



## MINI REVIEW

### Pathways of Decreasing Cured Temperature of Cathodic Electrodeposition Coating

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Cathodic electrodeposition (CED) coating has been developed a new type of industrial application of anti-corrosion coating. It has many merits such as little environmental pollution, no fire hazard, excellent corrosion resistance, high throwing power and degree of automation for coating. However, the curing conditions for conventional cathodic electrodeposition coating are that the cathodic electrodeposition coating is cured with the high temperature. The high temperature for curing is not helpful for the auto parts with plastic and rubber, which is easy to deform under such high temperature. Thus, the high temperature for curing is not beneficial to save energy. Therefore, it is essential to develop a novel cathodic electrodeposition coating, which is cured with low temperature. The pathways of decreasing the cured temperature of cathodic electrodeposition coating are reviewed. Furthermore, the practical questions to be solved to promote the development of cathodic electrodeposition coating with low cured temperature are pointed out.

**Keywords:** Cathodic electrodeposition coating, Resin, Cross-linking agent, Cured catalyst.

## INTRODUCTION

Cathodic electrodeposition (CED) coating has been developed a new type of industrial application of anti-corrosion coating from the mid 1970s. It has many merits such as little environmental pollution, no fire hazard, excellent corrosion resistance, high throwing power and degree of automation for coating. Thus, it is widely used in automobiles, light industry, agricultural machinery, household appliances, instruments, crafts, building materials and so on<sup>1</sup>.

Cathodic electrodeposition coating is often composed of the water-soluble cationic resin, pigments and material, solvent and neutralizer, which is made by grinding<sup>2</sup>. Usually, the blocked isocyanate is used as the curing and cross-linking agent in the conventional cathodic electrodeposition coating<sup>3-5</sup>. Furthermore, a certain amount of heavy metal salt is added as the catalyst of curing<sup>6,7</sup>. In this case, the curing conditions for conventional cathodic electrodeposition coating are that the cathodic electrodeposition coating is baked for 20-30 min with the high temperature of 170-180 °C. The high temperature for curing is not helpful for the auto parts with plastic and rubber, which is easy to deform under such high temperature. Of course, the high temperature for curing is not beneficial to save energy. Therefore, it is essential to develop a novel cathodic electrodeposition (CED) coating, which is cured with low

temperature<sup>8</sup>. At present, the novel cathodic electrodeposition coating, which is cured at the temperature of 150 °C, has been produced<sup>9-11</sup>.

From the view of curing mechanism, there are three pathways to decrease the curing temperature. Firstly, the polyfunctional curing agent is introduced. Secondly, the special sealer, which is decomposed under the low temperature, is developed. Thirdly, the low-temperature decomposition of urethane is developed<sup>12</sup>. In this paper, pathways of decreasing cured temperature of cathodic electrodeposition coating are reviewed. Furthermore, the practical questions to be solved to promote the development of cathodic electrodeposition coating with low cured temperature are pointed out.

### Pathways of decreasing cured temperature of cathodic electrodeposition coating

**Combination of different sealers:** The commonly used sealers such as  $\epsilon$ -caprolactam, methyl ethyl ketone oxime, diethyl malonate and 3,5-dimethyl-pyrazole, are de-blocked with low temperature. However, stability of cathodic electrodeposition coating and the surface smoothness of formed film can not be guaranteed when the de-blocked temperature is decreased and the reaction activity is improved further. Thus, it is difficult to guarantee the overall performances of cathodic electrodeposition coating when the sealer is used singly. The

combination of two different blocking agents can bring good performances of cathodic electrodeposition coating. Zhang *et al.*<sup>13</sup> prepared the cathodic electrodeposition coating which is cured with low temperature when the toluene diisocyanate (TDI) was blocked *via* combined use of ethylene glycol monomethyl ether and methyl ethyl ketone oxime. The good performance of the resultant film can be obtained *via* combination of these two different sealers. In their work, it was found that the de-blocked temperature is high and the surface of film is smooth when the ethylene glycol monomethyl ether is used singly. And the de-blocked temperature is low and the film is not uniform and accumulated partially when the methyl ethyl ketone oxime is used singly. Yang *et al.*<sup>14</sup> prepared the prepolymer which the de-blocked temperature is 140 °C and the de-blocked time is 20 min when the toluene diisocyanate is blocked by the combination of ethylene glycol monobutyl and caprolactam. The properties of the resultant film are good. Wu *et al.*<sup>15</sup> prepared the cationic epoxy resin which was cured at the temperature of 150 °C when the toluene diisocyanate was blocked with the combined sealer of ethylene glycol monobutyl ether and ethylene glycol monoethyl ether as a blocking agent. Wang *et al.*<sup>16</sup> synthesized the blocked toluene diisocyanate which was cured at the temperature of 140 °C when the toluene diisocyanate was semi-blocked with triethanolamine then blocked with *n*-butanol and 3,5-dimethyl-pyrrole, respectively. The blocked toluene diisocyanate was neutralized with the acetic acid. And the water-dispersible cationic cross-linking agent was obtained to improve the dispersion stability of cathodic electrodeposition coating. In addition, this blocked toluene diisocyanate was used as the curing agent in the fluorinated acrylate resin to prepare the cathodic electrodeposition coating. The average particle diameter of cathodic electrodeposition coating was 140-150 nm and the distribution of molecular weight of resin was narrow. The resultant cathodic electrodeposition coating can be cured at the low temperature of 130 °C<sup>17</sup>.

**Modification of resin:** The other pathway of decreasing the curing temperature is the modification of resin. The resin was modified by introducing the self-crosslinking group with high reaction activity into the molecular of resin. The commonly used self-crossing monomers were N-methylol acrylamide and hydroxylated acrylate. The methylol in the molecular of self-crossing monomer had high reaction activity, which can react with the epoxy resin under the condition of heating. Thus, the cured temperature of cathodic electrodeposition coating can be decreased. It was reported that the resin can be obtained when the mixed monomers of acrylate, hydroxymethyl acrylamide, hydroxypropyl acrylate, styrene and methyl methacrylate were copolymerized. The resultant resin had good water solubility and may be cured at a lower temperature<sup>3</sup> of 120 °C. Li *et al.*<sup>18</sup> introduced N-methylol acrylamide and acrylate monomers into the modified epoxy resin *via* grafting copolymerization. The resultant epoxy resin can be cured at the lower temperature of 130 °C. Wang *et al.*<sup>19</sup> prepared the modified epoxy resin *via* grafting when the mixed monomers of styrene and acrylate monomers and functional monomer of glycidyl methacrylate and the cross-linking monomer of diacetone acrylamide were used. In their work, the cathodic electrodeposition coating, which was cured at the lower temperature,

was prepared successfully when the cross-linking reaction was taken between the adipic dihydrazide and the ketone carbonyl group in the system and a small amount of blocked isocyanate was added. In addition, the novel resin, which was de-blocked at the lower temperature, was chosen to be the binder of cathodic electrodeposition coating. In this way, the cured temperature of cathodic electrodeposition coating can also be decreased. Kumar *et al.*<sup>20</sup> prepared the cathodic electrodeposition coating when the self-crosslinking water-soluble phenolic epoxy phenolic resin was used as the binder. Furthermore, any additional cross-linking agents were not added. The resultant cathodic electrodeposition coating can be cured at the lower temperature of 80 °C.

**Cross-linking agent:** The other important way to decreasing the cured temperature of cathodic electrodeposition coating was the modification of the cross-linking agents. Usually, the cross-linking agents were isocyanates. There are commonly two categories. One category was aromatics, such as toluene diisocyanate, diphenylmethane diisocyanate (MDI) and so on. Such cross-linking agents tended to have lower de-blocked temperature. However, it was easy to turn yellow for cathodic electrodeposition coating because of the presence of benzene ring. The other category was aliphatic, such as hexamethylene isocyanate (HDI). The film of cathodic electrodeposition coating was uniform when such a cross-linking agent was used. But the de-blocked temperature was high. In addition, there are also aromatic esters such as xylylene diisocyanate (XDI)<sup>21</sup>. The film was not easy to get yellow and the overall performance of the film was good and the de-blocked temperature was low when such a cross-linking agent was used. However, the price of such a cross-linking agent was high. Wang *et al.*<sup>22</sup> studied the influence of three different cross-linking agents of xylylene diisocyanate, hexamethylene isocyanate and on performance of cathodic electrodeposition coating. In the view of the de-blocked temperature, the de-blocked temperatures of hexamethylene isocyanate, xylylene diisocyanate and toluene diisocyanate were 150, 140 and 125 °C, respectively. From the overall view of de-blocked temperature, the appearance of the coating and emulsion stability, xylylene diisocyanate was an ideal cross-linking agent for cathodic electrodeposition coating. Liu *et al.*<sup>23</sup> adopted a method of a mixed cross-linking agent, *i.e.* the mixture of an aromatic isocyanate and an aliphatic isocyanate was used to achieve the low cured temperature. In this method, the overall performance of cathodic electrodeposition coating was good. He *et al.*<sup>24</sup> synthesized an isocyanate-terminated prepolymer when polyethylene glycol, isophorone diisocyanate and dimethylol propionic acid were used as raw materials. Then the prepolymer was fully blocked by N-methyl-diethanolamine and hydrophilic dimethylol-propionic acid was added to improve self-emulsifying ability. This resultant blocked macromolecular cross-linking agent was used as the cured agent at low temperature for the epoxy cathodic electrodeposition coating. Chu<sup>25</sup> used the epoxy amine adduct as the main resin. Then the melamine formaldehyde resin was chosen to be the cross-linking agent and a certain amount of metal catalyst was added. In this way, the cured temperature of cathodic electrodeposition coating may be at below 150 °C. Chung *et al.*<sup>26</sup> used a new type of cross-linking agent to cure cathodic electrodeposition coating. This new type

of cross-linking agent was tetramethylxylylene diisocyanate (TMXDI), which reacted with trimethylol propane. Then the oxime was used as the sealer. The cured temperature of cathodic electrodeposition coating can be decreased to 120-135 °C. TMXDI is the variety of xylylene diisocyanate, which two hydrogen atoms on the methylene in xylylene diisocyanate were replaced by a methyl group to form TMXDI. From the chemical structure, although it had an aromatic ring, the group of NCO group was away from the benzene ring. The electron cloud of benzene ring had little influence on the group of NCO<sup>27</sup>. Thus, the resistance to aging and UV light was improved and not easy to turn yellow.

**New type of catalyst for curing:** The de-blocked temperature of isocyanate and the cured temperature of cathodic electrodeposition coating can be decreased suitably when an appropriate amount of catalyst was added in the cathodic electrodeposition coating. The commonly used catalysts were amine catalysts, organometallic catalysts and composite catalyst<sup>28</sup>. The cured temperature of cathodic electrodeposition coating can be decreased 10-20 °C when high efficient catalyst was used. Miao and Wang<sup>29</sup> found that the cured temperature of cathodic electrodeposition coating can be dropped from 155 to 135 °C when the bismuth catalyst was used. Fang *et al.*<sup>30</sup> also found that the cured temperature of cathodic electrodeposition coating can be decreased when the catalyst of dibutyltin dilaurate was used. However, the conventional cured catalysts had a negative effect on environment. Thus, Zhong *et al.*<sup>31</sup> used alternative metal catalysts to replace the traditional catalyst. The result was satisfactory.

## Conclusion

In comparison with the conventional cathodic electrodeposition coating, the cathodic electrodeposition coating with low cured temperature has the following merits. It is suitable for finishing the auto parts with plastic and rubber, which is not to deform under such low temperature. Of course, the low temperature for curing is beneficial to save energy. However, cathodic electrodeposition coating with low cured temperature will be developed quickly when the following three practical questions to be solved:

- (1) Low-temperature dissociative of isocyanate is controlled suitably.
- (2) Low temperature curing and stability of cathodic electrodeposition coating is combined moderately.
- (3) Low temperature curing and smoothness of coating surface is combined fully. Only in this way, the performance of cathodic electrodeposition coating with low cured temperature can be guaranteed.

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