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The Effect of $Bi(OH)_3$ on Corrosion-Resistant Properties of Automotive Epoxy Primers

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In this study, we evaluated anti-corrosion properties of both commercial unleaded and lead epoxy primer for automotive substrate before applying to actual painting lines by salt spray test, and cyclic corrosion test, potentiodynamic test and electrochemical impedance spectroscopy. The difference in the corrosion resistance between automotive epoxy primers contained $Bi(OH)_3$ and leaded one was investigated. And it was also discussed the effect of zinc phosphate pretreatment to the epoxy primers. The specimen coated epoxy primer contained $Bi(OH)_3$ showed 0.5 V higher corrosion potential than that of bare steel. The result of salt spray test did not indicate remarkable difference of corrosion resistance in all specimens above 10 ㎛ thickness up to 1200 hours. In the cyclic corrosion test, epoxy primers contained $Bi(OH)_3$ on phosphated substrate performed good corrosion properties until 800 hours. The epoxy primer contained $Bi(OH)_3$ performed the equivalent corrosion resistance as leaded coating on phosphated steel, but slightly inferior to that of leaded on bare steel. These results show that the pre-treatment of zinc phosphate is effective as well as pigment changing in performing anti-corrosion properties in automotive bodies.

Keywords *: bismuth, lead, epoxy primers, electrochemical impedance spectroscopy, corrosion, salt spray test, cyclic corrosion test*

1. Introduction

Recently, two European directives very strongly influence surface technology in automobile production: the 'End of Life Vehicle-Direction'[1] does forbid from 2005 on the use of mercury, lead, cadmium and is limiting the content of hexavalent chromium compounds per car by 2g. Second, the 'Waste Electrical and Electronic Equipment amending Directive' also imposes a ban on lead from 2006.[2] But lead has been treated importantly in cataphoretic epoxy primers until up to recently, because it has performed deblocking agent of isocyantes, anti-corrosive pigment and protecting agent of steel facilities.[3] To overcome their regulations and problems, many researches and developments have not ended since the first lead free primers came out onto the market in the 1990s.[4)-6)] But as the unleaded epoxy primers which are only substituted pigments with lead were performed the insufficiency of anti-corrosion properties, commercial unleaded primers were also modified resins and additives to increase corrosion resistance of the coating systems by manufactures.[5]

In this study, we evaluated anti-corrosion properties of both commercial unleaded and lead epoxy primer for automotive substrate before applying to actual painting lines by salt spray test, and cyclic corrosion test, potentiodynamic test and electrochemical impedance spectroscopy.

2. Experimental Procedures

The anticorrosive epoxy primers were cationically deposited on cold roll steel plate. The conditions of substrate type, pretreatment condition, bath paint property, painting and coating thickness are summarized in Table 1. The test panels (70 ㎜×150 ㎜×0.8 ㎜) were pretreated by degreasing in basic solution, zinc phosphated in actual automobile painting line. One of coatings used lead as an anticorrosive pigment while the other was unleaded and $Bi(OH)_3$. Coated testing panel were manually scribed to 10cm length for SST and CCT.

Salt spray test was carried out in the salt spray test chamber for periods of 1200 hours and cyclic corrosion test was carried out for 400 hours and 800 hours by Fig. 1 conditions.

Photentiodynamic polarization has been carried out in 3.5% NaCl solution at R.T. without stirring. And all the potentials were referred to the saturated calomel electrode (SCE). And a.c. impedance spectroscopy was performed

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Table 1. Substrate, coating and painting conditions of the different samples tested

Sample ID	pretreatment	epoxy primers	thickness	bath paint property	painting condition
A	degreasing only (not zinc phosphated)	leaded	5, 10, 15, 20 25㎛	solid 20% pigments 20% (wt/wt)	Anode/cathode ratio 1 / 6 Painting temp. 28℃ Curing temp. 150℃×20min
B	degreasing only (not zinc phosphated)	unleaded			
C	zinc phosphated	leaded			
D	zinc phosphated	unleaded			

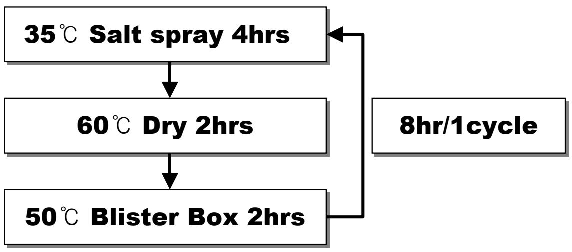


Fig. 1. The condition of cyclic corrosion test.

in 3.5% NaCl solution at 50℃ for 21days.

3. Results and discussion

The results of 1200 hours exposure tested panels by SST are presented in Fig. 2 Panels A and C are presented leaded epoxy primers type, and B and D are presented unleaded one. And A, B are coated on bare steel while C, D are coated on phosphated steel. Fig. 2 shows that leaded epoxy primers are superior to unleaded one at the 5 ㎛ thickness. But more than 10 ㎛ thickness, unleaded epoxy primers are on the same level with leaded one.

The results of 400 hours and 800 hours exposure tested panels by cyclic corrosion test(CCT, Fig. 1) are shown in Fig. 3 (a) is presented 400 hours exposure results, and (b) is presented 800 hours and A, C are leaded epoxy primers, and B, D are leaded one. Fig. 3 (a) shows that epoxy primers on bare panel have very severe blisters nearby scribed line, which are not concerned with thickness and type of coatings. Fig. 3 (b) shows on the same level between leaded and unleaded primers. It is affected that zinc phosphate protects substrate in the painting, and increases adhesion with coatings[7),8)] However, small blisters nearby scribed line are found more than 20 ㎛ thickness, that is more shown with increasing thickness. This shows

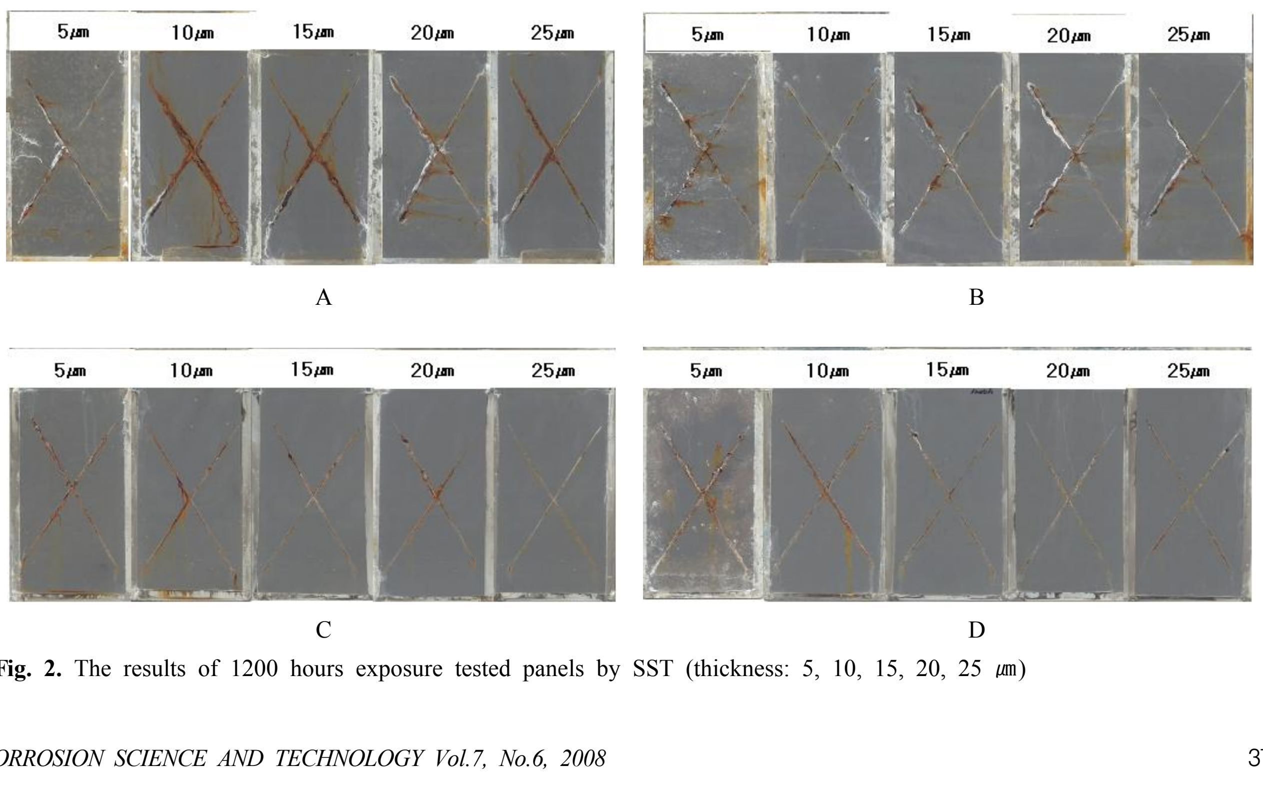
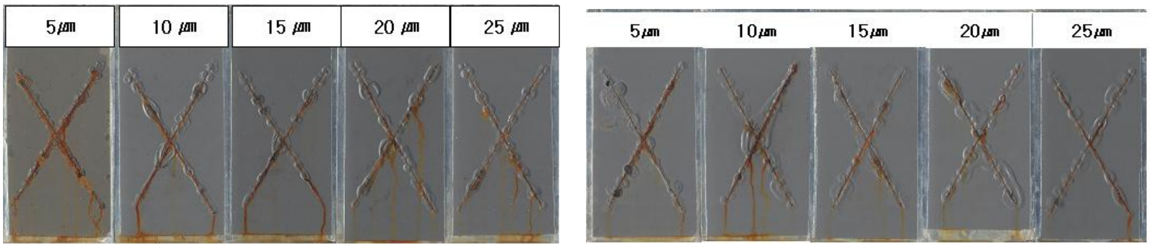
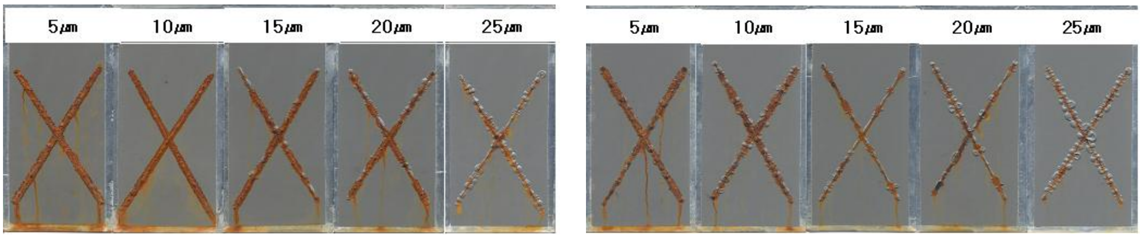


Fig. 2. The results of 1200 hours exposure tested panels by SST (thickness: 5, 10, 15, 20, 25 ㎛)



A B

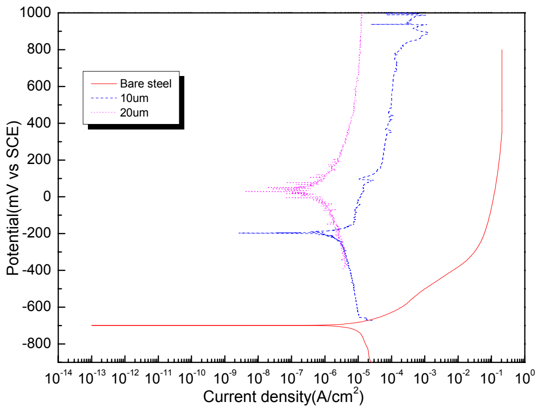
(a) The results of 400 hours (50cycle) exposure tested panels by CCT



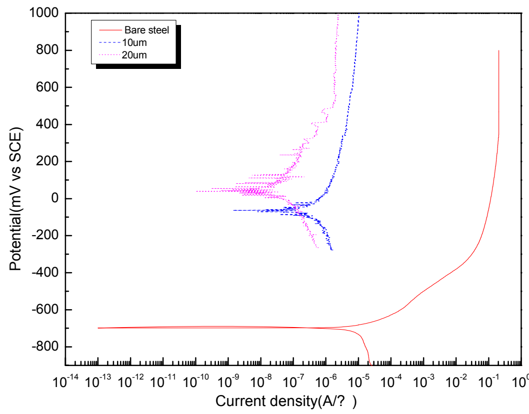
C D

(b) The results of 800 hours (100cycle) exposure tested panels by CCT

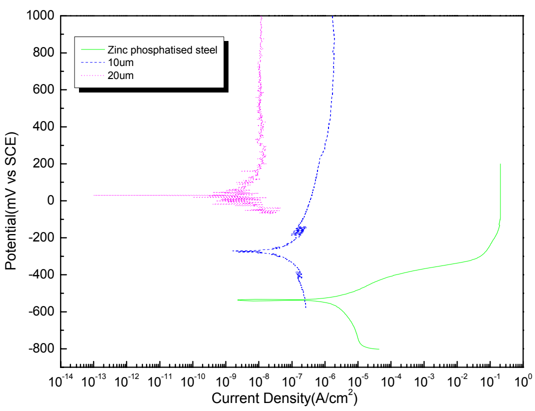
Fig. 3. The results of CCT exposure tested panels (thickness: 5, 10, 15, 20, 25 ㎛)



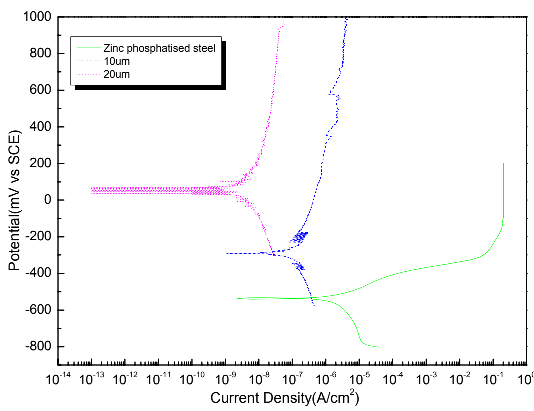
(a) Sample A (10, 20 µm)



(b) Sample B (10, 20 µm)



(c) Sample C (10, 20 µm)

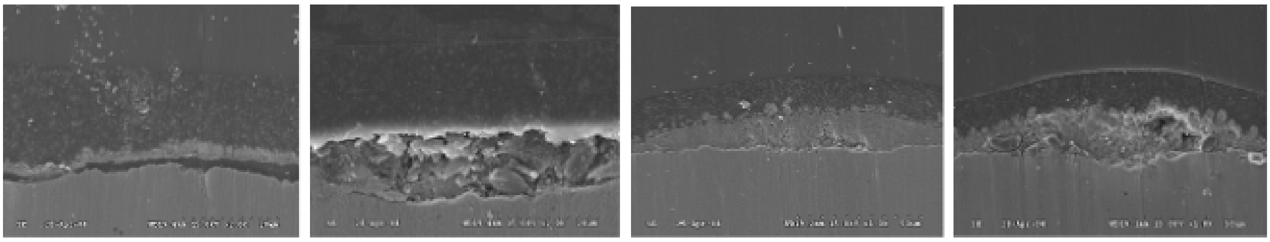


(d) Sample D (10, 20 µm)

Fig. 4. The results of potentiodynamic polarization with variable film thickness

Table 2. The electrochemical parameters derived from the potentiodynamic polarization curves

Sample (at 20㎛ build up)	E_{corr} (㎷)	i_{corr} (nA/㎠)	β_a (V/decade)	β_c (V/decade)	R_p (㏀ · ㎠)
Dgreasing only	-696.3	4,676	0.0575	0.2926	4
Zinc phosphated only	-535	1,990	0.0714	0.2926	13
A	-36.44	430	0.2159	0.2560	118
B	-47.76	56.2	0.4465	0.2639	1,283
C	30.79	2.2	0.1903	0.0851	11,429



A B C D

Fig. 5. The cross-sectional SEM images of different primer after 21days immersion at 50℃ with EIS performed.

that corrosion properties were not always improved by higher coating thickness that was affected by mechanical damages.

A summary of the electrochemical parameters derived from the potentiodynamic polarization curves (Fig. 4) are listed in Table 2 In Table 2, both of primer coated specimens were shifted about 500 mV- 600 mV to the positive direction relative to the uncoated specimen, which indicates that the corrosion property of the coated primers is better than that of uncoated one.

Fig. 5 show cross-sectional images of different primer after 21days immersion at 50℃ with EIS performed. All of primers exhibited corrosion product formation at primer-substrate interface.

Coated primes A,B on bare steel are shown deadhesion, but that of C, D on phosphated steel exhibited good adhesion at primer-substrate interface. It shows that the corrosion property of primers is more strongly affected by surface treatment than by pigment changes.

4. Conclusion

The anti-corrosion properties between leaded and unleaded epoxy primers for automobiles were investigated in this study. The specimen coated epoxy primer contained $Bi(OH)_3$ showed 0.5 V higher corrosion potential than that of bare steel. The result of salt spray test did not indicate remarkable difference of corrosion resistance in all specimens above 10 ㎛ thickness up to 1200 hours. In the cyclic corrosion test, epoxy primers contained $Bi(OH)_3$ on phosphated substrate performed good corrosion properties until 800 hours. The epoxy primer contained $Bi(OH)_3$ performed the equivalent corrosion resistance as leaded coating on phosphated steel, but slightly inferior to that of leaded on bare steel. In conclusion, unleaded epoxy coatings were slightly inferior to leaded one at less than 10 ㎛ thickness on the bare steel, but anti-corrosion resistance was same as level at more than 10 ㎛ on the zinc phosphated steel. And we confirmed that the pre-treatment of zinc phosphating is effective as well as pigment changing in performing anti-corrosion properties in automotive bodies.

Acknowledgement

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