

Adhesive Strength Improvement of Rapid Cure Paints

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Abstract

The advantages of catalyzed urethane paint systems include their paintability to substrates with high heat capacity, as well as those with cavities and other defects, and most importantly their ability to cure at low temperatures through the use of catalyst. However they have low adhesion, especially when they are exposed to water. To overcome this disadvantage, studies were made to improve the wet adhesion, by concentration polar groups onto metallic surfaces through the introduction of secondary hydroxyl groups to functional sites of the resin, for improved control of the reaction rate.

1. Introduction

In recent years, aluminum wheels have been increasingly used for design flexibility, as well as weight reduction. Cavities appears on the surfaces of aluminum wheels, because they are fabricated by machining aluminum castings. The holes cause formation of pinholes on the surfaces of baked paint films. We used the VIC (Vapor Injection Curing) system to try to prevent pinhole formation. Our results show the VIC system provides significant improvement in pinhole and edge covering powers and high-build capability, as well as good drying and handling performances leading to increased process rationalization.

However in the VIC technology, solvent volatilization is likely to cause strain induced stresses in the coating. This may have a detrimental effects on the adhesion in the water soak test. Surface treatment prior to coating also influences the wet adhesion of coated films.

Occasionally, less than optimal operating conditions may lead to insufficient chromate pretreatment of the substrate. We have found that even in these adverse conditions, urethane

paint which has the secondary hydroxyl group as the reactive part of the polyol component, enables the VIC system to give a good adhesion to the cured film.

2. Experiments

Two types of polyol resins were used. Either primary or secondary OH was introduced to the reactive radical of each resin. Studies were made of their adhesion, and curing reactions, as well as the strain-stresses and surface changes of the cured films.

2.1 Specimen

- 1) The reactive radical of acrylpolyol being primary OH introduced in polyol base resin.
- 2) The reactive radical of acrylpolyol being secondary OH introduced in polyol base resin.

2.2 Measurement of adhesion

Substrate: Aluminum die casting, AC 4CH

Pretreatment: Alkali degreasing/chromium chromate conversion coating. Substrates were subjected to pretreatment at conditions unfavorable for adhesion to give lower chromate coverage.

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Table 1 shows the surface composition of the specimen.

Painting method: VIC system (drying; 40°C x 20 min)

Film thickness: Primer/top coat 10/20 μm

Adhesion test: Crosshatch test; JIS K5400 8.5.2

Tensile peeling resistance; JIS K5400 8.7.

Wet adhesion test: After soak in de-ionized water for a specified time, a specimen, should exhibit no appearance damage and provide good secondary adhesion.

2.3 Reactivity

NCO agents are consumed in the urethane reaction. Therefore, the curing reaction rate of paint films can be determined by analysis of free NCO remaining.

•Titration method

The amount of isocyanate used as the curing agent in painted films can be determined by titration.

Titration: JIS, K7301 (1985)

Mixing ratio: NCO/OH=1/1

Amine=0.5 wt.% Tin catalyst=1.0 wt.%

•Rheological measurement (Orientech's DDV-OPA).

The curing reactivity was determined by use of a rigid pendulum type rheometer

Mixing ratio: Same as in titration method

2.4 Stress strain measurement

Aluminum foil was examined for changes in

shape due to stress after being painted and dried.

2.5 Substrate/Film analysis (Delaminated surface analysis)

The orientations of the polar groups on the substrate and film surfaces were analyzed XPS (X-ray Photoelectronics Spectroscopy).

3. Results

3.1 Adhesion

Crosshatch tests after water soaking indicated that primary OH induces delamination while secondary OH gives no detrimental results. Tensile peeling tests also show that secondary OH is superior to primary OH in both primary and secondary adhesion.

Introduction of secondary OH's into reactive sites of polyols clearly improves the adhesive strengths of coated films, as shown in Table 2.

3.2 Curing reactivity

•Secondary OH gives a slower rate of NCO reduction indicating a slower curing rate compared with primary OH (see Table 3).

•Viscoelastic property

Generally, with increased viscosity of a specimen, the attenuation rate of the pendulum motion increases but the period does not change. However, the period decreased in specimen with

Table 1 Surface composition of chromium chromate conversion coating by XPS.

pretreatment	surface composition at %							
	O	Al	C	Si	P	Cr	Na	F
unfavorable chromium chromate	30.9	8.1	50.3	6.4	1.4	0.9	1.3	0.7

Table 2 Paint adhesion

pretreatment	pretreatment	crosshatch test after water soak	adhesive strength	
			initial (kg/cm ²)	after water soak (kg/cm ²)
unfavorable chromium chromate	primary OH	poor	18.5	4.5
	secondary OH	good	27.5	>20.0

Table 3 Reduction of isocyanurate weight percent

composition	0 min.	20 min.	40 min.	60 min.	80 min.	100 min.
primary OH	100	69	45	31	22	17
secondary OH	100	83	68	55	48	41

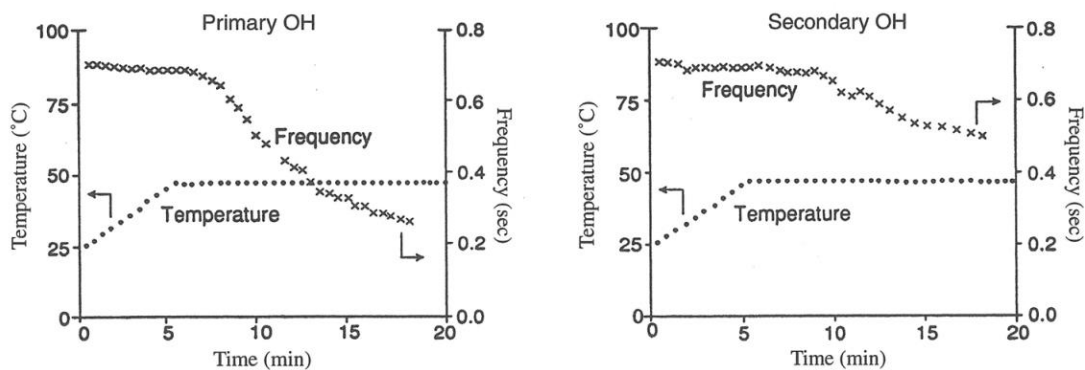


Fig. 1 Change in viscoelastic properties during curing

primary or secondary OH. This indicates the occurrence of curing reactions. With secondary OH, the period decreases at a slower rate, suggesting a slower curing speed. These results are shown in Fig. 1.

3.3 Stress strain property measurement

Primary OH induces inward (toward film side) deflection of painted films, while secondary OH induces no deflection. This suggests that the stress induced during film formation is significantly smaller when secondary OH is employed (see Fig. 2).

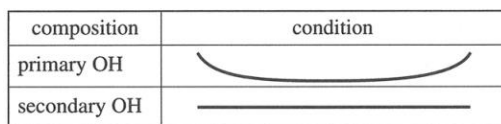


Fig. 2 Stress strain property

3.4 Analysis of delaminated surfaces (XPS)

According to XPS measurement, in both film and substrate delaminated surfaces, more polar groups such as C-O-C, C-OH, COO- and NH-COO components were determined in the case of secondary OH, compared with primary OH (see Table 4 and Fig. 3). This suggests that polar

Table 4 International composition of paint side determine by XPS

	primary OH		secondary OH	
	binding energy (eV)	Intensity ratio (%)	binding energy (eV)	Intensity ratio (%)
CH ₂	285.0	61.6	285.0	54.6
COC, COH	286.4	23.0	286.3	28.1
COO, NHCOO	287.6	15.4	287.5	17.3

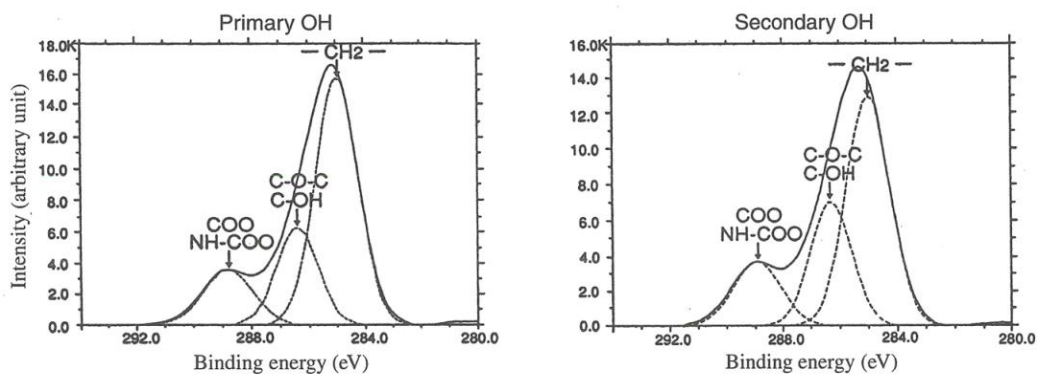


Fig. 3 C1s spectra of paint side interface after delamination.

groups and urethane bonding formed in the film are oriented toward the substrate.

4. Conclusions

In the VIC system, in which urethane paint is rapidly cured at low temperatures by use of catalysts, incorporation of secondary hydroxyls into the reactive sites of polyols used as the primer resin improves the adhesive strength, especially the wet adhesion, without sacrificing the advantageous rapid curability of the paint system.

The mechanism by which the adhesive strength is improved through the use of secondary hydroxyls was clarified. Stress measurement and delaminated surface analysis revealed that stress-induced strains are reduced and many polar groups are oriented towards the substrate. Slower curing rates provided sufficient time to allow polar groups to orient towards the substrate and develop a high degree of adhesive strength. Also, the stresses generated during the film formation are eased by the end of the curing, further leading to improved adhesive strength.