron microscopy work was performed on flat Q-Panels. Therefore, in the SEM photos, the rolling structure of the underlying steel is visible. The beam penetration in these photos is about 500 Å (0.05 microns). The films shown in the following SEM photos were grown at 92° F for a period of 70 seconds. These are typical times and temperatures used for this chemistry. Figure 1 shows the SEM photo of the black conversion coat only. The figure shows that the film is continuous without cracking, but has a high degree of roughness caused by porosity. The roughness is seen as light and darker areas. The light and dark areas show up because the electron beam is coming in at an angle and shadowing is occurring. The detector is relying on backscatter for the image. Figure 2 is a cross-section TEM of the underlying Zn layer with the black layer on top and the secondary passivate is the white layer above. The Zn is on the lower right side, the black layer is 2.86 microns and the secondary passivate is 0.810 microns. Several photos at various positions were made which show that the thickness is uniform of about 3 μ, with a very sharp interface along the Zn layer. The secondary passivate is consistently about 0.8 microns thick on this sample and also has a very sharp interface. Figure 3 shows a top down SEM of the secondary passivate on a layer which is very shiny. This photo shows that the smoothness has dramatically increased and porosity has decreased. This is most likely a desirable property for salt spray protection. Figure 4 is a high resolution photo of the secondary passivate showing that its growth actually occurs in layers. While the origin of these layers is not known, they may be growth artifacts caused by temporal depletions of solute near the growing interface due to turning or pumping of the parts in solution.

B: Composition – Solution compositions of the cations were made using a Varian 240FS atomic absorption unit. Fe and V vanadium weight percentage in the solutions were measured using new solutions and after 1 ft^2 of parts were run through the black coating solution of 100mL size. The difference in the cation concentrations between the two solutions was used to help estimate, along with SEM, the composition of the film. Table 1 below shows composite layer analyses based on both AA and EDX data.

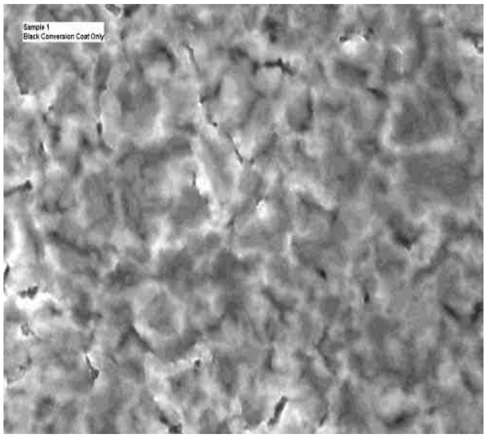

Figure 1. High resolution SEM of black layer. The layer is not cracked but has many pores.

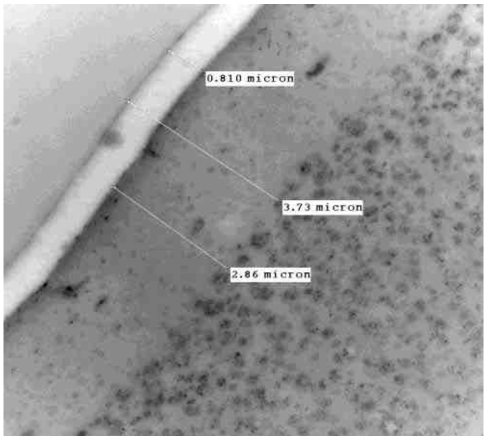

Figure 2. TEM cross section of the Zn (lower right), black layer (2.86 microns) and secondary passivate (white layer – 0.810 microns)

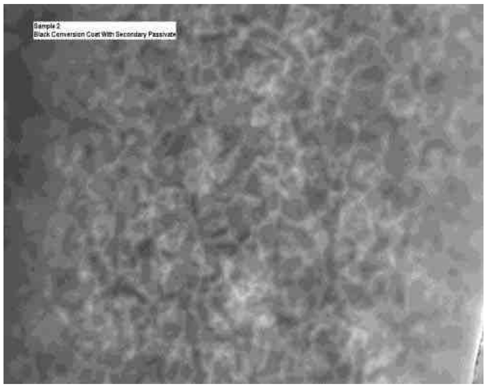

Figure 3. High resolution SEM of the top secondary passivate layer covering the black layer. Notice that the pores are closed off. The visual observation of this combination is a very shiny black surface.

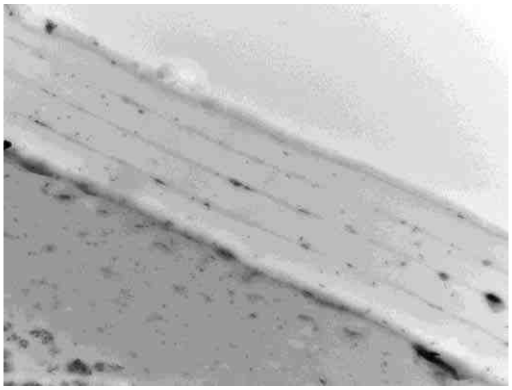

Figure 4. TEM view of the secondary passivate layer showing 5 distinct sublayers. We presently feel that these are growth artifacts caused by temporal solute depletion.

The form of combined analysis showed variations with the EDX yielding somewhat lower Fe concentrations in the film than would be calculated from the AA data based on the observed film thickness. However, the analysis seems to be consistent enough to serve as a general guide.

Table 1. Quantitative Analysis of Black Layers

Element	**Weight %** **Black Layer**
carbon	8
oxygen	9
vanadium	<.5
iron	3.3
chlorine	<.5
zinc	75

It should be remarked that there were traces of several other elements in solution and materials used for polishing and mounting for which traces showed up but are not included in this analysis. The secondary passivate is very much more complicated in composition. The composition demonstrates the presence of iron and vanadium-not part of the secondary passivate solution composition. Since the beam penetration is only 0.05 microns for the analysis, we ascribe the presence of these two ions to being actually in the layer.

4. Discussion: Compositional analyses with results such as these are difficult to interpret because of the large disparity between the Zn levels and Fe levels. Analysis to the depth of 0.05 microns, as in this paper, have been previously been performed on Cr conversion layers [3]. In that experiment the first few atomic layers appear to have a Cr concentration of several 10's of percent and then quickly drops off. This black film extends about an order of magnitude thicker than usually observed for conversion coatings. The fact that there was an agreement within the order of magnitude of Fe content between the SEM and the calculation from AA data and thickness indicates that the layer must be multiphase. In all probability the first phase is a Zn rich phase with little other cationic impurity. The second phase may be related to Zn ferrite or other spinel type materials. There is a possibility that the second phase could be Fe metal particles but we wouldn't think that to be the case based on electrochemical considerations. However, the high resolution SEM for which features can be seen, which are below 1 micron do not show evidence of particle clustering as seen by Song et. al. [4]. To further test for the possibility of a spinel phase, a small amount of Fe^{2+} was added to the highly Fe^{3+} black dip solution and caused a further marked darkening of the film. When the same molar amount of Fe^{3+} was added to the solution already containing Fe^{3+}, the effect was not nearly as pronounced. Therefore, we feel that tetrahedral sites in the ferrite structure may be preferentially filled by divalent iron while the Fe^{3+} goes to octahedral sites. The author's own experience with ferrimagnetic garnets [5] indicates that the 6 micron optical path for the light travelling through this type of structured ferrimagnetic film would be sufficient to observe deep blackening.

Salt spray studies of these layers by themselves showed that the black layer offered little resistance to the formation of white salts. While some of this behavior is attributable to porosity, a full calculation based on electrochemical potentials would need to be performed which would show if the black layer itself would be capable of strong salt spray protection.

As mentioned, both iron and vanadium were seen in the secondary passivate layer. This implies that when the second layer is applied in solution, the process of secondary passivation causes dissolution of the topmost layer of the black and a redeposition under conditions of supersaturation. This is the classic condition for a conversion coating. In neither the case of the blackening coat or the secondary passivate do we observe precipitation, although reversible color change is sometimes observed.

While we suspect complex trivalent iron hydroxyl species in the solution, we wanted to test if there was significant hydrate in the film product. We heated both the black layer by itself and the combined black layer/secondary passivate to 360°F (182°C) for 8 hours and found no change in the visual properties or salt spray properties. We therefore presume that the black films are composed mainly of oxides.

5. Conclusions:

We have developed a new decorative black passivation system which works well with both Cl/Zn and alkaline Zn systems. Extensive work has been performed on barrel loaded parts and attempts to cover large flat parts encountered in rack mounting have also produced good coverage.

The amount of iron (and other components) lost in the dipping process and gained in the film explains the long active tank life and excellent parts throughput. Since this blackening formula does not contain Cr^{3+} / phosphates, there is little tendency to form complexes which can alter the performance or cause irreversible chemical changes.

The slow loss of film components from dipping solution allowed us to develop a replenishment scheme which can be added over and over again for large parts throughput without having to change the underlying tank solution.

The combined black/secondary system has a salt spray resistance of about 100 hrs although the black layer by itself has less than 24 hrs of resistance. Because there is some porosity in the underlying black layer, improvement in the salt spray duration will probably be extended by decreasing the porosity, increasing the layer thickness of the secondary passivate and improving the electrochemical behavior of the combination. Efforts are now under way to accomplish this increase.

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