A Study on the Improvement of Surface Appearance in Electrogalvanized Steel Sheet

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In this study, zinc electrodeposits were polished 1-2g/m^2 in acid solution with various additives. Their effects on the whiteness and surface morphology of electrodeposits were investigated and mechanism for the improvement of surface appearance was also examined. Sulfuric acid solution and hydrochloric acid solution have a little effect on the improvement of surface appearance. But, the large increase of lightness and gloss was observed by the addition of hydrogen peroxide. From the microstructure observation, it was shown that sharp edges of thin zinc plates were altered into a smooth layered structure. Corrosion potential was shifted into the direction of positive potential and the dissolution of zinc electrodeposits was considerably accelerated by the addition of hydrogen peroxide. Nickel ion in plating bath decreased the lightness of zinc coating layer but iron didn’t affect it. Gloss was not affected by the existence of nickel and iron in plating bath. In the organic coated samples, polished sample had a better corrosion resistance and black patina resistance than not polished samples. It was shown that the lightness and gloss of organic composite coated samples were also largely increased even if zinc phosphate film and organic coating was performed on the polished surface.

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1. Introduction

Zinc coating is widely used on the various steel sheets for automobile and electronic applications owing to its sacrificial protection of steel. Thus zinc coating processes have been the subjects of numerous investigations. Organic composite coated electrogalvanized (EG) steel sheet which has double conversion coating layers of chromate and phosphate possess various merits such as good surface quality, corrosion resistance, fingerprint resistance and lubrication. However, since the toxicity of chromium was known to many people, the use of chromating treatment is in the atmosphere of prohibition from the viewpoint of global environmental protection. In the field of electrical appliances, customers also demand good electrical conductivity for accomplishing a stable ground property. As phosphate layer acts as insulator, new chromium free organic composite coated product is composed of zinc electrodeposits and a thin organic coating. In this case, the surface appearance was darkened and the lightness decreased by 5 to 7 compared to conventional organic coated product. Therefore, improvement of surface appearance was demanded from customers.

The appearance of zinc electroplated steel sheet is characterized by lightness and gloss of zinc electrodeposits. There are many factors affecting the appearance such as the characteristic of substrate, pretreatment, electroplating conditions and the composition of plating bath. Among these factors, electroplating conditions have a large effect on the crystal orientation and size which dominates the lightness and gloss of zinc electrodeposits. K. Ishii et al.1) studied effects of bath composition on the formability and appearance from the crystallographic point of view. According to their results, the gloss and lightness were increased with the basal plane orientation of zinc crystal. Similar tendency was also found in results of Y. K. Cho et al.2-3) The effects of plating condition and additives were investigated by M. Kawabe.4) It was also reported that the appearance of electrogalvanized steel sheet was improved by the predominant orientation of basal plane. It was shown that the lightness and gloss of zinc electrodeposits were influenced by substrate and pickling condition.5)

Therefore, this study was performed to increase the lightness and gloss of zinc coated product as a preceding work for the development of chromium free organic coated electrogalvanized product. Chemical polishing technique was introduced to improve the surface appearance of organic coated products. The modification of surface was investigated and the mechanism of reaction between zinc layer and etching solution was discussed

2. Experimental Procedure

Sample preparation

A commercial zinc electroplated steel sheet manufactured in continuous electrogalvanized line was used as a test sample. The specimen was cut into 100mm X 150 mm test pieces and was chemically polished in acidic solutions having various additives for 5 seconds at 25 . After surface modification was carried out, zinc phosphate films were formed and then organic composite coating with a thickness of about 1㎛ was performed by using a bar coater.

Analysis and estimation of properties

Surface appearance was estimated by measuring lightness and gloss with colorimeter and gloss meter. Microstructure and surface morphology were then observed by scanning electron microscope (SEM) and scanning prove microscope (SPM). The Chemical composition of zinc electrodeposits was analyzed by Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES). The crystallographic feature was examined by means of X-ray diffractometer using a copper target.

Corrosion test and humidity test

The specimens were cut into 150x70 mm test pieces. The edges and backs of the specimen were covered with adhesive tape. A salt spray test 35℃ was performed as specified in the Standards ASTM B117. Humidity test was also carried out in 90% humidity for 120 hours at 60℃. Black patina was evaluated by the difference of lightness before and after the test

Electrochemical measurement

Electrochemical experiment was conducted to examine the dissolution behavior of zinc electrodeposits. Corrosion potential to time curves was measured with respect to a saturated calomel electrode (SCE) in various acidic solution having additives at 25℃. Specimen was first placed in corrosion test cell containing demi-water and then the experiment was started. After beginning the experiment, polishing solution was injected into a test cell in order to be adjusted to a set concentration and pH.

3. Results and discussion

Surface appearance with the variation of etching solution

Fig. 1 and Fig. 2 show the difference of lightness and gloss with the variation of acidic solution and pH.

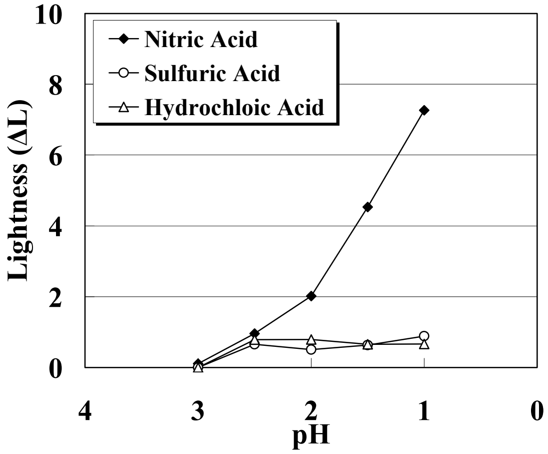


Fig. 1 Results of difference of lightness with etching solution and pH

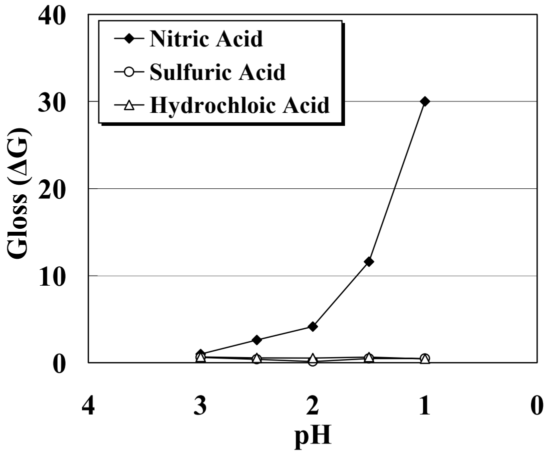


Fig. 2 Results of difference of gloss with etching solution and pH

As the pH of polishing solution was lowered, gloss and lightness was increased. It was shown that sulfuric acid solution and hydrochloric acid solution have a little effect on the improvement of surface appearance. But, nitric acid remarkably increased the lightness and gloss of zinc electrodeposits.

Fig. 3 represents the effect of addition of hydrogen peroxide to sulfuric acid on the surface appearance. It is generally known that hydrogen peroxide is a powerful oxidizing agent and is not harmful. The large increase of lightness and gloss was observed by the addition of hydrogen peroxide. Especially, the addition of even small amount has a large effect on the improvement of surface appearance. When hydrogen peroxide and sulfuric acid is separately used to polish zinc electrodeposit, lightness and gloss was not increased. It can be thought that hydrogen peroxide exhibits the synergistic effect on polishing the surface.

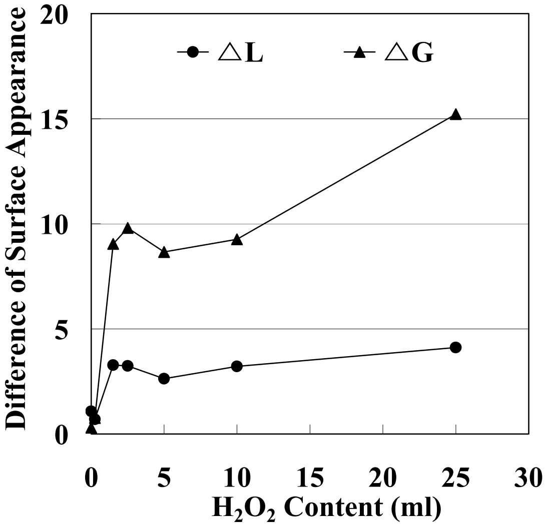


Fig. 3 Effects of the addition of hydrogen peroxide on the surface appearance

(Polishing condition: pH 1.5, Sulfuric acid + X ml H_2O_2))

Influences of the addition of hydrogen peroxide to nitric acid at pH 1.5 were shown in Fig. 4. Similar tendency to results of sulfuric acid solution containing hydrogen peroxide was observed. However, in spite of a large improvement of surface appearance in nitric acid base solution, its effect was smaller than that of sulfuric acid base solution.

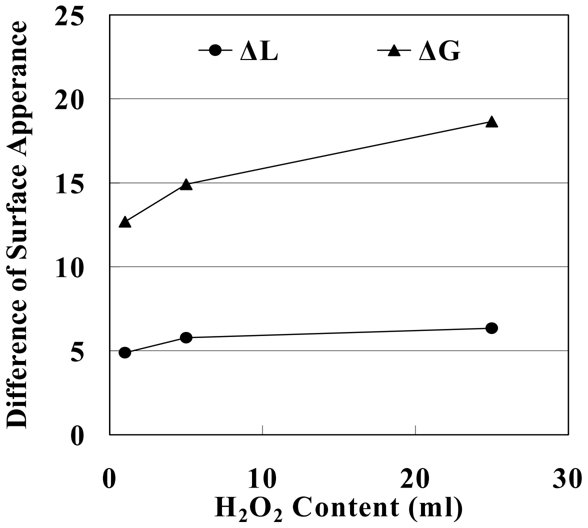


Fig. 4 Effects of the addition of hydrogen peroxide on the surface appearance

(Polishing condition: pH 1.5, nitric acid + X ml / l H_2O_2))

Fig. 5 shows the surface morphologies of zinc eletrodeposits before and after polishing test. In the no polished state, the deposits are formed by the layer-by-layer growth mechanism on (002) plane zinc electrodeposits. That is, sharp edges were observed on a well developed layered structure. When samples was polished in sulfuric acid and hydrochloric acid solution, the morphologies of layered structure having sharp edges were little changed. In the case of polished samples in nitric acid, sharp edges of uneven layers were altered into a smooth layered structure. This change of surface was also observed in sulfuric acid containing hydrogen peroxide. From these results, it was found that lightness and gloss of zinc electrodeposit could remarkably be improved by the addition of hydrogen peroxide to acid solution. The sample, which was polished in the solution of nitric acid and hydrogen peroxide, has a smooth morphology by the severe dissolution of zinc electrodeposits. But, it is not desired that the excessive dissolution of zinc electrodeposits have a bad effect on the corrosion resistance of zinc electrogalvanized steel sheet. From the observation of 3-dimensional microstructure by scanning prove microscopy such as Fig. 6, it was also verified that uneven steps of zinc electrodeposits was changed to smooth surface. It was found that this modification of uneven step in zinc electrodeposits contributed to the improvement of surface appearance.

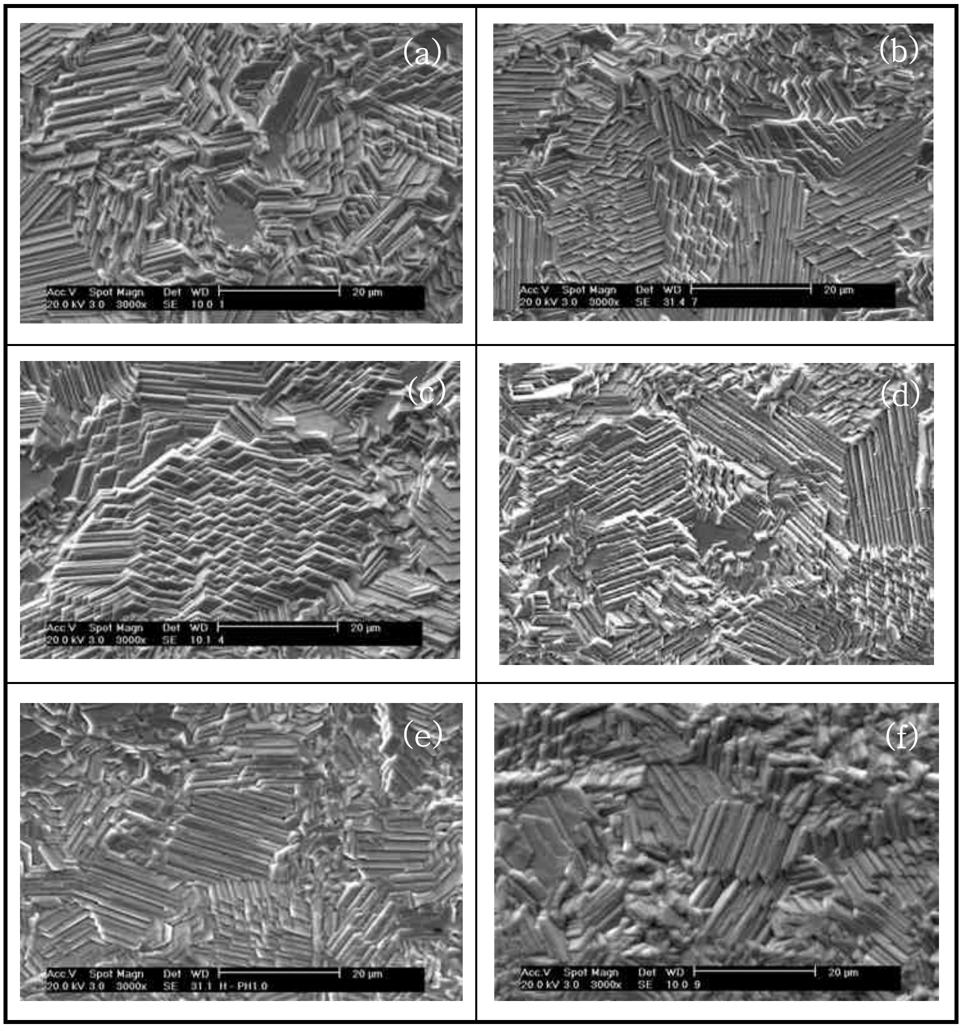


Fig. 5 Surface morphologies of polished zinc elelectrodeposits in various polishing solution

(Polishing condition: pH 1.5, acid solution + 5 ml/l H_2O_2)

(a) Not polished (b) HCl (c) H_2SO_4

(d)H_2SO_4 + H_2O_2 (e) HNO_3 (f) HNO_3 + H_2O_2

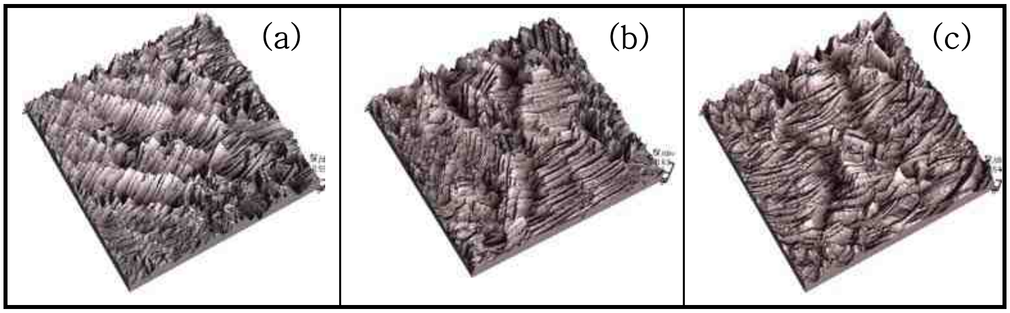


Fig. 6 3-dimensional SPM morphology of polished surface

(a) H_2SO_4 (b) $H_2SO_4 + H_2O_2$ (c) $HNO_3 + H_2O_2$

Fig. 7 gives the results of X-ray diffraction analysis. From this result, it was shown that zinc crystal orientation was not varied by polishing treatment of surface.

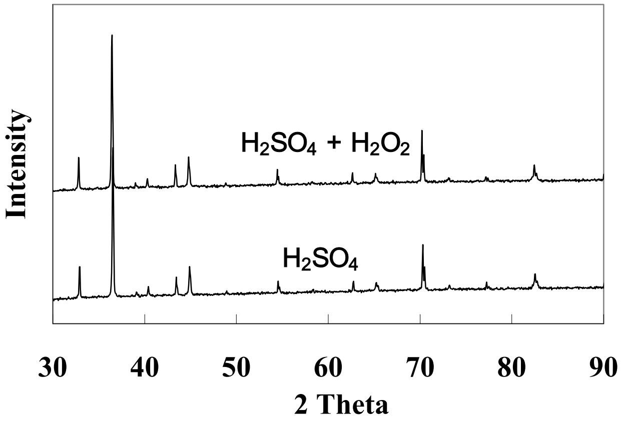


Fig. 7 Results of X-ray diffraction analysis

(Polishing condition: pH 1.5, sulfuric acid + 5 ml/l H_2O_2)

Result of electrochemical test

Corrosion potential to time curve was measured to examine the dissolution behavior of zinc electrodeposits in acidic polishing solution. It was shown in Fig. 8. Corrosion potential of zinc electrodeposits was about -1020mV (SCE) in the sulfuric acid solution and about -770mV (SCE) in hydrogen peroxide solution.

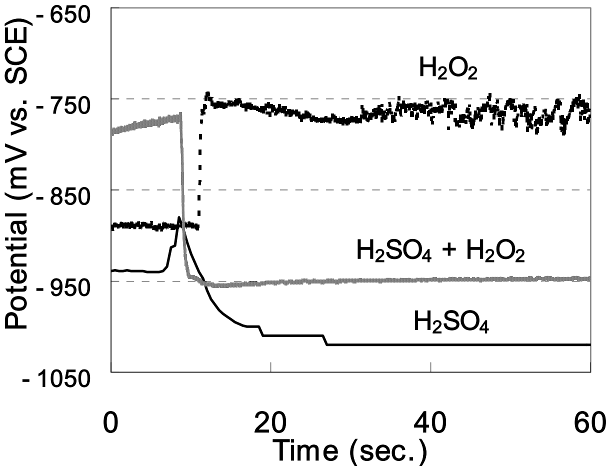


Fig. 8 Corrosion potential to time curves

Therefore, when hydrogen peroxide was added to sulfuric acid solution, hydrogen peroxide plays an important role in the dissolution of zinc electrodeposits. Its function can be explained in Fig. 9 by anodic polarization curve. As the corrosion potential of zinc electrodeposits in hydrogen peroxide solution is higher than that in sulfuric acid solution, corrosion potential is shifted to the direction of positive potential in the solution of sulfuric acid and hydrogen peroxide. Accordingly, corrosion potential is moved from E^0 to E^1, but the increment is small. A dissolution rate is increased from i^0 to i^1. As the horizontal axis of dissolution rate is logarithmic scale, the dissolution of zinc electrodeposits was considerably accelerated above several hundred times.

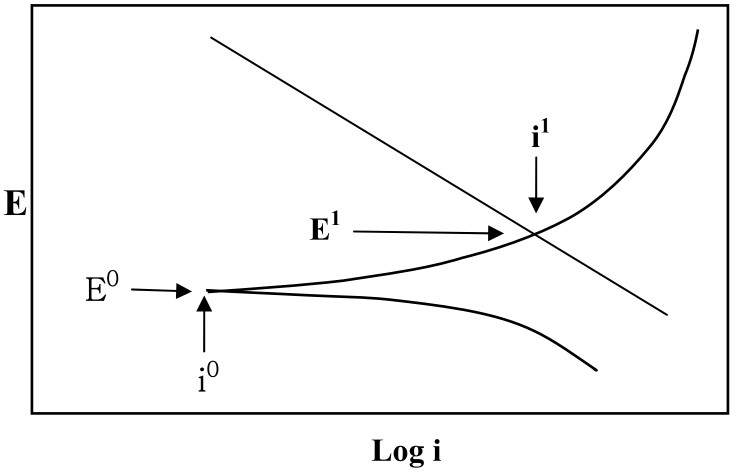


Fig. 9 Schematic diagram for illustration of corrosion potential shift by the addition of hydrogen peroxide

Properties of organic composite coated steel sheet

Polished samples were coated with zinc phosphate film and organic composite resin. Their properties were measured and summarized in Table 1. The lightness and gloss was largely increased by polishing in the solution of sulfuric acid and hydrogen peroxide even if zinc phosphate film and organic coating was treated on the polished surface. The black patina resistance of polished sample was slightly larger than that of no polished sample. It was shown that polishing was very effective in the improvement of surface appearance and the decrease of discoloration in humid atmosphere. The result of salt spray test also showed that polished sample had a better corrosion resistance than no polished sample. It is thought that this corrosion behavior is related with the composition and morphology of surface. A lot of small voids were observed in the phosphate film of not polished sample, but little in polished sample. It seems that these small voids affect corrosion resistance.

Table 1 Properties of organic composite coated steel sheet

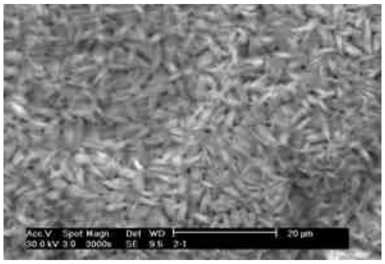
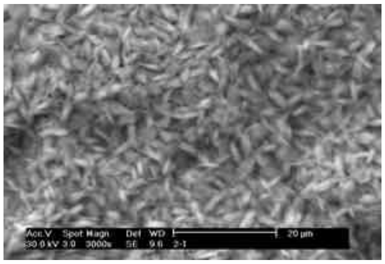
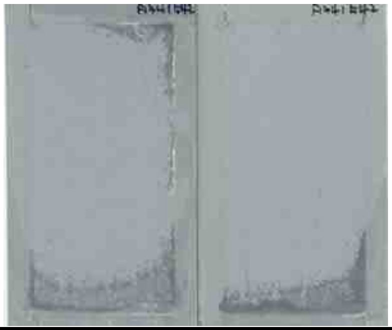
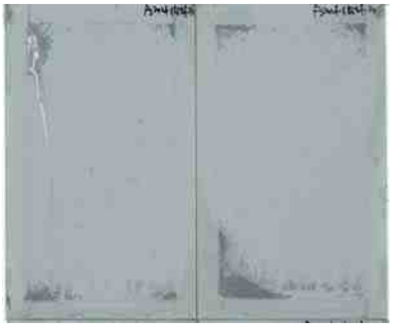
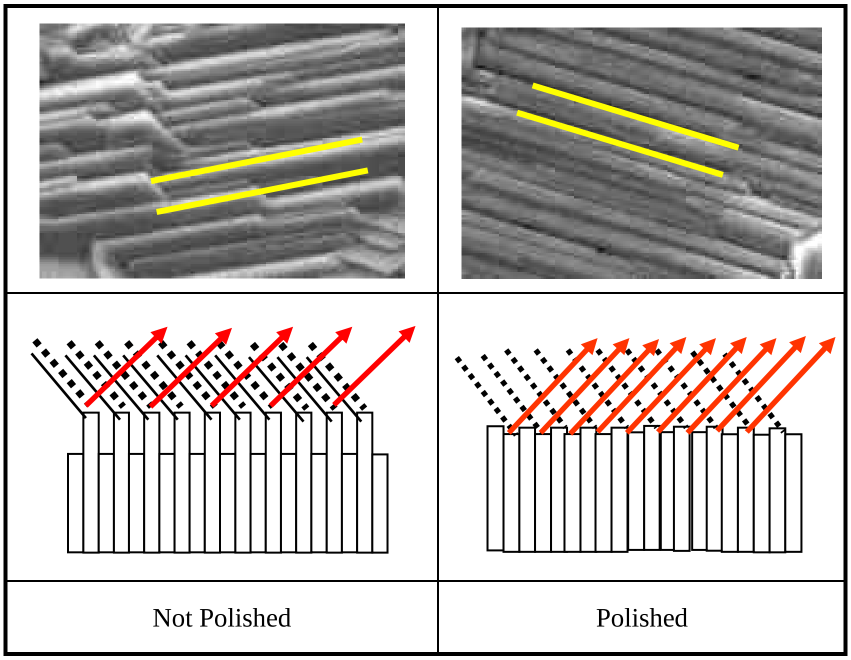
Contents	Not polished	Polished
Lightness (L)	72 ± 2	78 ± 2
Gloss (G)	2.5 ± 1	5 ± 1
Humidity Test	△L : 1.53 ± 0.2	△L : 1.15 ± 0.2
Microstructure		
Salt Spray Test (180Hrs)		

Illustration for the improvement of surface appearance and properties

Fig. 10 shows the microstructure of zinc electrodeposits. Zinc electrodeposits are in the shape of thin layered plates. The edges of them are parallel to specific crystal orientations and many crystals of the same orientation were stacked into a layered packet. Zinc crystals grow laterally on the edge of an each thin layer. There is always a micro-roughness on the surface of zinc electrodeposits. The part of incident light is not reflected on the surface by shadow effect. In the polished specimens, it can be considered that zinc coating layer was preferentially dissolved on the edge of thin layered plates. As the micro-roughness of zinc electrodeposits was evened by polishing, a larger part of incident light will be reflected on the surface. Therefore, surface appearance such as lightness and gloss can be improved by the above mentioned reason.


Not Polished

Polished

Fig. 10 Illustration for the improvement of surface appearance of zinc electrodeposits

The content of each chemical species dissolved into the polishing solution was analyzed to investigate the dissolution behavior of electrodeposits by ICP. Fig. 10 shows the dissolved coating weight and the concentration of impurity. Dissolved coating weight of zinc electrodeposits increased linearly with the concentration of hydrogen peroxide up to 10ml/l. In our factory, zinc products and Zn-Ni products are produced in the same electrogalvanized line. Accordingly, nickel was inevitably contained in zinc electrodeposits as an impurity. It was known that this impurity decreased the surface quality. Nickel was also dissolved as a similar aspect to dissolved coating weight. Therefore, the nickel concentration was theoretically recalculated by assuming the general dissolution from coating layer. Both theoretical and real measured concentration were compared to examine the dissolution behavior.

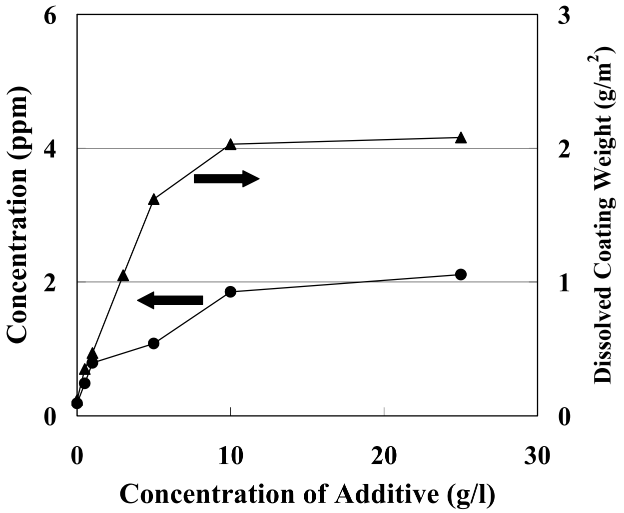


Fig. 10 Variation of dissolved coating weight and nickel content with hydrogen peroxide

Fig. 11 shows the schematic diagram to calculate a theoretical concentration. All the concentration is expressed by normalized value and the formula is as follows.

$$\text{Real Value}(\times 100) = \frac{C1_{Ni}}{C1_{Ni} + C2_{Zn} + C3_{Fe}} \times 100 \quad (1)$$

$$\text{Theoretical Value}(\times 100) = \frac{C0_{Ni}}{C0_{Ni} + C0_{Zn} + C0_{Fe}} \times \frac{m_i}{20} \times 100 \quad (2)$$

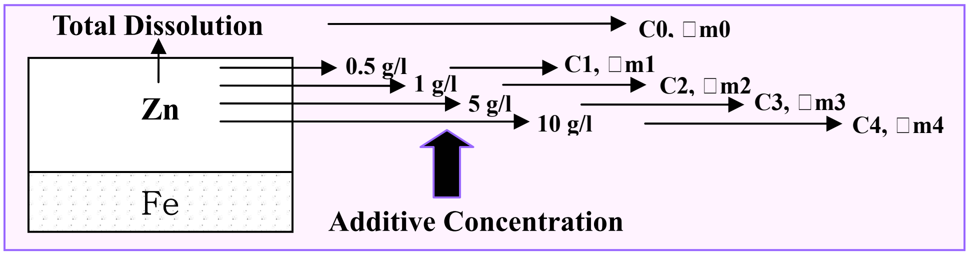


Fig. 11 Schematic diagram to calculate the theoretical concentration

Fig. 12 and Fig. 13 show the recalculated concentration of iron and nickel. In the initial stage of dissolution, it was observed that nickel and iron was selectively dissolved from zinc electroplated layer. As the increasing addition of hydrogen peroxide dissolved a larger coating layer, it was difficult to experimentally analyze the selective dissolution of impurity in the high concentration range of hydrogen peroxide.

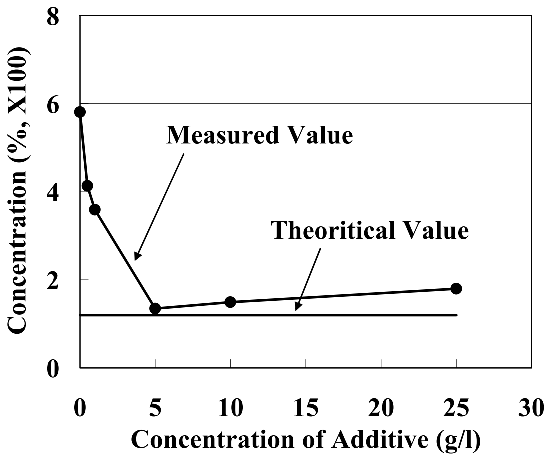


Fig. 12 Theoretical and measured concentration of nickel

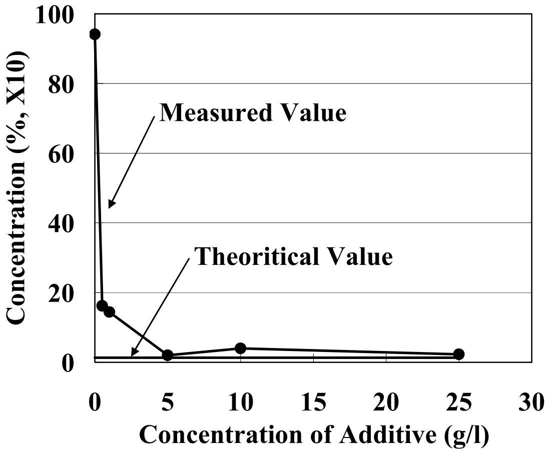


Fig. 13 Theoretical and measured concentration of iron

Fig. 14 and Fig. 15 show effects of nickel and iron in plating bath on the lightness. As the nickel ion in plating bath decrease from 100ppm to 60ppm, lightness increased by 2 to 3. On the other hand, iron ion was maintained in the concentration of constant range. From these results, it can be concluded that nickel ion in plating bath and zinc electrodeposit decrease the lightness of zinc coating layer and iron don't affect it.

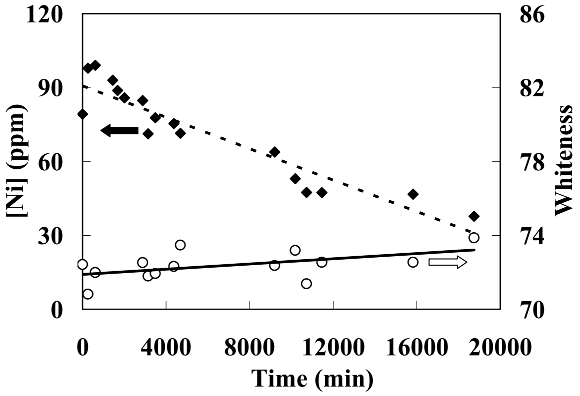


Fig. 14 Variation of lightness with nickel concentration in electroplating bath

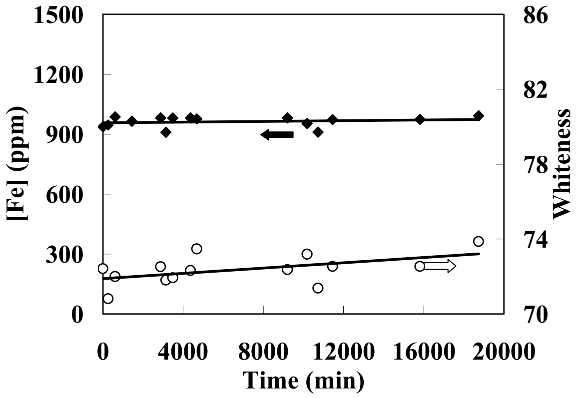


Fig. 15 Variation of lightness with iron concentration in electroplating bath

Fig. 16 represents the variation of gloss with nickel concentration in plating bath. Gloss was not varied with nickel concentration. Iron concentration of plating bath was maintained in the concentration of constant range. Therefore gloss was not affected by the existence of nickel and iron in plating bath. Strictly speaking, it is correct that gloss was not affected in investigated concentration range of impurity

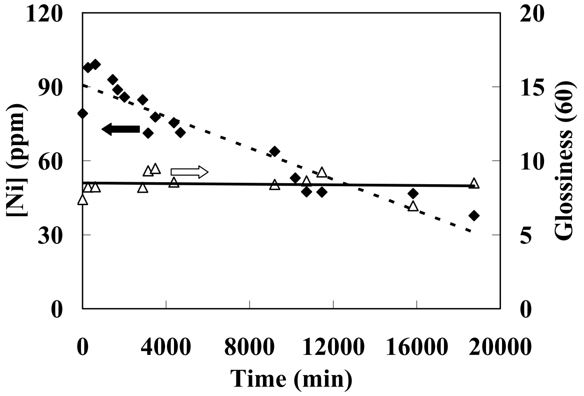


Fig. 16 Variation of gloss with nickel concentration in electroplating bath

4. Conclusions

1. Sulfuric acid solution and hydrochloric acid solution have a little effect on the improvement of surface appearance. But, the large increase of lightness and gloss was observed by the addition of hydrogen peroxide. From the microstructure observation, it was also shown that sharp edges of thin zinc plates were altered into a smooth layered structure.

2. Corrosion potential was shifted into the direction of positive potential and the dissolution of zinc electrodeposits was considerably accelerated by the addition of hydrogen peroxide.

3. It was shown that the lightness and gloss of organic composite coated samples were also largely increased even if zinc phosphate film and organic coating was performed on the polished surface. The black patina resistance of polished sample was slightly larger than that of no polished sample.
The result of salt spray test also showed that polished sample had a better corrosion resistance than no polished sample

4. Nickel ion in plating bath decreased the lightness of zinc coating layer but iron didn’t affect it. Gloss was not affected by the existence of nickel and iron in plating bath.

5. References

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