# Preparation and Characterization Of a Colored Anodic Coating on Hot Dip Galvanized Steel

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This study reports a method by which a colored anodized layer can adhere to hot dip galvanized steel by utilizing an alternating current power supply that automatically controls and maintains proper current and voltage values. To be effective, this anodizing process was divided into two stages. A solution containing 0.75 M sodium hydroxide, 0.2 M sodium borate, 0.75 M sodium silicate and 0.03 M cobalt salt was used as an electrolyte. An alternating current of 60 Hz at a constant 60 V was utilized in the first stage for 10 min. A milky white film was formed on the structure as a barrier layer to the passage of zinc species from the electrode to the solution, which further provides a sufficient barrier layer for the subsequent coating formation. In the second stage, the current density was kept at 10 A/dm<sup>2</sup> and the temperature was maintained at 10 °C for 10 min. The anodic coating appeared fairly smooth and the colors were attractive. Multi-color variations were obtained, such as blue, green, brown, white, gray, etc. The hardness of the anodic coating is about 20 percent higher than that of pure zinc layers. Microscopically, two distinct structures were observed—one islandlike, the other like fritted glass. Anodic coating of the hot dip galvanized steel offers excellent resistance to saline environment and is significantly better than the untreated galvanizing steel, based on the results of the salt fog test.

inc is an amphoteric metal that is very active electrochemically; therefore it can be used sacrificially when coupled with steel. For this reason, many commercially available products, made of ferrous metals, such as home appliances, automobile bodies, bridge structures, and electric power transmission equipment, utilize zinc as an indispensable medium against corrosion. Zinc coating



Fig. 1—Variation of current density and temperature with time for hot dip galvanized steel at 60 V, in an electrolyte of 0.75 M NaOH, 0.2 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 10H<sub>2</sub>O, 0.75 M Na<sub>3</sub>O<sub>2</sub>Si<sub>4</sub>, 0.03 M cobalt salt.

layers are often soft and therefore susceptible to wear, corrosion or both. The atmospheric corrosion rates of galvanized steels normally increase in the presence of soluble chlorides, especially near the seacoast.<sup>1</sup>

Conventional hot dip galvanized steel articles appear a silver grey that lacks aesthetics and limits the field of usage. There are several methods usually employed to improve the color of the surface of the zinc layer, as well as to reduce the zinc consumption of the galvanized items.<sup>2,3</sup> For instance, the zinc surface is usually treated with a chemical conversion coating or organic coating. Although these coatings have been used extensively, there are problems yet to be resolved.<sup>4,5</sup>

Anodic treatment of galvanized steels is the authors' present interest because of their improved corrosion resistance, combined with providing attractive colors. There are some references disclosing proprietary and non-proprietary processes for color anodizing of zinc and its alloys.<sup>6-8</sup> Guttman has reported that the APCF process (based on the use of a nearly neutral electrolyte containing **A**mmonium hydroxide, **P**hosphoric acid, **C**hromic acid, and hydro**F**luoric acid or ammonium **F**luoride), can be carried out by using either alternating current or direct current, but alternating current was often preferred.<sup>9</sup> The working temperatures involved are



Fig. 2—SEM surface morphology of barrier layer operating at 60 V for 10 min at (a) 10  $^\circ C;$  (b) 20  $^\circ C.$ 



Fig. 3—Time dependence of the current density and film thickness during the barrier film formation at 60 V and 10 °C in the following electrolytic baths: (1) Potassium silicate,  $K_2SiO_3$  (water glass), 0.75 M; (2)  $K_2SiO_3$ , 0.75 M + NaOH, 0.375 M; (3)  $K_2SiO_3$ , 0.75 M + NaOH, 0.75 M; (4)  $K_2SiO_3$ , 0.75 M + NaOH, 0.75 M + Sodium borate, Na<sub>3</sub>BO<sub>3</sub>, 0.06 M; (5)  $K_2SiO_3$ , 0.75 M + NaOH, 0.75 M + Na<sub>3</sub>BO<sub>3</sub>, 0.12 M; (6)  $K_2SiO_3$ , 0.75 M + NaOH, 0.75 M + Na<sub>3</sub>BO<sub>3</sub>, 0.21 M; (6)  $K_2SiO_3$ , 0.75 M + NaOH, 0.75 M + Na<sub>3</sub>BO<sub>3</sub>, 0.22 M.

# TableResults of Salt Spray TestFor Various Colored Anodic Coatings

Galvanized Panels		240 hr		480 hr		1200 hr		2640 hr		4080 hr	
	Color	RR	AA	RR	AA	RR	AA	RR	AA	RR	AA
Anodic Coating	Green Blue Brown Gray White	10 10 10 10 10	N N N N N N	10 10 10 10 10		10 10 10 10 10	F N N N N	10 10 10 10 7	F N N F	6 10 9 10 5	F P N F
HDG	Silver Gray	7	Р	4	Р	0	R	0	R	0	R

\*RR, Rust rating (ASTM B117). AA, Appearance; P, Zinc patina; F, Fade away; N, No fade away and zinc patina; R, Serious corrosion; HDG, Hot dip galvanized steel.



Fig 5—Anodized hot dip galvanized parts.14



Fig. 4—Spark discharge on hot dip galvanized steel as a function of time.

high enough to fuse the coating into a fritted structure. A solution containing sodium silicate, sodium borate, sodium tungstate and sodium hydroxide has been recommended by Murphy.<sup>10</sup> When a zinc surface is anodized in this solution, the anode voltage rises at constant current. At 100 V, sparks appear, forming thick rough films at the edges of the surface. Before spark initiation, films were gray and smooth; after sparking, glossy globules appeared on the film. Coloring was unsuccessful except that the grayish film changed to yellowgreen from addition of dichromate. Under humid conditions, white and dark spots were formed after six weeks. Weisbergen and Erikson have reported their newly developed bath, from which different colors were produced from a single solution, made by varying the applied voltage.<sup>11,12</sup> Pushpavanam reported that electrolytic treatment of zinc in solutions of sodium hydroxide and sodium nitrate produced different metallic colors.13 Higher temperatures and current densities led to flaking and non-uniform coating. Moreover, the interferencecoloring alloys produced with these methods were relatively thin and had poor corrosion resistance. Considerable uncertainty and ambiguity in the reports of the films were observed in earlier work. It was therefore of interest to study the nature of a wide variety of anodic films formed on hot dip galvanized steels, including a process of two stages for anodizing<sup>14</sup> and the conditions for coloring in an electrolytic process.

#### **Experimental Procedure**

Cold rolled structural steel panels (SS-41, 50 x 30 x 3 mm) were galvanized at 460 °C by dipping in a commercial galvanizing process bath. The steel surface was completely covered by a uniform zinc coating and a zinc-iron alloy layer with a thickness of about 60  $\mu$ m, as measured by scanning electron microscopy (SEM). The temperature of the anodizing solution was maintained at 10 °C by using a water bath. The heat generated during anodizing is significant and must be effectively removed to maintain the temperature in the recommended range. All the galvanized steels were



Fig. 6—Optical micrograph of cross section of hot dip galvanized steel layer.



Fig. 7—SEM photomicrograph of cross section of anodic coating on hot dip galvanized steel.

degreased by dipping in trichloroethylene. The subsequent acid cleaning was performed in 5 wt percent Hcl at 25 °C for 10 sec, followed by rinsing in distilled water. A three-phase alternating current power supply was used for anodizing. An automatic power control to maintain proper current and voltage value was provided by a silicon controlled rectifier (SCR) unit. Galvanized steels, used as electrodes, were immersed in a doping solution containing 0.75 M sodium hydroxide, 0.2 M sodium borate, 0.75 M sodium silicate and 0.03 M cobalt salt. An alternating current (60 Hz, constant 60 V) was used in the first stage of the process for 10 min. In the second stage, the current density was increased to 10 A/dm<sup>2</sup>, to raise the voltage beyond the spark potential and to control the temperature at 10 °C. The duration of the second stage was 10 min, after which the article was rinsed with distilled water and dried. A uniform, non-reflective blue anodic layer with a thickness of 30 µm was obtained. Surface hardness was measured with an applied load of 20 grams. Exposure tests



Fig. 8—Surface morphology of anodic coating showing (a) island-like structure and (b) fritted glass structure.



Fig. 9—(a) Fritted glass structure formed irregularly in a pit; (b) X-ray mapping of silicon; (c) X-ray mapping of cobalt; (d) X-ray mapping of zinc.

in a salt spray cabinet were conducted according to the procedures of ASTM B 117, using 3.5-percent sodium chloride solution with a pH value adjusted to 7. After a period of exposures, the degree of rusting was evaluated according to ASTM D 1654. In this method, ratings from 0 to 10 are assigned, with 10 meaning no failure and zero meaning failure over at least 75 percent of the area.

#### **Results and Discussion**

#### Influence of Anodizing Temperature

Figure 1 shows the current-time curves for hot dip galvanized steel at a constant 60 V in the anodizing solution. Loose, white coating precipitates were observed on the surface after the electrodeposition at 5 °C. The precipitates were identified and consisted mainly of  $\gamma$ -zinc hydroxide and a small quantity of colorless oxides. This finding is consistent with the formation of zinc hydroxide that can be precipitated from the electrolyte solution at lower alkaline concentration and lower temperature.<sup>15</sup> When the electrolyte temperature increased to 10 °C, mixed translucent and smooth opaque films were obtainable on the surface of the specimen, but a dark film was formed on the back side. The film formed at 10 °C proves to be zinc oxide, which was revealed by x-ray analysis. The film formed at 20 °C can accumulate the darkening agent. Part or all of the dark films formed at 20 °C were detached in the form of flakes. The tendency to form flakes was enhanced at high temperatures and current densities. The duration of maximum current density increases at higher electrolyte temperature (Fig. 1). Often the high current density through those regions where the surface is covered by dark oxide films resulted in destruction of the film and consequent dissolution into soluble products. High current density in this case did not increase the thickness of the oxide film. Moreover, this oxide film would be flaked off easily from the specimen's surface at higher current density, as a result of intensified gas evolution on the top edges of the specimen.

As discussed in a previous paper,<sup>15</sup> dark films on zinc have been studied by a number of authors, and were identified as zinc oxide.<sup>16-18</sup> They were also the subject of intensive investigation by Huber, who showed that the darkening was associated with the presence of excess zinc.<sup>19</sup> Figures 2a and 2b show the surface morphology of the barrier layer obtained at two different electrolyte temperatures. A dendrite-like structure of zinc is shown in Fig. 2a, while a porous and all-dark film is shown in Fig. 2b, in which holes and crevices can be seen. It is clear from Fig. 2, in pH 12 electrolyte, and at lower voltage, that zinc at first dissolves actively into solution, the structure of the electrode remains bright and the development of etch patterns is visible. As time and potential increase, a milky white film is formed. At 60 V, the dissolution process becomes retarded by the formation of a film on the structure that acts as a barrier layer to passage of zinc species from the electrode to the solution.

#### Effect of Additives on the Barrier Layer

The addition of sodium borate to alkaline electrolyte produced significant changes of the current density at all times and had an appreciable effect on the deposit barrier layer. Figure 3 shows the current density decreasing markedly with increasing borate concentration in the range from 0.06 M to 0.2 M. The current density reached 27 A/dm<sup>2</sup> in 0.06 M sodium borate and gradually decayed to low current density after the formation of an excellent barrier layer that is more compact if formed directly on the surface rather than by precipitation. This observation is related to the idea that electrochemical potential affects the adsorption of oxygen, particularly on the substrate surface. Sodium hydroxide and sodium borate are the non-oxidizing substances that indirectly facilitate the passivation of zinc by providing a condition more favorable for the adsorption of oxygen.<sup>20</sup> The mechanism of passivation is similar in that high concentrations of OH<sup>-</sup> displace hydrogen adsorbed on the metal surface, thereby decreasing the probability of the reaction between dissolved O<sub>2</sub> and adsorbed H. The excess oxygen is then available to be adsorbed instead, producing passivity. The optimal range of solution concentration appears to be 0.2 M sodium borate and 0.75 M sodium hydroxide, with current density of 10 A/dm<sup>2</sup>.

#### Properties of Anodic Coatings after Spark Discharge

In the second stage, the current density is kept at galvanostatic conditions (*i.e.*, by applying a constant current to the galvanized article). The corresponding voltage increases linearly to keep current density constant during the second-stage process. The potential finally reaches 90 V, at which some light sparks are initiated. The sparks are generally small and highly mobile at first, but are replaced by large, less mobile sparks as the voltage increases toward 118 V over a period of about 10 min. Orange sparks were observed over the whole barrier film, as shown in Fig. 4. This effect has been noted previously for aluminum and studied in detail.<sup>21</sup> These

events are apparently associated with ionization of the cobalt salts; cobalt ions adhered to the galvanized steel, as indicated by formation of a bluecolored anodic layer. These events are also frequently accompanied by voltage and current pulses, as well as copious gas evolution and other phenomena.

The anodic coating was fairly smooth with various attractive colors on the products, as shown in Fig. 5. When cobalt salts are replaced by other metal salts, such as manganese, chromium, iron, tin, etc., various colors (brown, green,



Fig. 10—EDS observation of (a) island-like structure; (b) fritted glass structure.

white, and gray will be observed on the surface of the zinc anodic layer. Such coatings can effectively reduce light reflection and enhance surface corrosion resistance.

#### Microstructure and Chemical Distribution

Figure 6 shows a cross-sectional view of a typical galvanized coating, consisting of a progression of zinc-iron alloy layers bonded metallurgically to the base steel, starting with a relatively pure zinc outer layer, known as the *eta* layer, about 15  $\mu$ m thick. Figure 7 is a SEM photomicrograph of a cross-sectional coating on galvanized steel. The anodic coating forms an integral bond with the substrate and the top layer is easily distinguished from the *eta* layer of the galvanized steel. This coating is of duplex nature, consisting of a porous outer layer over the barrier layer. The anodic coating thickness varies from 30 to 40  $\mu$ m, with about 10  $\mu$ m penetration, or a dimensional increase from 20 to 30  $\mu$ m. The hardness of the colored anodic layer is greater than 100 VNH<sub>20</sub>, measured on cross section, which is 20 percent higher than that of the outer *eta* layer.

Two types of surface morphology of the anodic coating were observed—island-like structure and fritted glass structure, as shown in Fig. 8a and 8b. No apparent agglomeration of semi-fused particles was found (Fig. 8b). All the island-like particles were identified as silicon-containing substances on the surface. Negative charging from the insulation characteristic of silicon took place and repelled more secondary electrons to the detector of the SEM, causing brighter imaging of

the protruding areas on the surface. It appears that the basilar surface was constructed of multiple layers of the fritted glass structure, as shown in Fig. 9a. The particle was irregularly grown in a pit on the surface. Careful examination of Figs. 9b and 9c indicates that the distribution of transition metals actually follows the silicon distribution. This also demonstrates the effect of direct adsorption of transition metal ions by spark discharge process. Figure 9(d) shows that the distribution of zinc is quite uniform on the surface of the anodic coating. Results from EDS observation in Fig. 10a indicate that the island-like structure is silicon-enriched. Zinc and silicon are almost equally enriched, however, in the fritted glass structure, as shown in Fig. 10b. Microscopically, the chemical composition of the anodic coating is mainly silicon and zinc, mingled with transition metals homogeneously distributed in these two structures and which exhibit a unique color accordingly.

#### Accelerated Corrosion Tests

The corrosion resistance of both untreated and anodic galvanized steel was tested in a salt spray cabinet for 4000 hr. The results indicated that zinc patina and rust spots were formed on the surface of untreated galvanized steel after a short period of exposure. The galvanized panels showed noticeable corrosion of the steel substrate after 240 hr of test. Anodic coatings proved to be the most corrosion resistant and did not show any breakdown during the accelerated corrosion test. The anodic zinc coating is slightly dulled by a faint white film on the surface after 2640 hr salt spray test, as shown in the table. The deposit on the anodic zinc coating was identified as  $Zn(OH)_8Cl_2 \cdot 2H_2O$  by XRD.

## Conclusions

- Two stages were utilized to anodize the galvanized steel. In the first stage, a milky white film was formed on the structure that provides a sufficient barrier layer for subsequent coating formation. In the second stage, a fairly smooth and attractive colored anodic coating was obtained.
- Two kinds of structure were formed on the anodic coating surface—island-like structure and fritted glass structure. The island-like structure is silicon enriched. Zinc and silicon are almost equally enriched in the fritted glass structure.
- Optimum composition and operating conditions were found as follows:

Sodium hydroxide	0.75 M
Sodium borate	0.2 M
Sodium silicate	0.75 M
Cobalt salt	0.03 M
Temperature	10 °C
Voltage	60 V (at first stage)
Current density	10 A/dm <sup>2</sup> (at second stage)
Duration	10 min.





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- 4. Multi-color variations are available, such as blue, green, brown, white, gray, etc. The hardness of the anodic coating is 20 percent higher than that of pure zinc layers.
- 5. An anodic coating on the surface of hot dip galvanized steel offers excellent corrosion resistance against saline environments and is therefore significantly better than untreated galvanized steel, as evaluated by the salt fog test.

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