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PROCESS OF TREATING SURFACES OF SHAPED ARTICLES OF POLYACETALS WITH CAMPHOR-SULFONIC ACID

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3 Claims. (Cl. 156—2)

It is known to use high molecular weight polyacetals as thermoplasts for the manufacture of shaped articles, such as tubes, profiles and injection moulded material. Owing to the good resistance to chemicals of polyacetals, however, the shaped articles cannot be bonded or lacquered with satisfactory strength. Therefore, various methods have been proposed to treat the surfaces of shaped articles of polyacetals.

Experiments to roughen the surface mechanically with the aid of grinding cloth and analogous grinding agents, or to subject the shaped articles to an electronic pretreatment under reduced pressure, or to treat the surface with an oxidizing flame did not result in a sufficient improvement of the bonding strength of adhesives and lacquers.

Better results are obtained when the shaped articles are immersed in a solution containing an oxidizing acid. It is known, for example, to roughen the surface of shaped articles of polyoxymethylene by dipping them for 10 minutes into a solution of about 20° C. of 11 grams of potassium bichromate in 400 parts of sulfuric acid of 95–98% strength and 14 parts of water so that it can be well wetted with water and thus bonded and lacquered. However, the process has considerable drawbacks in that it can only be applied when the area of the shaped article to be treated is free from frozen in or forced stresses (latent stress) since otherwise it breaks under the action of the acid. Shaped articles can be produced very seldom without stress and it is, therefore, necessary to subject the shaped articles to a heat treatment before treating them with the oxidizing acid. Moreover, it is rather difficult to treat limited areas of the surface.

According to another proposal shaped articles which are under stress can be treated with a mixture containing p-toluene-sulfonic acid. For this purpose the shaped article is dipped for 10–30 seconds into an agitated mixture of 75–120° C. consisting of 0.3% by weight of p-toluene-sulfonic acid, 96.2% by weight of perchloroethylene, 3.0% by weight of dioxane and 0.5% by weight of kieselguhr, then placed for 1 minute in a furnace having a temperature of 120° C., rinced with water and dried in the air. After said treatment the surface of the articles can be bonded and lacquered. However, it is not uniformly roughened because the amount of p-toluene-sulfonic acid adhering to the surface after dipping is non-uniformly distributed on the said surface in spite of the addition of kieselguhr, especially when articles of complicated shape are concerned. With this process, too, it is difficult to limit the pretreatment to definite areas of the surface.

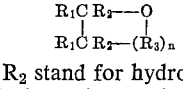
The present invention provides a process for improving the property of being bonded and lacquered of surfaces of shaped articles of polyacetals which comprises contacting the dry surface for a period of time ranging from 15 seconds to 30 minutes at 70–150° C. with dry pulverulent camphor-sulfonic acid. After the removal of the loosely adhering acid, for example by blowing it off with air, the surface of the shaped article of polyacetal has a uniformly mat appearance, it can be wetted with water

and has a good bonding strength for adhesives and lacquers. It is especially advantageous that according to the process of the invention shaped articles with strong latent stress can be treated without heat treatment or other pretreatment. Moreover, parts of the surface can be covered and thus readily protected against the action of the acid. Panels, for example can be treated on one side only or parts can be protected by covering them with adhesive foils.

In special cases, for example when larger amounts of shaped articles are to be treated in continuous manner, it may be of advantage to treat them with dry pulverulent camphor-sulfonic acid fluidized with a hot carrier gas, for example hot air.

Owing to the fact that camphor-sulfonic acid does practically not decompose at high temperatures, it can repeatedly be used for the surface treatment of shaped articles of polyacetals. It is possible to effect a dry treatment of the surfaces of plastics also with p-toluene-sulfonic acid. However, it is disadvantageous that. the latter acid decomposes during the first use and must be washed off with water.

According to the process of the invention any kind of shaped articles of polyacetals can be treated. By polyacetals there are to be understood homopolymers of formaldehyde or trioxane and the copolymers thereof with cyclic ethers of the formula



in which R_1 and R_2 stand for hydrogen or low molecular weight alkyl radicals, or low molecular weight, halogen-substituted alkyl radicals, and R_3 represents a methylene, an oxymethylene, or a low molecular weight alkyl- or halogen-alkyl-substituted methylene or a low molecular weight alkyl- or halogen-alkyl-substituted oxymethylene radical and n is one of the numbers 0, 1, 2, and 3. Especially suitable are polyacetals such as polyoxy-methylenes the terminal groups of which may have been esterified or etherified.

The following examples serve to illustrate the invention but they are not intended to limit it thereto.

Example 1

Pulverulent camphor-sulfonic acid was spread on panels of polyoxymethylene by means of a fine-meshed sieve in a manner such that the surface was uniformly covered. The covered panels were then heated for 3 minutes at 120° C. After having removed the powder and washed off the adhering traces of acid with water, the panels dried in air had a mat surface. They could be bonded with one another and with panels of wood, iron and other plastic materials by means of polyisocyanate/polyester adhesive. The adhesive joints had a tensile shear strength of 100 kp./cm., whereas untreated polyoxymethylene panels could not be bonded with the said adhesive.

Example 2

A panel of polyoxymethylene was heated at 130° C. and dipped for 45 seconds in pulverulent camphor-sulfonic acid having a temperature of 130° C. After removal of the powder and washing off the adhering traces of acid with water, the panel was dried in air. The panel which had a mat appearance was lacquered with a lacquer on the basis of polyisocyanate/castor oil. The lacquer could not be peeled off when the surface was scratched.

Example 3

2 mm. thick sheets (5 x 2.5 cm.) of polyoxymethylene were bent to an extent such that both ends could be inserted in a U-shaped profile 1.3 cm. wide. The bent sheets were treated as described in Examples 1 and 2

without stress crazing being observed. A pretreatment of the bent sheets with sulfuric acid bichromate solution was not possible because in contact with the acid stress crazing occurred at once.

We claim:

1. Process for improving the property of being bonded and lacquered of surfaces of shaped articles of polyacetals, which comprises contacting the dry surface for a period of time ranging from 15 seconds to 30 minutes at 70 to 150° C. with dry pulverulent camphor-sulfonic acid.

2. The process of claim 1, which comprises treating the shaped articles by dipping them in dry camphor-sulfonic acid fluidized with a hot carrier gas.

3. The process of claim 1, which comprises treating shaped articles containing high molecular weight polyoxymethylene.

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