Article ID: 1003 - 6326(1999)03 - 0510 - 04

Composite hydrophilic coating for conditioner aluminum fins①

Gan Weiping(甘卫平), Ji Dongying(吉冬英), Pang Xin(庞 欣)
Department of Materials Science and Engineering
Central South University of Technology, Changsha 410083, P. R. China

Abstract: To solve the so-called "white rust" and 'water bridge" problems of the aluminum fins for heat exchanger of automobile air conditioner, aimed at nationalizing the art of hydrophilic coating technology, the choice of coating forming and curing materials was investigated. By measuring the water contact angle, SEM surface scanning and ingredients analysis of the coating, optimal parameters and composition are acquired. The coating forming mechanisms of the composition was also expatiated. The coating obtained has good hydrophilic and other properties.

Key words: aircondition equipment; aluminum fins; hydrophilicity; coatings **Document code**: A

1 INTRODUCTION

Aluminum alloys have become the first-choice materials for making heat exchanger with its good properties, at present 95 % automobiles made in Japan use aluminum heat exchangers[1]. Since the outside environment is very severe, the natural oxide on the untreated aluminum fin surface will gradually become powdered under the alternative effect of the sunshine, rain, acid dew, dust and produce the so-called "white rust", contaminating the environment; and the surface temperature of the condenser is below the dew point of air when working, the water drops collected on the fins will present in the form of semicircle and even form "water bridge" between the narrow spacings, thus blocking the smooth flow of the air, reducing the heat exchanger surface, increasing noise and energy consumption and shortening the use time[2,3].

Ever since the 1970, with the spacing of the fins getting smaller and smaller, the "white rust" and "water bridge" phenomena became more and more obvious. How to solve this problem has been an emergent project in the last two decades of the contury.

An effective way to do this is to improve the wettability of the fin surface by hydrophilic-coating. Thus treated aluminum fins can effectively solve the above mentioned problems and bring considerable economical benefits. There are organic, inorganic and composite hydrophilic coating methods, and each has its good and bad points, but with the high anticorrosive property of the organic materials and the good hydrophilic property of inorganic materials, composite coating has the best performance. At present Japan stands in advance in this field with patent technology[8~12].

But the research has just begun in China, several imported coating-lines is waiting this art to be nationalized. With this object, the paper select the composite method, decide the composition proportion, optimize the technical parameters and discuss the curing mechanisms.

2 EXPERIMENTAL METHODS

2.1 Anticorrosive underlayer treatment

Immersing the washed 1050 aluminum sheet in a solution, containing Cr^{3+} 1.8 g/L, Cr^{6+} 1.5 g/L, F^- 0.4 g/L, PO_4^{3-} 5.0 g/L for 1 ~ 3 min, then drying in hot air at 40 ~ 60 ℃ to

① Received Sept.17, 1998; accepted Jan.6, 1999

gain the phosphate-chromate anticorrosive coating.

2.2 Composite sclection

Almost all the polymer organic compounds used in related patents and other documents, have been considered, and the acrylic resins was chosen for its wide-use, excellent coat forming ability and availability. 100% water soluble acrylic ester polymer and its cross-linking agent poly-amino resin, self-made in our laboratory, were also selected. Besides the compound of zinc, zirconium, the inorganic coating materials mainly used is water glass, the cheap, widely used, well-adherent sodium water glass was chosen, but sodium water glass can not form good coating itself and needs hardener[4]. Because of the strict demands for the coat forming ability, excellent hardener must be used here. Therefore this paper focused on the choice of suitable hardeners to improve the coat forming ability and other properties.

2.3 Property tests

By measuring the water contact angle, SEM surface scanning and ingredient analysis, the property and quality of the coatings obtained were compared and analyzed. The optimal parameters were also selected on the basis.

3 EXPERIMENTAL RESULTS AND ANALYSIS

3.1 Organic hardener glyoxal

Mixing the acrylic, amino resin, water glass and glyoxal proportionally to make 5% water solution, using the orthogonal method to find the optimal value of the immersing time, hardening time and temperature, the best coating surface quality was obtained by immersing the chromated sheet 6 min in the solution then drying it 10 min at 160 ℃. But all the samples were brittle and appeared white colour to some degree, which means glyoxal can not help sodium water glass to form good coating. and the ingredients analysis also showed that the silicon content on the surface was below 1%, indicating water glass just took little part in the coat forming. This is because coating of industrial water glass is poor in anti-water ability and needs modification by other materials[13,14]. Zinc oxide is a very common one to do it.

3.2 Inorganic hardener ZnO

The dissociation equations of sodium water glass are

$$Na_2SiO_3 + 3H_2O \rightarrow Si(OH)_4 + 2Na^+ + 2OH^- \quad (1)$$

$$Si(OH)_4 + 2OH^- \rightarrow Si(OH)_6^{2-} \quad (2)$$

ZnO is amphoteric oxide and can dissolve in NaOH easily, $Zn(OH)_4^{2-}$ is formed after it is mixed with Na_2SiO_3, pH is decreased and silicone acid is deposited.

$$ZnO + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-} \quad (3)$$

The existence of Eqn.(3) makes the reaction develop toward the direction of Eqn.(1). during the dehydration process, $Si(OH)_4$ particles come close to each other, the hydrated layer disappear gradually, and the Si-OH group on the surface of colloid particles closing each other will condense, a three dimensional web-form structure with —Si—O—Si—O— as the main chain is thus formed. But if too much water is lost and the volume decrease is too large, the coating will crack easily. Polymer compounds can disperse to the gap of the structure, the acrylic resin in the composite just had this property.

Mixing the water glass and ZnO proportionally and diluted them by water. After sticking it in 80 ℃ for 7 h, the transparent part is used with acrylic and amino resins to coat the aluminum sheets, after drying, the thickness of the coating is different and the contact angle is small in the thick part and big in the thin part. Ingredient analysis is made on the different parts, the results showed that the quality of the coating is still not good enough.

3.3 Inorganic hardener aluminum tripolyphosphate

According to documents, aluminum tripolyphosphate is a good hardener of water glass. but it is very difficult to make. The aluminum tripolyphosphate used is self-made in the laboratory, but the particle is not small enough

because of the limited condition. After mixing the acrylic, amino resins, water glass proportionally, 0, 0.5, 1.0, 1.5, 2.0 g/L aluminum tripolyphosphates were added to the above mixture respectively and samples 1#, 2#, 3#, 4#, 5#, were defined and tested with the results as Tables 1, 2.

Table 1 Average contact angle with water

Sample No.	Contact angle/(°)
1#	24
2#	21
3#	17
4#	15
5#	10

Table 2 Silicon content of 5#

Element content	Mass fraction, %	Mole fraction, %
Na	0.68	0.81
Al	91.55	92.71
Si	3.26	3.17
P	2.65	2.34
Cr	1.86	0.98

Because silicon is brittle in itself, the silicon content should not be high, 3% silicon of 5# is moderate, aluminum sheet treated like 5# showed good anticorrosive, anti-heating properties, the water contact angle was 10° in general.

4 COAT FORMING MECHANISMS

4.1 Aluminum tripolyphosphate hardening mechanism

In aluminum tripolyphosphate, phosphate groups stands in the center of the tetrahedron structures which are like silicon acid group tetrahedron structures. The structures next to each other lose water and co-use the oxygen, and the result is: all the tetrahedrons are connected in the forms of web or chain structure. But the co-oxygen direction of the two groups are different, the silicon group has four directions and will lead to the crack of the coating while the phosphate group has only three directions with the web in a surface. This property of phosphate is very important, the insert of P-O structure limits the development of Si-O structure, thus controlling the powdery of the coating, therefore the improvement of aluminum tripolyphosphate to water glass coating is without doubt.

The existence of multi-valenced cations also has effect on the coating and Al^{3+} is the most effective one because of the coordination between O^{2-} and Al^{3+}. The insert of Al-O to the chains of SI-O, P-O changes the property of them. And the entrance of Al^{3+} into octahedron, cross-links the chains and hasten the hardening.

But when aluminum tripolyphosphate is used alone, the operation is difficult to control, the coating is not ideal, if aluminum tripolyphosphate and transition metal oxides are used together, the curing effects will be better. The co-use of such materials can be the direction to further improve the coat forming ability and stability of the sodium water glass.

4.2 Curing mechanisms of organic composition

The transition of the coating material from liquid to the amorphous solid state on the coated subject is called the curing process of the coating, which is mainly done by the evaporation of the solvent, the physic and chemical changes such as condensation and polycondensation. The mechanisms are different with the composition.

In this experiment, the curing process is achieved by the reaction of the active groups in the resins. Because of the connection of the groups (—OH, COOH— etc), an insoluble web structure is formed thus providing good coating performance. The equations of the cross-linking reaction are as follows:

$$—N—CH_2OR + R'—OH \longrightarrow —N—CH_2OR' + ROH \quad (1)$$

$$—N—CH_2OR + R'—COOH \longrightarrow —N—CH_2OCR' + ROH \quad (2)$$

At the beginning of the cross-linking process, the reaction is mainly co-condensation, with the increase of the temperature, the velocity of the self-condensation increases with reaction like the following:

$$—N—CH_2OCH_3 + —N—CH_2OCH_3 \longrightarrow —N—CH_2—N— + CH_3OCH_2OCH \quad (3)$$

From above, it is obvious that the hydrophilic coating is a highly-connected web structure by the process of co-condensation and self-condensation.

4.3 Effect of the acrylic resin

Fig.1 is the obverse of the phosphate-chromate coating (~ 3 μm), which shows the concave-convex submicroscopic structure. Such structure can adhere resins with good flowing and permeating properties and obtain excellent

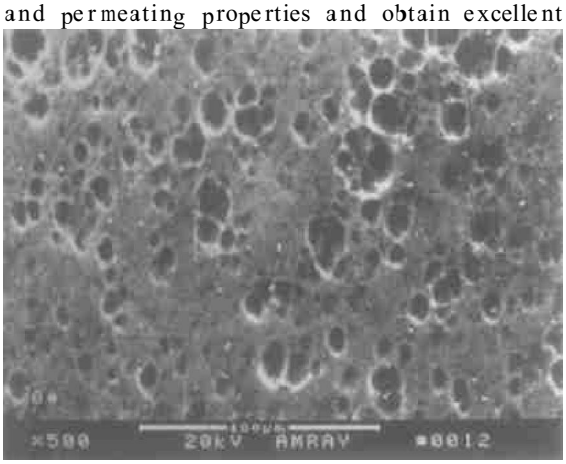

Fig.1 P-Cr coating obverse

adherent interface performance, and guarantee the strong bond between the chromate and the upper layer. Fig.2 is the microscopic side face of the composite coating which shows that the organic resins has dispersed equally to the spacing of SI—O—SI—O— chains; the addition of the organic materials not only help to improve the poor anti-water property of the water glass, but also improve the surface quality of the coating, strengthen the connection of the chains and decrease the brittleness and increase the hardness and plasticity of the coating. Thus greatly improve the anticorrosive ability of it.

5 CONCLUSIONS

(1) In the composite coating containing both acrylic resin and water glass of coating, the surface quality and the performance of the coating are both poor if glycol is used alone as the water glass hardener.

(2) The coat forming ability of the water

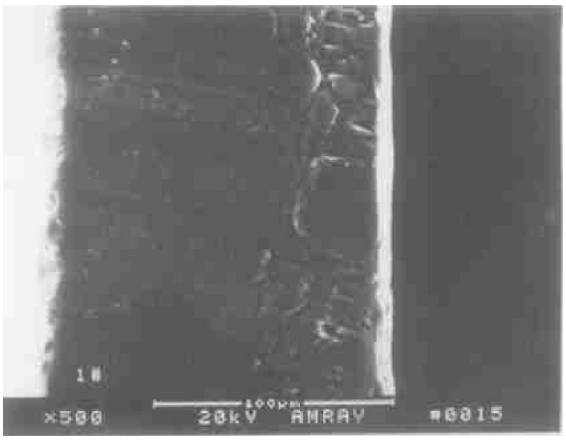

Fig.2 Side face of composite coating

glass was improved obviously after it was improved by ZnO.

(3) The comprehensive performance of the composite hydrophilic coating improved greatly when aluminum tripolyphosphate is used as the water glass hardener.

(4) The use of polymer compound greatly improved the anticorrosive ability and the strength and plasticity of the coating.

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(Edited by Zhu Zhongguo)