

METHOD FOR SURFACE TREATMENT OF POLYACETAL RESINS

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The present invention relates to a method for the surface treatment of polyacetal resins. More particularly, the invention relates to a surface treatment method which is preferably adopted as the pre-treatment of polyacetal resins to be carried out prior to plating.

Polyacetal resins have excellent thermal, mechanical and chemical properties. At the present time, however, since they are relatively expensive, they are mainly used as engineering resins for the manufacture of functional parts.

Looking to the future from the point of view of the raw materials for resins, it is expected that polyacetal resins formed by using methanol as the starting material will become one of the cheapest resins.

Therefore, it is expected that polyacetal resins will be applied even in those fields where ABS resins and the like are now applied, such as, for example, the manufacture of shaped articles decorated by plating and coating. In this field, however, the surface inactivity which is a merit of a polyacetal resin in the conventional uses becomes a defect. Therefore, the surface treatment of polyacetal resins is an important technical problem. By the term "surface treatment" is meant treatment which renders the surface hydrophilic so that plating or coating becomes possible.

It is said that polyacetal resins can be surface activated by etching with a chromic acid mixture, phosphoric acid, sulfonic acid or the like. However, although the surface is roughened by carrying out the etching according to such a conventional method, complete activation is impossible.

We carried out research on the relationship between changes of the surface by etching of a shaped article of a polyacetal resin and the kinds of treating agents, and to our great surprise, it was found that
5 when a polyacetal resin is treated with a liquid mixture of hydrochloric acid and sulfuric acid good activation can be attained although use of each acid singly does not result in good activation, even with a thin depth of etching of less than several μm .

10 According to the present invention therefore, a method is provided for the surface treatment of a polyacetal resin characterised in that the resin is treated with an acidic solution containing chloride ions and sulfate ions.

15 A polyacetal resin shaped article etched according to the method of the present invention can be plated by the same steps as those adopted for the plating of ABS resins. The plated article obtained has a high adhesion comparable to that of a plated ABS resin
20 article and a heat resistance superior to that of a plated ABS resin article. Furthermore, the treated article can be surface-decorated and bonded, for example by coating, vacuum deposition or sputtering.

We have also carried out research on the composition
25 of the polyacetal resin to be treated, and have found that a polyacetal resin containing calcium carbonate is especially preferred. By the use of this polyacetal resin, the effects of the present invention can be further enhanced.

30 More specifically, in accordance with the present invention, there is provided a method for the surface treatment of polyacetal resins, which comprises treating a shaped article of a polyacetal resin, preferably a polyacetal resin containing calcium carbonate, with an
35 acidic solution containing chloride ions and sulfate ions.

In one embodiment of the present invention, a shaped article is prepared from a polyacetal resin according to a customary procedure, and the treatment of the present invention then carried out, preferably
5 after annealing and degreasing. The treatment is ordinarily accomplished by dipping a shaped article of a polyacetal resin for a predetermined time in an acid solution of sulfuric acid containing chloride ions. For example, in the case of a liquid mixture of 1 part
10 by volume of concentrated hydrochloric acid, 1 part by volume of concentrated sulfuric acid and 2 parts by volume of water (about 8.6% by weight of HCl plus about 35.3% by weight of H_2SO_4), the treatment is accomplished within 5 to 30 minutes at 25°C. The article treated
15 according to the invention is subjected to neutralization and washing with water. It is then conveniently plated in the same was as in the case of ABS resin, that is by sensitization treatment, the activation treatment, the catalyst treatment including the sensitization treatment
20 and the activation treatment in combination, the non-electrolytic plating treatment and the electric plating.

The polyacetal resin for use in the present invention may be, for example, a homopolymer, a copolymer or a modified acetal. Especially when a
25 polyacetal resin contains calcium carbonate, the treated surface is appropriately rough and highly active, and therefore, the plating adhesion is remarkably high. The effect of improving the plating adhesion by calcium carbonate is highest when the content is 3% to 5%, and
30 if the content is higher than this level, a good adhesion can be obtained stably. The addition of calcium carbonate results not only in stabilizing the plating adhesion but also improves the rigidity and reduces the dimensional change in the shaped article.
35 A filler such as, for example, powder glass, silica,

talc or pumice exerts similar effects. However, such filler involves a risk of reducing the surface gloss of the plated article. The calcium carbonate to be used in the present invention can be light calcium carbonate, chalk or heavy calcium carbonate. Fine particulate products smaller than heavy calcium carbonates have a reduced action of degrading the gloss, but coarser particles are preferred from the viewpoint of the plating adhesion. Accordingly, when the surface gloss is important, it is preferred that the amount of calcium carbonate added be up to 10%, and when the rigidity and reduction of the dimensional change are important, it is preferred that the amount of the filler added be 10% to 60%.

The treating solution that is used in the present invention is ordinarily prepared from hydrochloric acid and sulfuric acid. However, the method of incorporation of chloride ions and sulfate ions is not limited to mixing of the acids per se. For example, salts such as for example calcium chloride, sodium chloride and sodium sulfate may be added to an acidic solution to supply all or part of the necessary ions.

When such salts are used for formation of the acidic treating solution or when the treatment of a polyacetal resin containing calcium carbonate is repeated, it sometimes happens that precipitates are formed in the solution. In order to smooth the surface of the treated article, it is preferred that these precipitates be removed by filtration.

According to the surface-activating treatment of the present invention, the surface layer is etched preferably to a depth of 0.5 to 50 μm , more preferably 1 to 20 μm . A similar etching effect can be attained by the treatment using sulfuric acid or hydrochloric acid alone, but then the degree of activation is insufficient. It is considered that since the shaped

article is simultaneously subjected to both the action of hydrochloric acid, having a relatively low etching activity but a high permeability, and the action of sulfuric acid, having a strong etching activity but a low permeability, the surface layer of the treated article is appropriately decomposed to form an active layer. However, the scope of the present invention is not limited by this conjecture. In general the conditions of treatment according to the invention depend on the composition of the treating liquid, the temperature and time of treatment and on any plating process subsequent to treatment. When the temperature and time of treatment are appropriately adjusted, the composition of the treating solution that is used for the treatment of the present invention can be changed within a broad range. For example, when the treatment temperature is 0°C to 70°C., the treatment time is up to 1 hour and the solution is prepared from commercially available hydrochloric acid and sulfuric acid, it is preferred that the hydrogen ion concentration in the solution be 0.6 to 1.5 equivalents per 100 g $[0.02 \times \text{H}_2\text{SO}_4 \text{ (wt.\%)} + 0.027 \text{ HCl (wt.\%)}]$, especially 0.8u to 1.3 equivalents per 100 g, the hydrogen chloride/sulfuric acid weight ratio be from 1/20 to 20/1, especially from 1/10 to 1/1 and that the concentration of hydrogen chloride in the hydrochloric acid used be up to 30% and this hydrochloric acid be mixed with concentrated sulfuric acid (the especially preferred hydrogen chloride concentration being 7% to 25%). A solution having the intended composition may of course be prepared by mixing concentrated hydrochloric acid and concentrated sulfuric acid with water. The above-mentioned concentration range is not particularly critical, but this concentration range may be broadened if the treatment temperature is higher or lower than the above-mentioned temperature or the treatment time is shorter or longer. Phosphoric acid

ions, sulfonic acid ions, boric acid ions, other halogen ions, halogenic acid ions, nitric acid ions, silico-fluoric acid, borofluoric acid, organic acids such as for example formic acid, and organic materials such as for example surface active agents may be incorporated, so far as the effects of the present invention are not reduced.

The present invention will now be described with reference to the following Examples and Comparative Examples.

Comparative Example 1

A plate having a side of 5 cm and a thickness of 3 mm was prepared from a polyacetal resin (Duracon M90 manufactured by Polyplastics Kabushiki Kaisha) by injection moulding. The shaped article was annealed at 140°C. for 1 hour and degreased with methylene chloride.

The degreased shaped article was treated at room temperature (25°C) for 20 minutes with a liquid mixture comprising 1 part by volume of concentrated sulfuric acid and 1 part by volume of water, and was neutralized with a solution of sodium hydroxide, washed with water and treated at 25°C. for 3 minutes with Catalyst manufactured by Kizai Kabushiki Kaisha (1 part by volume of a catalyst, 1 part by volume of concentrated hydrochloric acid and 5 parts by volume of water) and at 25°C for 2 minutes with a solution comprising 1 part by volume of concentrated hydrochloric acid and 3 parts by volume of water. Then, the article was non-electrically plated with a solution manufactured by Kizai Kabushiki Kaisha (1 part by volume of chemical nickel plating solution A, 1 part by volume of chemical nickel plating solution B and 2 parts by volume of water) and electrically plated with copper (a solution comprising 220 g/l of copper sulfate and 55 g/l of concentrated sulfuric acid). The plated article was dried at 80°C for 1 hour and the adhesion force was

measured. It was found that the adhesion force was lower than 100 g/cm. The adhesion force was determined by forming a scar having a width of 1 cm with a knife so that the scar was extended to the resin layer from the plating surface and measuring the load necessary to peel the plated layer from the polyacetal.

Comparative Example 2

The plating treatment was carried out in the same manner as in Comparative Example 1 except that a treating solution comprising 1 part by volume of water was used. The adhesion force of the plated article was substantially zero.

Example 1

The plating treatment was carried out in the same manner as in Comparative Example 1 except that a treating solution comprising 1 part by volume of concentrated sulfuric acid, 1 part by volume of 35% hydrochloric acid and 2 parts by volume of water was used. The adhesion force of the plated article was 700 g/cm.

Examples 2 to 16

Polyacetal resins shown in Table 1 and treated under conditions shown in Table 1 were plated in the same manner as in Example 1. The results obtained are shown in Table 1.

Table 1.

<u>Example No.</u>	<u>Base Resin</u>	<u>Additive</u>	<u>Amount (%) of Additive</u>	<u>Treating Solution (volume ratio)</u>	<u>Treatment Conditions</u>	<u>Adhesion Force (Kg/cm)</u>
2	Delrin	-	-	sulfuric acid (1), hydrochloric acid (1), water (2)	25°Cx20min	0.5
3	Duracon M90	heavy calcium carbonate	1	ditto	ditto	above 1
4	ditto	ditto	5	ditto	ditto	above 2
5	ditto	ditto	10	ditto	ditto	above 2
6	ditto	ditto	20	ditto	ditto	above 2
7	ditto	ditto	30	ditto	ditto	1.9
8	ditto	ditto	10	ditto	25°Cx10min	1.9
9	ditto	ditto	10	ditto	25°Cx30min	1.7
10	ditto	ditto	10	ditto	35°Cx 5min	1.1
11	ditto	ditto	10	ditto	45°Cx 5min	1.2
12	ditto	ditto	10	sulfuric acid (2), hydrochloric acid (1), water (2)	25°Cx 5min	1.1

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Table 1 (continued)

<u>Example No.</u>	<u>Base Resin</u>	<u>Additive</u>	<u>Amount (%) of Additive</u>	<u>Treating Solution (volume ratio)</u>	<u>Treatment Conditions</u>	<u>Adhesion Force (Kg/cm)</u>
13	Duracon M90	heavy calcium carbonate	10	sulfuric acid (1), hydrochloric acid (2), water (2)	25°Cx10min	1.3
14	ditto	Hakuenka DD*	30	sulfuric acid (1), hydrochloric acid (1), water (2)	25°Cx20min	1.5
15	ditto	heavy calcium carbonate	5	ditto	ditto	1.8
		glass beads	30			
16	ditto	Uniber*	30	ditto	ditto	1.9
<u>Note</u>						

*: finely divided calcium carbonate manufactured by Shiraisai Kogyo

CLAIMS

1. A method for the surface treatment of poly-acetal resin characterised in that the resin is treated with an acidic solution containing chloride ions and sulfate ions.
2. A method according to claim 1 characterised in that the polyacetal resin contains a filler.
3. A method according to claim 2 characterised in that the filler is calcium carbonate.
4. A method according to claim 3 characterised in that the resin contains 3% to 5% of the calcium carbonate.
5. A method according to any of claims 1 to 4 characterised in that the surface of the resin is etched by the treatment to a depth of 0.05 to 50 μm .
6. A method according to claim 5 characterised in that the surface of the resin is etched to a depth of 1 to 20 μm .
7. A method according to any of claims 1 to 6 characterised in that the treatment temperature is 0°C to 70°C, the treatment time is up to one hour and the acidic solution is prepared from commercial hydrochloric and sulfuric acids, the hydrogen ion concentration in the solution being 0.6 to 1.5 equivalents per 100 g., the hydrochloric acid/sulfuric acid weight ratio being from 1/20 to 20/1 and the concentration of hydrogen chloride in the hydrochloric acid being up to 30%.
8. A method according to claim 7 characterised in that the hydrogen ion concentration is 0.8 to 1.3 equivalents per 100 g., the hydrochloric acid/sulfuric acid weight ratio is from 1/10 to 1/1 and the hydrogen chloride concentration in the hydrochloric acid is 7% to 25%.



9. A method according to any of claims 1 to 8 characterised in that the treatment is carried out after annealing and degreasing of the surface.

5 10. A method according to any of claims 1 to 9 characterised in that the resin is in the form of a shaped article.

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