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Effect of a mixed aqueous solution of HCl and $CaCl_2$ on adhesion of coating to evaporated indium layer

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Abstract

The effect of a mixed aqueous solution of HCl and $CaCl_2$ on the adhesion of a coating with an evaporated indium layer was evaluated. Peeling was observed between the evaporated indium layer and the clear-coat after dipping a coated panel in the mixed aqueous solution, and the coating films were seen to lose their metal gloss. Observation of the evaporated indium layer with scanning electron microscope (SEM) revealed various particle sizes of indium. A higher area ratio of indium particles in the indium layer led to faster peeling after dipping the coated panels in the mixed aqueous solution.

The effect of the cross-linking density of clear coating film on the peeling between the indium layer and the clear-coat was investigated. A clear coating film with a lower cross-linking density resulted in a shorter peeling time in the mixed aqueous solution.

It was considered that the peeling was caused by condensation of water in the spaces where indium was dissolved by penetration of the HCl from the HCl/$CaCl_2$ aqueous solution into the evaporated indium layer.

Keywords: Indium; Vacuum evaporation; Adhesion; Urethane coating; Viscoelasticity; Moisture permeability

1. Introduction

The performance of automotive coatings is affected by various chemical substances such as acid rain, bird droppings, sap, iron powder and inorganic salts. In a previous paper, we reported that: (1) peeling occurred in adhesion tests of coated films after washing the chrome-plating substrate with water containing inorganic salts[1,2]; (2) iron powder adhesion occurred under high temperature and humidity, adhering easily to a coating film with high moisture permeability[3]; (3) whitening of melamine-cured coating film occurred by addition of inorganic acid and a light stabilizer[4]; and (4) cracking of melamine-cured coating film was affected by the affinity of the 2-methylheptane to the melamine resin and also cracking of the coating film occurred in a shorter time when there was a higher affinity [5].

Recently, soft plastic substrates are used as parts for items such as radiator grilles for more stylish automobile design. Surface treatment with evaporated indium is performed on these substrates, as properties such as impact resistance are not obtained in surface treatment with rigid chromium plating and evaporated aluminum. However, indium coatings have poor acid resistance and thus are not suitable for automobiles in contact with acid rain or $CaCl_2$ snow-melt salts.

This paper reports on the effect of a mixed aqueous solution of HCl and $CaCl_2$ on the adhesion of coatings with an evaporated indium layer.

2. Experimental

2.1. Sample preparations

Indium was evaporated onto an acrylate-isocyanate cured primer, and an acrylate-isocyanate cured clear-coat was

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applied and cured. The primer and clear-coat had dry film thicknesses of 20 and 30 μm, respectively. Both the primer and the clear-coat were force dried for 60 min at 80 °C. The evaporation occurred under conditions of 0.1, 0.2 and 0.3 g of applied evaporated indium and at vacuum pressures of 1.33×10^{-1}, 1.33×10^{-2} and 1.33×10^{-3} Pa.

2.2. Dipping test in a mixed aqueous solution of HCl and $CaCl_2$

A mixed aqueous solution of HCl and $CaCl_2$ was prepared by mixing 30 mL of 12 N HCl and 55 g of $CaCl_2$ in 1000 mL of distilled water. Crosscut test pieces were dipped in the solution of HCl and $CaCl_2$ for 72, 168 and 240 h at 50 °C. Peeling was investigated after drying at room temperature. The peeling test was performed by pulling off tape adhered to the crosscut section, and the width of peeling indicated by the distance from the crosscut line.

2.3. Observation of evaporated indium layer

Indium was evaporated from 0.1, 0.2 and 0.3 g of indium and at vacuum pressures of 1.33×10^{-1}, 1.33×10^{-2} and 1.33×10^{-3} Pa. The surface and cross-section of the evaporated indium layers were observed using a Hitachi S-4000 scanning electron microscope. The samples were prepared by platinum sputter with a 15-kV accelerating voltage. The area ratio of indium particles on the evaporated indium layer was determined by portrait analysis of an SEM micrograph focused on the indium evaporation layer.

2.4. Cross-linking density of clear coating film

The free films, without the indium or primer layers, were prepared by peeling off the coating films after coating by drying forcedly at 80 °C for 60 min on tin foil. The dry free films were 50 μm thick. The viscoelasticity of the free films was measured using a Rheology DVE-V4 dynamic viscoelasticity automatic measurement apparatus. Cross-linking density was obtained from the equation, $E = 3nRT$ (E = Young's modulus, n = cross-linking density, R = gas constant, T = absolute temperature) [6–8].

2.5. Measurement of moisture permeability

A moisture permeability cup (JIS 0208 standardized) was kept for 0, 4, 8, 12 and 24 h under 50 °C and 50% relative humidity. The moisture permeability weight was measured and plotted against time. The moisture permeability was calculated using the slope of the best-fit line and a free film thickness of 30 μm.

2.6. Analysis of dissolution of indium layer

The solution of HCl and $CaCl_2$ was analyzed after the dipping test using an ICP Optical Emission Spectrometer.

3. Results and discussion

Adhesion testing of the coating evaporated was performed under various conditions after dipping in the HCl/$CaCl_2$ solution. Table 1 shows the conditions and results of the coating system with the evaporated indium layer. The results revealed that both peeling and loss of metal gloss occurred, and that the degree of peeling varied. A higher weight of indium applied via evaporation and a lower vacuum pressure resulted in a longer width of peeling from the crosscut section. The longest width of peeling occurred under conditions of 0.3 g applied indium and at 1.33×10^{-1} Pa vacuum pressure.

The evaporated indium layer on the primer was observed with SEM. The results of SEM observation are shown in Fig. 1a, b, d and e. It was found that various particle sizes of indium were deposited on the primer. Fig. 1c indicates that there were no particles but instead the indium had formed a film. A higher vacuum pressure led to smaller particle

Table 1
Results after dipping test in a mixed aqueous solution of HCl and $CaCl_2$[a]

Substrate	Primer		Indium evaporation conditions			Clear-coat		Width of peeling (mm)	Metal gloss[c]
	Paint	Film thickness (μm)	Weight (g)[b]	Vacuum pressure (Pa)	Film thickness (μm)	Paint	Film thickness (μm)		
Thermo-polyurethane	Polyurethane	20	0.1	1.33×10^{-1}	50	Polyurethane	30	0.9	Yes
				1.33×10^{-2}	30			0.3	Yes
				1.33×10^{-3}	40			0.3	Yes
			0.2	1.33×10^{-1}	100			7.0	Yes
				1.33×10^{-2}	70			0.3	Yes
				1.33×10^{-3}	70			0.3	Yes
			0.3	1.33×10^{-1}	90			30	Yes
				1.33×10^{-2}	100			0.3	Yes
				1.33×10^{-3}	100			0.3	Yes

[a] Test time was 168 h.
[b] Weight applied via evaporation.
[c] Yes: metal gloss was partially lost (confirmed by visual inspection).