PROGRESS IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir

Prog. Color Colorants Coat. 7(2014), 139-145

Ministry of Science, Research and Technology
Institute for Color Science and Technology

Organic/Inorganic Hybrid as an Anticratering Agent in Cathodic Electrocoating

S. Seraj[1], Z. Ranjbar[2*] and A. Jannesari[3]

[1] M. Sc., Faculty of Surface Coatings and Novel Technologies, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran.

[2] Professor, (a) Center of Excellence for Color Science and Technology and (b) Department of Surface Coatings and Corrosion, Institute for Color Science and Technology(ICST), P.O. Box: 16765-654, Tehran, Iran.

[3] Assistant Professor, Department of Resins and Additives, Institute for Color Science and Technology(ICST), P.O. Box: 16765-654, Tehran, Iran.

ARTICLE INFO

Article history:
Received: 23-03-2013
Final Revised: 02-06-2013
Accepted: 10-06-2013
Available online: 10-06-2013

Keywords:
Cathodic electrocoating
Crater defect
Organic/inorganic hybrid
Anticrater agent
Glycidoxy propyl trimethoxy silane

ABSTRACT

Many surface defects may appear in electrophoretic coatings. One of the most important defects in automotive coatings is cratering. An improved aqueous electrocoating composition containing an anticrater additive which is a reaction product of silane component based on glycidoxy propyl trimethoxysilane and polyoxypropylene diamine. The synthesized compound is used to reduce crater numbers in the final electrocoated car bodies. Prepared samples were characterized using infrared spectroscopy and optical microscopy. The number of craters in the electrocoated sample was evaluated by GM9532p standard. The final anticrater-containing electrocoat produced coating with a smoother surface and fewer craters. Prog. Color Colorants Coat. 7(2014), 139-145. © Institute for Color Science and Technology.

1. Introduction

Cathodic electrocoatig is a common used technique for the application of primer in the automotive industry [1-3]. Many surface defects may appear in electrophoretic coatings. One of the most important defects in automotive coatings is cratering. Cratering is small crater shaped depressions [4,5]. Surface defects are caused by unwanted surface flow and developed due to the presence of surface tension gradients [6]. Cratering results from a contaminant with low surface tension which is on the substrate in the coating or is deposited on the wet film. In most cases, the source of crater is not recognizable. The craters are formed and electrocoats should be crater resistant. Craters are formed resulting in the presence of incompatible compounds in the coating. These compounds can be the oil contaminants which are remained on substrates due to improper treatment. In addition, after electrocoating of surface and before baking of the films, these incompatible compounds may be present in the air and can be deposited on the wet film accumulated in coating/air interface and cause crater. Some of the low surface tension contaminants dissolve in

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*Corresponding author: ranjbar@icrc.ac.ir the film, as a result of Marangoni effect [7, 8]. Flow occurs from the low surface tension parts to high surface tension parts of the film. However, evaporation of solvent causes an increase in viscosity which impedes flow leading to form crater [9-11]. Surface defects like cratering are caused by unwanted surface flow and developed due to the presence of surface tension gradient. Alternatively, surfactants may be added to reduce the interfacial tension between the incompatible component and the coating [6, 20, and 21].

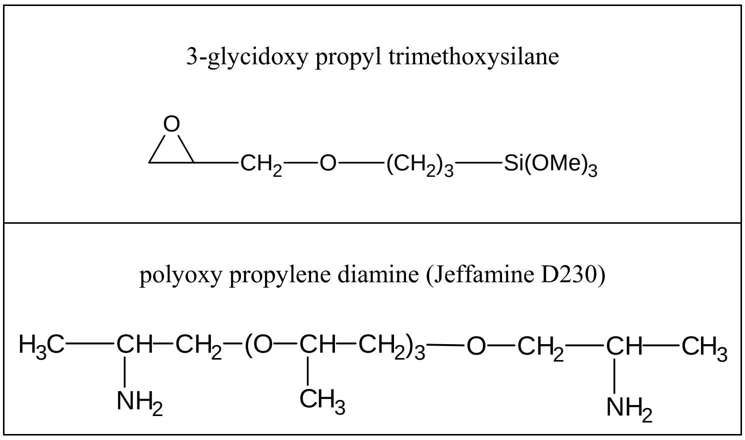
Anticratering agents can be oriented in various ways, they aggregate at various interfaces like coating/air and substrate/coating interfaces due to the hydrophobic effect. At the instant, a coating is electrodeposited on a substrate, the anticrater agent based silicone surfactants in the coating will begin to diffuse to and absorb at the newly created coating/substrate interface and at the coating/air interface. It takes a finite time for the interfacial tension at these interfaces to reduce. By reducing the surface tension, wettability of the contaminant by coating will be improved. As a result, surface tension gradient will not be created and cratering is prevented [6, 15, 16].

According to Schwartz and coworkers studies, crater resistance of an electrocoating improves by using surface active agent which reduces the interfacial tension and prevent surface tension gradient [6]. Allisa Gum and coworkers synthesized an anticrater agent based on silicone compound and used it in electrocoating bath to reduce the number of craters. They concluded that the synthesized additive acts as surfactant which is adsorbed at the coating/air and coating/substrate interfaces and reduces the surface tension and the number of craters [20]. Troy and coworkers synthesized the anticrater agent. Synthesized compound acts as a surfactant and reduces surface tension. The final electrocoat contains anticrater agent produces coating having a smoother appearance with fewer craters [21].

In the present work, glycidoxy propyl trimethoxysilane-polyoxy propylene diamine has been prepared as an anticratering agent for cathodic electrocoating.

2. Experimental

Glycidoxy propyl trimethoxysilane (Glymo, Merck), acetic acid (Merck) and polyoxypropylene diamine (Aldrich) were used as raw materials. Cathodic electrocoating (BASF Co.,Germany, Cathogaurd 500). The oil used for crater resistance test (according to GM9532p standard) was supplied by Digital equipment corporation, USA. It was oil based lubricant with code number 9981831. Chemical structure of ingredients is illustrated in Figure 1.



$$H_3C-\underset{NH_2}{CH}-CH_2-(O-\underset{CH_3}{CH}-CH_2)_3-O-CH_2-\underset{NH_2}{CH}-CH_3$$

Figure 1: Chemical structure of the raw materials.

Glycidoxy propyl trimethoxysilane and polyoxy propylene diamine were mixed in weight ratio of 2:1 at 59°C for 2 hours. Under these conditions, glycidoxy propyl trimethoxysilane was reacted with polyoxy propylene diamine to form the glycidoxy propyl trimethoxysilane-polyoxy propylene diamine adduct containing tertiary amine groups. The product was neutralized by acetic acid to stabilize cathodically depositable dispersion in deionized water. Electrocoating bath was prepared according to the following formula:

- Pigment to resin ratio: 0.16
- Resin solids: 40%
- Pigment paste: 67.5%
- Paint baths solid: 15%

The electrocoating bath was stirred for 24 hours under stirring, and then filtered by appropriate filter. A certain amount of greasy oil and synthesized anticrater was added to all baths except for reference bath (Synthesized additive and oil contents are shown in Table 3. Subsequently, normal steel substrate was sanded by suitable sandpaper and cleaned by isopropyl alcohol before cathodic process. The temperature bath was maintained at 28˚C. The normal steel panel was connected to the cathode and the stainless steel anode of the DC power supply and placed 5.5 cm apart, and then voltage of 190 V was regulated. After 2 minutes, cathode was removed from the bath and washed with DI water. Samples have been baked for 20 minutes at 162±2 ˚C. The films thickness was measured by the Elcometer thickness gauge (UK). The thickness of different parts of the film was measured and then the average thickness of the film without anticrater and with anticrater was calculated.

3. Results and discussion

Figure 2 shows the reaction between epoxide ring of glycidoxy propyl trimethoxysilane and amine groups of polyoxy propylene diamine.

Table 1: Variation of absorption peak intensity (normalised on $-CH_2$ peak intensity)

Sample code	(C-O) group in oxiran ring ($907 cm^{-1}$)	Secondary amine ($1625 cm^{-1}$)	(C-N) group ($1100 cm^{-1}$)	OH group ($3420 cm^{-1}$)
G	0.96	-	-	-
P	-	-	1.06	-
GP	0.79	0.49	1.94	0.84

Figure 2: Reaction between glycidoxy propyl trimethoxysilane and polyoxy propylene diamine.

Infrared spectra (Figure 3) showed that the glycidoxy propyl trimethoxysilane-polyoxy propylene diamine network structure has been formed. The reaction between epoxide ring of glycidoxy propyl trimethoxysilane and amino group of polyoxypropylene diamine has been confirmed by the disappearance of epoxy bond at 907 cm^{-1} and the appearance of hydroxyl bond at 3420 cm^{-1}. Variation of the adsorption peak intensity of the functional groups is shown in Table 1.

The intensity reduction of absorption peak of epoxide ring and the intensity increase of absorption peak of hydroxyl group and (C-N) bond confirm the ring opening reaction of epoxy and secondary amine compound. The absorption peak appeared at 1625 cm^{-1} confirms the presence of secondary amine groups.

Particle size distribution of the synthesized additive was evaluated by optical microscopy (Figure 4).

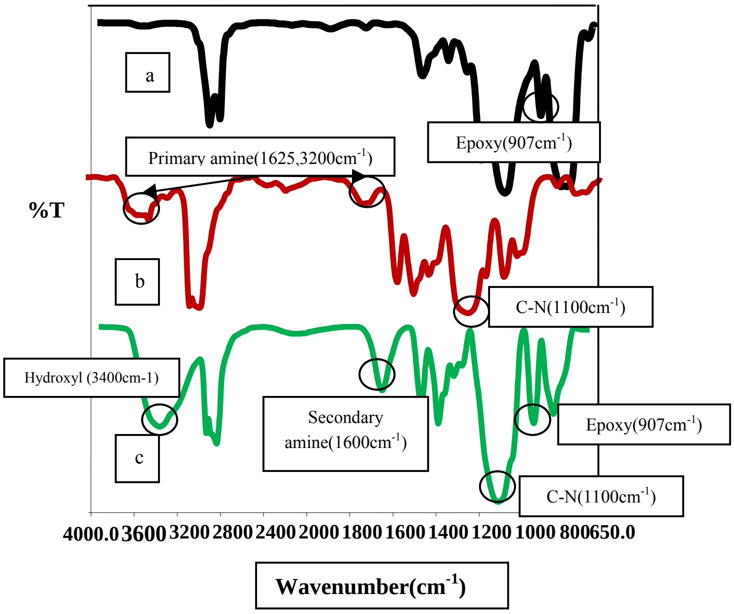


Figure 3: Infrared spectra of Glymo (a), polyoxy propylene diamine (b) and glycidoxy propyl trimethoxysilane-polyoxypropylene diamine after 2 hr(c).

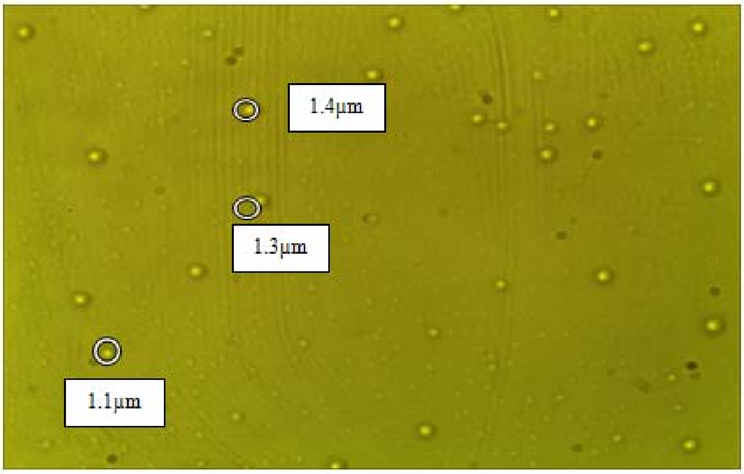


Figure 4: Particle size distribution of glycidoxy propyl trimethoxysilane-polyoxy propylene diamine(400x).

The particles were dispersed in water. Results manifest that particles have an uniform distribution and the average particle size was equal to 1.25 µm.

Crater resistance of samples was evaluated according to GM9532p standard. This standard belongs to General motor Corp (Crater resistance test for sheet metal forming lubricants). This standard describes a method for evaluating the crater resistance properties of sheet metal forming lubricants on electrocoating primers (ELPO). The greasy oil in this study acts as a contamination which is adsorbed on the substrate or in the bath and prevents the electrocoating from wetting the substrateand forming the crater. Crater resistance of the prepared additive in electrocoating dispersion has been evaluated. For this purpose, 5 baths were prepared containing varying amounts of prepared additive. A certain amount of oil contaminant (0.04wt %) was added to all baths except for the reference bath according to GM9532p standard. After electrocoating process and curing, the number of craters on the cathode surface was counted. According to the GM9532p standard test method, electrocoatings containing various amounts of additive were ranked with respect to lowest to highest crater level (Table 3). The number of craters is reduced in the presence of the prepared organic-inorganic additive in 0.2-0.6 wt%. The results are shown in Table 3.

Table 2: Ranking based on the number of crater according to GM9532p.

Rating scale	
10 = NO CRATERS	5 = 16-25 CRATERS
9 = 1-2 CRATERS	4 = 16-50 CRATERS
8 = 3-5 CRATERS	3 = 51-75 CRATERS
7 = 6-10 CRATERS	2 = 76-100 CRATERS
6 = 11-15 CRATERS	1 = 100+ CRATERS

Table 3: Crater counts on panels containing different amounts of the synthesized additive.

Sample code	A(weight% of bath volume)	B(weight% of bath volume)(4)	Crater number	Grades[22]
1	0	0	2	9
2	0	0.04	55	3
3	0.2	0.04	31	4
4	0.4	0.04	4	8
5	0.6	0.04	3	8

*A: Anticratering agent concentration

*B: Oil concentration

*Crater resistance was rated according to rating scale of 1-10 where 10 illustrares no craters on the panel.

During the cathodic electrocoating process, anticratering additive based on surfactants may reduce the interfacial tension between the incompatible component (oil contaminant) and polymer binder, thus the ability of the electrocoating for wetting the incompatible component (oil contaminant) increases. Prepared anticrater agent may adsorb to the air/coating and coating/substrate interface due to having hydrophobic groups and surface activity. Hydrophobic parts of compound (methyl group) are oriented to the non-polar air molecules or incompatible compound which is on the substrate (Si-O bond due to high flexibility and bond angle speeds the orientation of non-polar molecules in air). Hydrophilic parts of the compound (neautralized amine groups with acetic acid and ethylene oxide groups) are oriented. By adsorption of the surfactant (anticrater additive) in the interface of an aqueous dispersion, hydrogen bonds between polar molecules reduce. As a result, surface tension decreases and the wettability of the contamination by electrocoating may enhance, therefore surface tension gradients are prevented and the number of craters is reduced. The performance of a surfactant (anticrater additive) is typically tracked by plotting surface tension versus log of bulk concentration of the surfactant. Surface tension versus concentration curve for the surfactant based on glycidoxy propyl trimethoxy silane-polyoxy propylene diamine is shown in Figure 8.

As it is clear from Figure 8, surface tension decreases by increasing the concentration of surfactant. The break point in this curve typically represents critical micelle concentration (CMC). It appears at approximately 0.5wt% of anticrater agent; it shows a micelle agglomoration form. According to the calculations made for 0.1 to 0.5 wt% (for instance 0.4wt%), the prepared additive concentration should be below the CMC point. when the surfactant is added above the CMC point, no further reduction occurs in surface tension because it is not in the monomeric form which is surface active. So when the prepared additive is under the CMC point; can adsorb contaminants. As a result, surface tension gradients of coating film and incompatible component are reduced and wettability of the coating film increased, so the number of craters in the final electrocoat reduced. Above CMC point (for instance 0.6 wt%) it is expected that the additive is not surface active and it is in micelle agglomoration form. At this value, the concentration of the prepared surfactant (anticrater additive) at the coating/air interface has been saturated. As a result, the prepared additive at this value can not reduce the number of craters significantly [6, 19-21].

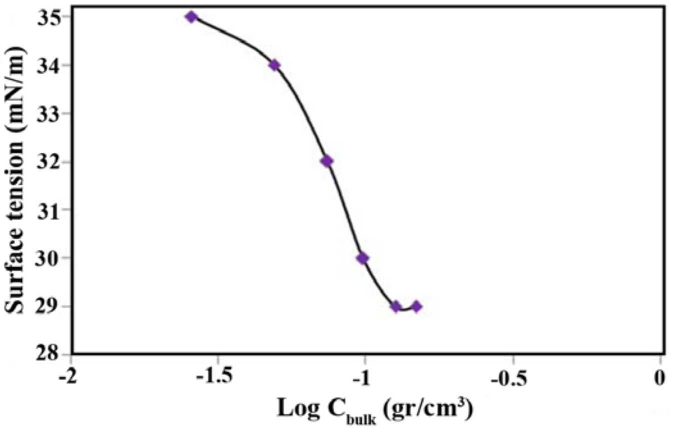


Figure 5: Surface tension versus concentration curve for the surfactant based on glycidoxy propyl trimethoxysilane-polyoxy propylene diamine.

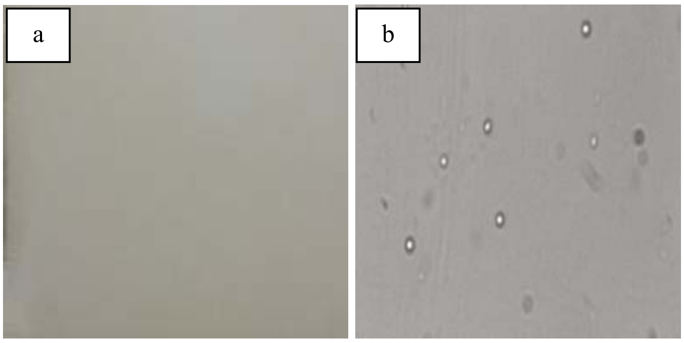


Figure 6: Image of a sample (a) without and (b) with crater.

To understand the advantageous effect of the anticrater agent, the image of a sample with and without craters is shown in Figure 6.

4. Conclusion

Glycidoxy propyl trimethoxysilane-polyoxy propylene diamine was synthesized as an anticratering agent for cathodic electrocoating. Electrocoating bath with different additive concentrations were utilized to investigate the optimum concentration of silane based additive on decreasing the crater number in electrocoating films. Results showed that in amounts less than 0.5 wt% (CMC point), surfactants are in monomeric state so the surfactant does not agglomerate and remains active. In these values, the maximum reduction in the number of craters was observed.

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