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Effect of technology of aminated epoxy acrylic cationic resin on properties of eletrodeposition

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Abstract: Using diethanolamine as aminating agent and glacial acetic acid as neutralizing agent, aminated epoxy acrylic cationic resin was prepared. The effect of technology of aminated epoxy acrylic resin on properties of eletrodeposition was studied by conductivity meter and electrophoresis apparatus. It was shown that, conductivity firstly decreased, and then increased with aminating temperature increase. In contrast with putting polyacrylic resin into thin acetic acid solution, the more compact film could be achieved by neutralizing polyacylic resin with glacial acetic acid and then add it into water. When neutralizing temperature was enhanced, the speed of electrodepsidon was found to increase, and the film was also more compact. Increasing the DN leads to enhanced conductivity and smaller particle size. When DN equaled to 80%, the smoothest film could be achieved.

Key words: acrylic cationic resin; glycidyl methyacrylate; conductivity; cathodic eletrodeposition coatings

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0 Introduction

Electrophoretic finishing is a new type of technology, derived from 1960s. Electrocoating is a process where by the migration of electrically charged particles under the action of an electrical potential difference between a conducting object to be coated and a counter electrode takes place[1]. Electropainting easily forms a uniform film as compared with the conventional coating techniques. Because the deposited film possesses high resistance, the electropainting shows high throwing power which is the ability to deposit a uniform film on a complex-shaped surface. This system has been widely used in industries due to such advantages, such as car body, badge or glasses frame.

Basic resins for cathodic electropainting includes epoxy resins[2], acrylic resins[3], polybutadiene resins[4] and polyurethane resins[5]. Epoxy resins have excellent corrosion resistance, durability and adhesive power, but have very poor weather resistance. Therefore, epoxy resins are only used as primer. Although transparent acrylic resins have good weather resistance and finishing, thin films are unfavorable for corrosion protection. Epoxy acrylic resins can be achieved by copolymerizing acrylic monomers with epoxy functional group. This type of cathodic electropainting possesses excellent properties in weather and corrosion resistance, which reached the aim of the bottom and top combined electrophoretic finishing. In this paper, the effect of technology of aminated epoxy acrylic resin on performances of cathodic eletrodeposition coatings will be dicussed.

1 Experimental

1.1 Materials

methyl methacrylate, butyl acrylate, 2-hydroxyethyl methacrylate, glycidyl methyacrylate and

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Biography: Zhou Xin-hua (1974-), male, doctoral candidate, mainly research on fine chemical engineer.

curing agent are all of commercial product. Benzoyl peroxide, diethanolamine, and acetic acid are of C. R. Grade.

1.2 Synthesis of aminated epoxy acrylic cationic resins

Aminated epoxy acrylic cationic resins were prepared using the reaction scheme as show in figure 1. A 500 mL flask equipped with a condenser and mechanical stirring was filled with solvent and heated. Epoxy acrylic solvents were prepared by solvent polymerization under monomer-starved conditions at reflux temperature. Monomer solutions containing methyl methacrylate, butyl acrylate, 2-hydroxyethyl methacrylate, benzoyl peroxide were introduced into the reaction flask at a constant rate over three hours. Stirring was continued for 2 hours and tertiary amine was added. The reaction mixture was maintained for two hours, then glacial acetic acid and curing agent were added under intensive stir condition. A transpatent solution with 60 *wt*% solids content was produced.

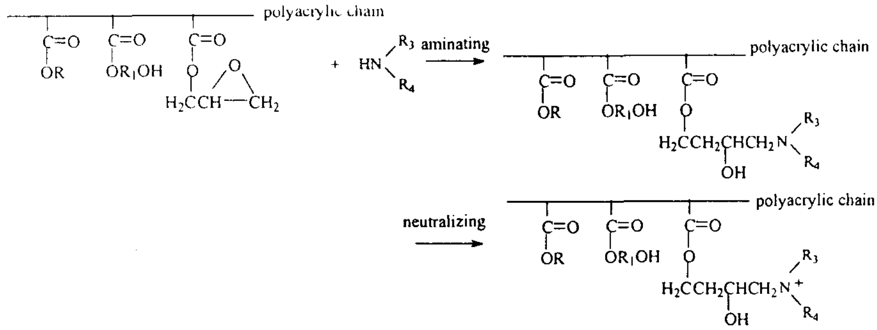

Fig. 1 Reaction scheme for the preparation of aminated epoxy acrylic cationic resins

1.3 Electrodeposition

The prepared aminated epoxy acrylic cationic resins were applied to the substrates by a cathodic eletrodeposition technique. The deposition was accomplished by the aid of a direct current at a bath temperature of 30℃. The cathode to anode ratio was 1 : 1, the solid content being 12%. The separation distance between the cathode and the anode was 5 cm and a magnetic stirrer stirred the bath continuously. A steel panel(the cathode) was immersed into the electrodeposition cell having the above mentioned bath composition. After connecting the electrodes, the time 120 s and voltage 20 V were set and then applied.

2 Rresults and discussion

There is a complex process for preparing aminated epoxy acrylic cationic resins and too many factors affects properties of electrophoretic solution. The effect of reactive conditions of diferent stage on conductivity and current density was discussed in this paper.

2.1 Aminating temperature

Aminating was referred as secondary amine reacting with epoxy on the side chain of polyacrylic resin. This reaction generated hydroxy used for cross-linking group and tertiary amine providing hydrophilic group. The results indicates that water solubility of cationic acrylic resin are very bad if aminating temperature is under 40℃. There is much white floccule in electrophoretic solution when acrylic resin is dispersed in water. When n (epoxy) : n (secondary amine) = 1 : 1, aminating temperature-conductivity curves are shown in Fig. 2. Fig. 2 illustrates conductivity first decrease, and then increase with aminating temperature increase at different neutralize degree. As the temperature is raised to about 90℃, conductivity gets its lowest value. Low conductivity can be explained as complete aminating reaction which decreases electrolyte strength of small molecule. Therefore aminating temperature at 90℃ will be suitable.

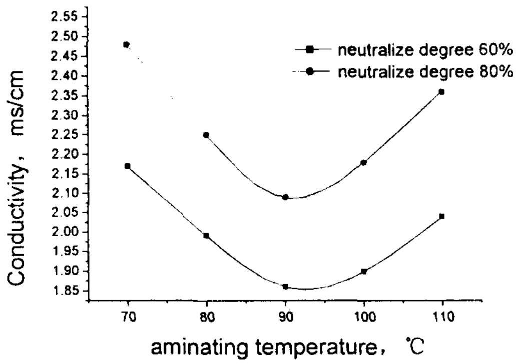

Fig. 2 Plots of the neutralizing temperature vs. conducticvity

2.2 Neutralizing technology

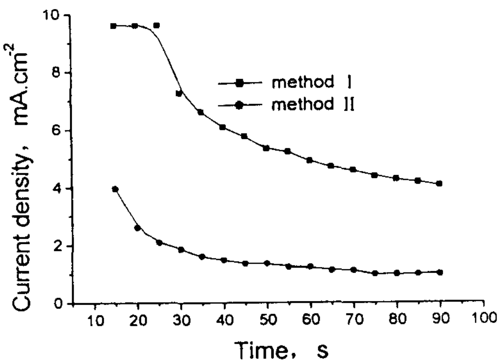

Fig. 3 Time dependence of current density using different neutralizing technology

Glacial acetic acid is used to neutralize tertiary amine on polyacrylic chain which provides required water solubility. There are two ways of adding acetic acid: putting polyacrylic resin into thin acetic acid solution (method Ⅰ) or neutralizing polyacrylic resin with glacial acetic acid and then add it into water (method Ⅱ). We examine the conductivity of these two neutralizing teclnology. The conductivity of method Ⅰ is 2.160 ms $\cdot$ cm^{-1}. While conductivity of method Ⅱ is 1.972 ms $\cdot$ cm^{-1}. Fig. 6. illustrated that there is a long induction time before current density begins to decrease sharply in method Ⅰ. While in method Ⅱ, current density decreases slowly after decreased sharply from beginning to 40 s. Due to insulating film depositing on surface, increase of resistance decreases current density. At the end of electrophoresis, current density of method Ⅱ is lower than that of method Ⅰ which also illustrates that method Ⅱ has more compact film and higher throwing power. Therefore, method Ⅱ is more suitable for neutralizing stage.

2.3 Neutralizing temperature

Amine belongs to easily coloured group. When neutralizng temperature is too high, tertiary amine is oxidated which results in the resin becoming into deep color. While neutralizing temperature is too low, high viscosity polyacrylic resin is hard to be neutralized by acetic acid completely. These unreacted acetic acid will be disadvantage to electrodepostion and corrosion resistance of the resin. The results of conductivity showed that the conductivity of neutralizing temperature of 50 ℃, 70 ℃ and 90 ℃ was 1.791 ms $\cdot$ cm^{-1}, 1.854 ms $\cdot$ cm^{-1} and 1.870 ms $\cdot$ cm^{-1}. By increasing neutralizing temperature, the ionic sites on the surface of the particles will increase which resulted in decreasing the probability of the ionic sites being present within the bulk of the particles. As Fig. 4 showed, the electrodeposition at higher neutralizing temperature showed a lower current density, as the film becomes more insulating. Higher the nertralizing temperature is , more rapidly the current density decreased. When the neutralizing temperature being at 100℃ above, the color of polyacrylic resin will become deep yellow.

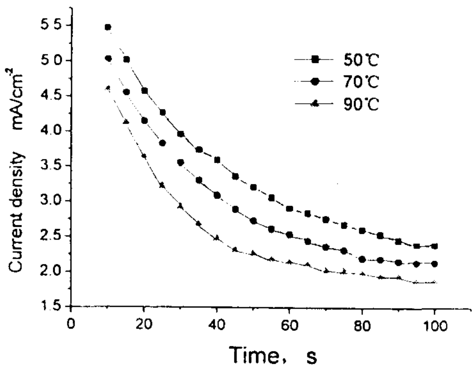

Fig. 4 Time dependence of current density at different neutralizing temperature

2.4 Degree of neutralization(DN)

Tab. 1 and Fig. 5 show the effect of DN on properties of bath solution and film. The neutralizing acid distributes itself between the dispersed and the aqueous phases and since the pH values are obtained only for the aqueous groups retain the largest part of the neutralizing acid and so it is present in the dispersed phase. The more the DN the lower the pH, which demonstrates that there is more free acid present in the aqueous phase. Increasing the DN results in a higher ionic strength per unit area and unit weight of the resin leading to enhanced conductivity. At the same time , the decrease in the DN will give rise to an increase in particle size which leads to lower hydrophilictiy. Fig. 5 illustrates the increase and then decrease in film thickness with increasing DN. This effect can be attributed to the difference of conductivity and particles. When DN is less than 70%, the poor hydrophilicity results in the larger particle size which make the deposited film coalescence poorly. While DN is greater than 90%, there are some addititonal free hydrogen ions in the bath, which increase the conductivity even further and decrease the velocity of particle deposition. Therefore, DN euqals to 80% which is suitable for this electropainting.

Tab. 1 The effect of pH on properties of bath solution and film

DN/%	110	100	90	80	70	60
pH	4.3	5.0	5.3	5.5	5.8	6.0
particle size/nm	87.3	102.5	116.0	127.3	138.7	155.3
conductivity/ms · cm^{-1}	1.125	1.065	1.027	0.982	0.873	0.726
film appearance	shrinkage void	orange peel	good	very good	orange peel	stacking

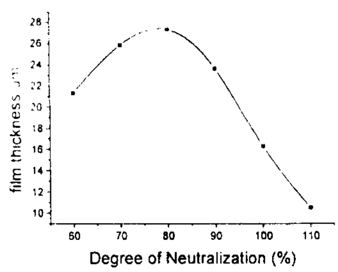

Fig. 5 The effect of DN on film thickness

3 Conclusions

Conductivity first decreases, and then increases with aminating temperature increase. There is the lowest conductivity value at 90℃.

Contrast two kinds of neutralizing technology, that is, putting polyacrylic resin into acetic acid solution(method Ⅰ) and neutralizing polyacrylic resin with acetic acid, and then add it into water (method Ⅱ). While there is a longer induction time in method Ⅰ, method Ⅱ has more compact film and higher throwing power.

Conductivity increases with increaseing aminating temperature. The electrodeposition at higher neutralizing temperature showed a lower current density.

The more the DN, the lower the pH, which demonstrates that there is more free acid present in the aqueous phase. Increasing the DN leads to enhanced conductivity. When DN equals to 80%, the smoothest film can be achieved.

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胺化环氧丙烯酸阳离子树脂合成工艺对电沉积性的影响

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摘要:以二乙醇胺为胺化剂、冰醋酸为中和剂，合成了胺化环氧丙烯酸阳离子树脂. 采用电泳仪和电导率仪，研究了胺化环氧丙烯酸树脂合成工艺对阴极电泳涂料电沉积性的影响. 结果表明，随着胺化温度的增加，电泳液电导率先下降后上升. 将冰醋酸加入树脂中中和，后用水稀释，比树脂在醋酸稀溶液中中和，电沉积性能更好. 电沉积速率随着中和温度的上升而增加，电沉积膜致密性相应增加. 中和度(DN)愈高，电泳液电导率愈大，粒径越小，而涂膜外观在中和度为 80%时达到最佳.

关键词:丙烯酸阳离子树脂;甲基丙烯酸缩水甘油酯;电导率;阴极电沉积涂料

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