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Surface & Coatings Technology 200 (2006) 4897 – 4903

SURFACE & COATINGS TECHNOLOGY

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Premature darkening problem and its prevention in galvanized sheet surface

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Received 19 February 2005; accepted in revised form 27 April 2005
Available online 18 January 2006

Abstract

Studies were undertaken in detail to identify the root cause of the darkening problem in unpassivated as well as laboratory simulated passivated hot dip galvanized steel sheet having regular spangle with the help of corrosion studies,i.e., salt spray, humidity chamber, atmospheric exposure and electrochemical tests. The samples were characterized by using Scanning electron microscopy/energy dispersive X-rays analysis (SEM/EDX), Auger electron spectroscopy (AES) and also measuring the volume percentage of bright and dull spangles on galvanizes sheet by a new technique developed in our laboratory. Based on the laboratory results, a special passivating solution was developed and implemented in our continuous galvanizing line (CGL), in order to improve the darkening behaviour of galvanized sheets. The sample from CGL with special passivating solution was tested and results were further corroborated by potentiodynamic polarization and SEM/EDX studies.

Keywords: Galvanized; Spangle; Darkening; Chromating

1. Introduction

In the engineering and construction sectors, hot-dip galvanized steel sheets are preferred by users for their beautiful appearance consisting of large flowery grains termed "spangles"; originating from the solidification pattern of the zinc layer. These spangles are obtained by adding minor quantities of lead, bismuth or antimony to the zinc bath. In addition to the surfactants, the spangle formation is also affected by cooling rate, roughness and cleanness of the steel sheet. Depending on the solidification condition, the zinc coating films show mirror finish brightness because of the presence of large number of very smooth and reflective spangles (bright spangles) in some cases while in other cases they reveal dull appearance due to high percentage of rough and poor reflectivity (dull spangles). The dull spangles not only detract the galvanizing coating appearance but also adversely affect surface reactivity. Chang and Shin classified the spangles as dull or bright and found that dull spangles were more sensitive to corrosion attack [1]. To eliminate the darkening and white rusting problem, practically all galvanized sheets are given a post-galvanized treatment (chromatizing). Usually the chromate treatment is very effective but often, premature darkening of the surface does occur.

Helwig studied this problem extensively and observed that bright coating with few rough spangles have much more resistance to blackening than dull coating with many rough spangles [2]. This observed difference in surface reactivity suggests that the dull spangle have a different surface composition than bright spangle and some evidence of this has been reported in literature. Waitlevertch and Hurwitz analyzed bright and dull spangle by emission spectrography using a hallow cathode source. They observed that the dull spangles contained more lead and antimony than bright spangles [3]. Frank, Conduti, and Smith obtained similar results using ion scattering spectrometry and, in addition, observed that the dull spangles also contained more

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doi:10.1016/j.surfcoat.2005.04.044

antimony [4]. Zopponi et al. concluded that the darkening is produced by the presence of antimony oxide in the surface and appears mainly in dull spangles as the result of greater diffusion of antimony and faster oxidation [5].

This darkening problem was reported when sheets are kept in the coil condition or are stacked. Similar but less pronounced blackening occurs in atmospheric exposure. The exact cause of blackening is not known but it was suggested that uneven distribution of alloying element on the dull spangle surfaces creates galvanic cells that makes the surface more reactive under the thin film of electrolyte. Various methods have been proposed to eliminate the darkening problem such as flashing treatment of galvanized sheet with Ni, Co, prior to its chromate treatment [6].

We observed blackening problem in one of our galvanizing line product where as another line product was free from such defects. The galvanized sheets showed premature darkening within 4–8 weeks during transit and storage. Although the same chromating solution was used in both galvanizing line products but the darkening problem was persisted in only one line product. Hence, a detail studies were taken first done to understand the causes of darkening and subsequently to eliminate darkening of galvanized sheet. A laboratory based chromate solution was made to understand the darkening problem.

2. Experimental

2.1. Chromate passivation

The conventional chromate solution was collected from plant at two different concentrations; here called as conventional A and B. Also a chromate passivating solution was made in laboratory here; after refer as lab chromate. Both the conventional and laboratory chromate solutions were characterized by measuring of total chromium, hexavalent chromium, their ratio and pH. The measured data are given in Table 1. The 150×100 mm^2 steel panels (0.6 mm thick) with a 60 g/m^2 hot dip galvanized spangled coating were collected from plant. These unchromated galvanized sheets were cleaned by magnesium powder followed by acetone washing. The panels after the dip chromating process were passed through a set of squeeze rolls immediately and finally dried in oven. The above mentioned chromate solutions were used separately to chromate the galvanized sheets by varying the chromate dipping time and oven drying temperature.

Table 1
Chromium concentration and pH of the passivating solution

Chromate solution	pH	Cr^{+6} (mg/100ml)	Total Cr (mg/100ml)	Cr^{+6}/Cr^{+3}
Conventional A	1.5	305	551	1.24
Conventional B	1.3	433	911	0.90
Lab chromate	1.3	463	697	1.97

Table 2
Laboratory chromatizing process parameter for galvanized samples

Solution	Chromatizing time (s)	Oven drying temp. (°C)	Oven drying time (s)
Conventional A	3	80	60
Conventional A	6	120	60
Conventional B	3	80	60
Conventional B	6	120	60
Lab chromate	3	80	60

2.2. Surface characterization

Both dull and bright spangles were analyzed separately by Scanning Electron Spectroscopy (SEM) instrument. JEOL-6400 SEM attached with Energy dispersive Spectroscopy (EDS) detector was used for surface analysis of galvanized surface in unchromate and chromate condition for dull and bright spangles.

The AES analyses was performed on the unchromated galvanized surface at an accelerating voltage of 10kV and the thickness of oxide was measured by depth profiling using 3.5 keV Ar^+ ion sputtering in the Auger system. The sputter rate was 25 nm/min as measured on Ta_2O_5. Both types of spangles were analyzed separately to study the distribution of elements on the spangles surface.

2.3. Corrosion study

The potentiodynamic electrochemical tests (Tafel analysis) were performed in 5% sodium chloride solution on unchromated galvanized sheet. Test was conducted on Bright as well as dull spangles to find out the influence of each type of spangle on corrosion behaviour.

The chromated samples were exposed in high humidity–high temperature conditions, salt spray chamber and atmosphere to study the darkening phenomenon. For simulating high humidity–high temperature cycle, five samples were put together, wrapped in volatile corrosion inhibitor (VCI) paper and kept at 40 °C temperature and 90% humidity. Salt spray test was carried out as per ASTM B-117 in 5% sodium chloride solution to evaluate the white rust resistance properties. In atmospheric exposure test, the samples were kept on the industrial atmosphere at the building top at an angle of 45 °C to horizontal facing southward exposure.

Table 3
Failure result (in h) for different exposure test

Chromate solution	Atmospheric (blackening) (h)	High humidity–high temperature (blackening) (h)	Salt spray (5% white rust h)
A	480	70	50–60
B	480	70	70–80
Lab chromate	Not blackening till 480 h	Not blackening till 480 h	70–80

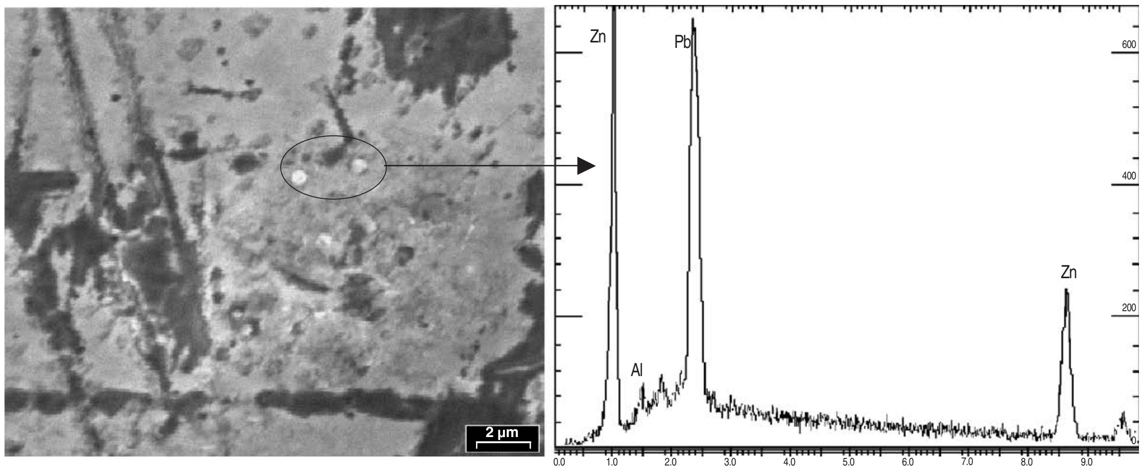

Fig. 1. SEM/EDX studies on the dull spangle area of unchromated sheet.

2.4. Spangle ratio measurement

The overall brightness of the spangle sheet depends on the ratio of dull and bright spangle distribution on sheet surface which in turn relates to sheet darkening. Therefore, a precise measurement technique was developed to find out the ratio of dull to bright spangles on galvanized sheet surface. An area of 90×80 mm^2 was taken to calculate dull and bright spangles using a transparent graph sheet. The dull and bright spangles were sketched and its area was measured. This new technique gave an accurate value of area fraction of dull and bright spangle.

3. Result and discussion

3.1. Chromate passivation process: lab simulation study

The chromate solutions mentioned in Table 1 gave a colorless chromate coating on galvanized sheet surface. The chromating process parameters were varied to study the influence of various chromate solutions on corrosion behaviour as mentioned in Table 2. The dipping time was changed from 3 to 6 s to observe the zinc dissolution rate in the acidic passivating solution. The sample weight before and after chromating was found almost similar which indicated that the amount of zinc dissolved was compensated by the chromium deposition during chromating. Similarly the drying temperature was varied from 80 to 120 °C in a heating furnace without any air circulation inside the furnace. The typical values obtained from these test were compiled and are given in Table 3. The conventional chromated samples exposed to salt spray, atmospheric exposure and high humidity–high temperature, did not give any conclusive evidence of changing the process parameters on surface properties. However, a very remarkable observation was also made during the above exposure tests that the dull spangles became more blackened than the bright spangles. The chromate treatments were most effective in preventing blackening on galvanized coating which had minimum dull spangle.

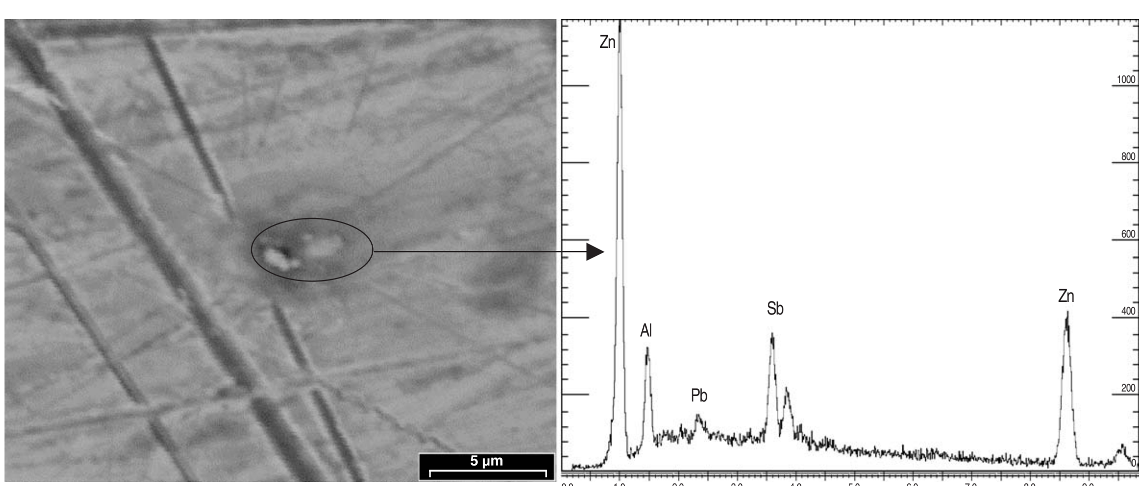

Fig. 2. SEM/EDX studies on the bright spangle area of unchromated sheet.

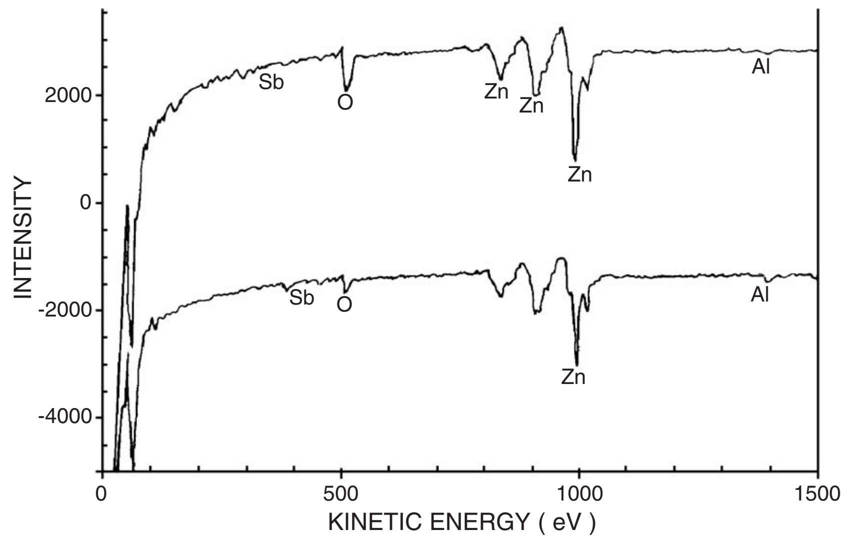

Fig. 3. AES studies on the dull spangle area of unchromated sheet.

3.2. Surface characterization

The unchromated galvanized surface was analyzed by SEM/EDX to find out the distribution of solute elements like lead, antimony and aluminum. It was observed that the dull spangle contained more of these elements than smooth spangle which was relatively pure. Large number of lead precipitates was observed at the dull spangle surface as a result of solute rejection and reaction with atmosphere during the solidification of zinc coating. The pure lead globules were found in the dull spangles area as shown in Fig. 1. Lead and antimony were found in the bright spangle surface but the size and the population were very small in comparison to dull spangles as shown in Fig. 2. The AES analysis revealed that antimony and aluminum were present in both dull and bright spangle of unchromated sheets as shown in Figs. 3 and 4, respectively. Initially antimony was observed in both the spangles but after sputtering, the antimony was found only in dull spangles. Similarly, after three minute of sputtering, aluminum washed out from the bright area surface whereas in the dull area it persisted. This indicated that the aluminum oxides distribution was almost uniform all over the surface but its adhesion and thickness was very high in dull area. It has been reported that the thickness of aluminum oxide film, of the order of 5 nm, remained same for both bright and dull coatings and independent of zinc spangle roughness [7].

3.3. Corrosion studies

Electrochemical potentiodynamic test in 3.5% sodium chloride medium on unchromated galvanized samples

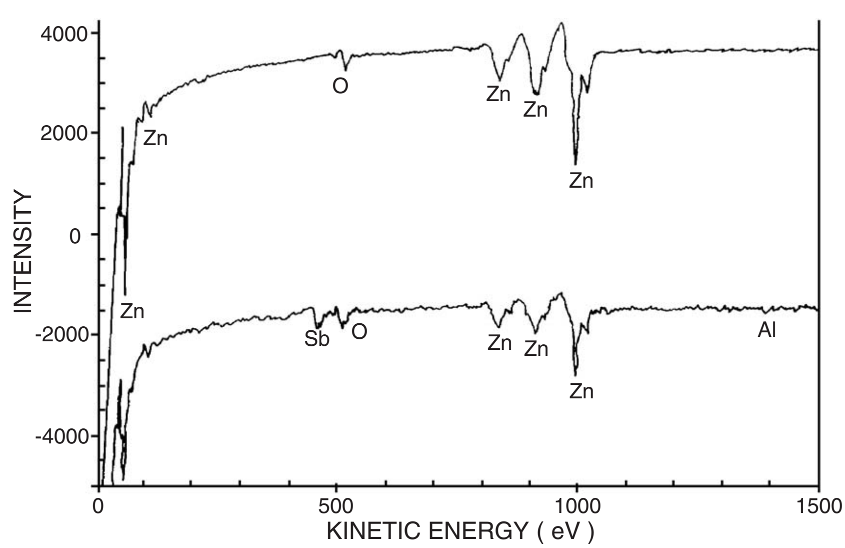

Fig. 4. AES studies on the bright spangle area of unchromated sheet.

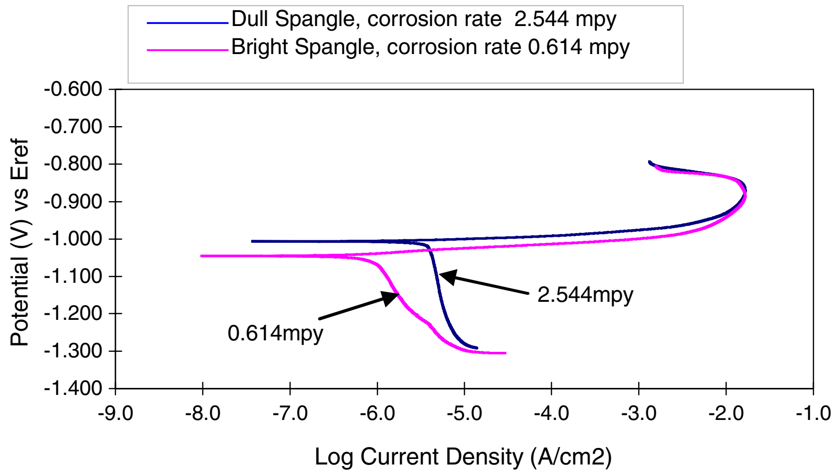

Fig. 5. Comparison of corrosion rate of dull and bright spangle area of galvanized sheet.

depicted that the corrosion rate of dull spangle was approximately two times more than the bright spangle. This bright spangle contained smooth and pure zinc surface, thereby giving lower corrosion rate than dull spangles. This finding revealed that the dull spangles were more prone to corrosion attack than bright spangles in unchromated condition as shown in Fig. 5.

3.4. Spangle distribution on surface

From the corrosion test, SEM and AES analysis it was found that the dull spangles were more prone to blackening. The blackening appearance enhanced with the increase in number of dull spangle. This led to find out the spangle distribution in both bright and dull appearance product.

The spangle ratio measurement showed that the galvanized sheet surface having overall brightness contains 68% of bright spangle and 32% dull where as the galvanized sheets having overall dull appearance contains 30% bright spangle and 70% dull spangles as shown in Fig. 6. This two opposite spangle distribution ratio was for two different plant samples. Furthermore, no darkening problem was observed on the samples having overall brightness. This helped in addressing the spangle related surface deterioration effects like blackening and white rusting of the galvanized steel.

3.5. Improved chromate process: lab study

The SEM-EDS and AES study clearly revealed that the dull spangle contained comparatively more lead, antimony and aluminum than bright spangles which makes the galvanic cell with zinc and caused the premature darkening of the galvanized sheet. Bright spangle is relatively pure than dull and hence less susceptible to blackening [8]. In X-ray mapping on conventional chromate coated dull spangle, it

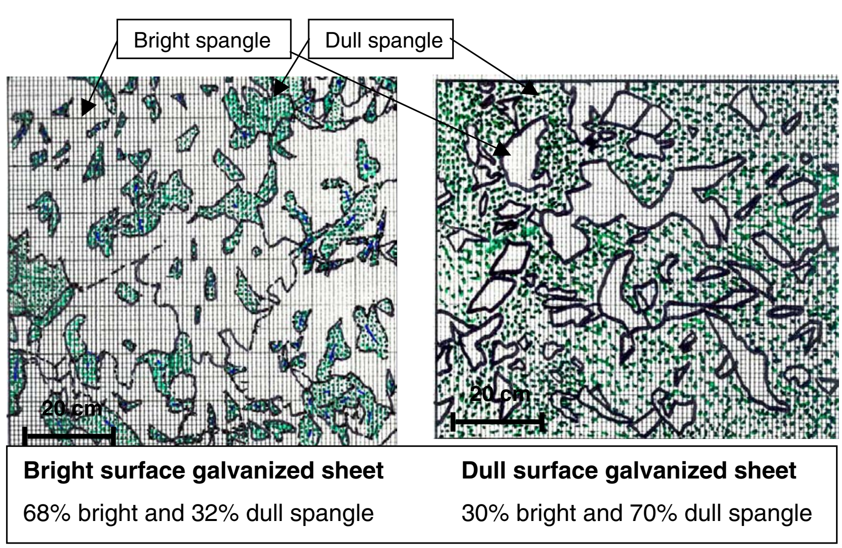

Fig. 6. Dull and bright spangle distribution on two sheets.

was observed that the dull spangle contained large number of lead and antimony surrounded by the chromate coating. This indicated that the conventional passivating solution was not effective in dissolving lead and antimony from the surface as shown in Fig. 7. Therefore, we focused our attention on the dull spangles only and our aim was to dissolve the solute particles from the dull spangle during the chromate coating and make it purer like bright spangle. With this objective, a chromate based passivating solution was made in laboratory to dissolve preferentially the alloying element particularly lead, antimony and aluminum from the spangled surface. Other objective of this chromate formulation was to enhance white rust resistance after chromating of galvanized sheets.

The chromating passivation solution consisted of chromic acid. The chromic acid is a very strong oxidizing agent, it passivates a metal surface and a chromate film is not formed. To inhibit the passivation of galvanized surface, sulphuric acid was added in the chromating formulation.

Now for the selectively and preferably dissolution of lead during chromate coating of galvanized sheet surface, nitric acid was added in the chromating formulation. The basis of choosing the nitric acid was based on the lead compound and its solubility in different acid as shown in Table 4. Similarly, fluorosilicic acid was added in the chromating formulation which gives hydrofluoric acid and silicate ions. The solubility of antimony fluoride was found to be very high compare to other compound of antimony. The dissolution of aluminum was very high in fluorosilicic acid which is greater than 50 mils per year which indicate that the faster and preferential dissolution of aluminum layer [9]. In this way the fluorosilicic acid serves the purpose of dissolving both the aluminum and antimony from the galvanized surface where as the nitric acid preferentially dissolve the lead only.

3.6. Performance of laboratory developed chromating solution

The above developed chromate coating formulation was applied on galvanized sheet. The X-ray mapping shown in Fig. 8 indicated that the new formulation was effective in dissolving the lead and antimony globules during chromating. The population of solute particles was drastically reduced and only at few points small lead globules were observed. The antimony was not observed in the mapping of the steel sheets. This revealed that the surface was not completely free from solute particles but it removed the major part of the solute present in the surface.

In salt spray tests the samples gave better performance than conventional chromate coating. It passed 90 h in salt spray test without any white rust formation where as the conventional chromate galvanized samples passed up to 60 h only. The samples exposed in atmosphere showed no blackening even after two months of exposure in industrial atmosphere.

Table 4
Several compounds and their solubility

Compound	Formula	Solubility at 25 °C
Lead chromate	PbCrO4	1.8×10^{-4}
Lead fluoride	PbF2	3.7×10^{-8}
Lead nitrate	$Pb(NO_3)_2$	Soluble 60 g/100 ml
Lead sulphate	PbSO4	1×10^{-8}
Antimony fluoride	SbF2	447.7

4. Conclusions

In the present study, hot-dip galvanized steel sheet with regular spangles were subjected to corrosion tests, SEM/EDX, AES and measurement of volume fraction of bright as well as dull spangles in order to identify and suggest some remedial measures to overcome the early darkening problem. The results of our findings can be summarized as follows:

1. The darkening problem of thin-transparent chromate film on hot-dip galvanized surface was highly influenced by the type of the spangle. Salt spray, humidity cabinet and atmospheric exposure tests revealed that the samples with dull appearance gave the higher percentage of corrosion products than those with bright appearance. The corrosion rate measured from electrochemical technique in 5% sodium chloride solution also confirmed the higher rate of corrosion in the area of dull spangle.

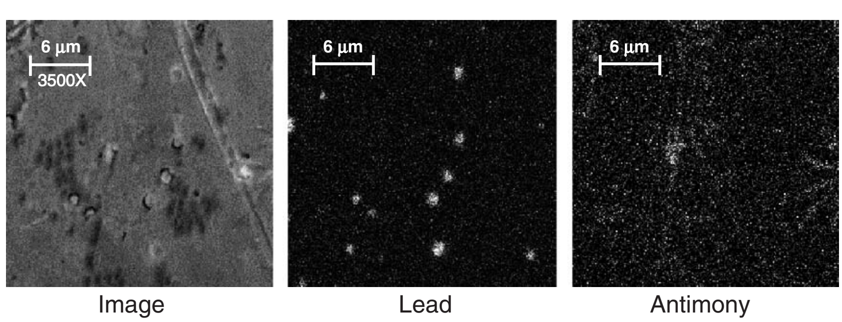

Fig. 7. SEM X-ray mapping of conventional lab chromated dull spangle.

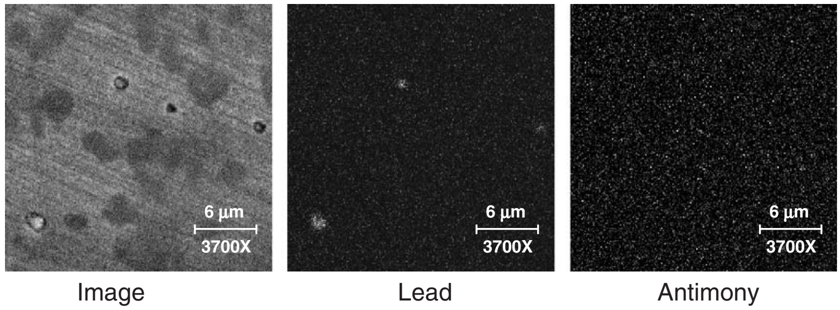

Fig. 8. SEM X-ray mapping of lab chromated dull spangle.

2. The SEM-EDX and AES study clearly revealed that the poor reflective dull spangle contained comparatively more lead, antimony and aluminum than highly reflective bright spangle. The higher concentration of these solute rejected elements form galvanic cell with zinc, causing early darkening of galvanized sheets.
3. The spangle ratio measurement showed that galvanized sheet surface having overall brightness contains 68% of bright spangle where as overall dull appearance sheet showed only 30% of bright spangle.
4. The laboratory formulated passivating solution worked very effectively in minimizing the early darkening problem in galvanized sheet by dissolving lead and antimony selectively. This was further confirmed by EDX mapping and well supported by corrosion tests.

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