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SURFACE CONDITIONING SYSTEM FOR POLYMER STRUCTURES

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ABSTRACT OF THE DISCLOSURE

An improved surface conditioning and release system is provided for all casting processes in which a polymerizable material is deposited on a casting surface by a surface conditioning layer applied to the casting surface. The surface conditioning layer comprises a water soluble film forming material such as gelatin or carboxymethyl cellulose which is essentially insoluble in the polymerizable material and which will remain water soluble under the conditions used to polymerize the polymerizable material. The layer also contains a water-soluble film-extending agent which is polyvinyl alcohol or a mixture of polyvinyl alcohol and a polyether glycol.

BACKGROUND OF THE INVENTION

1. Field of the invention

This invention relates to a surface conditioning system and process for use in casting polymerizable materials. More specifically, it relates to a system and process for treating a casting surface to allow both release of the cast material from the casting surface and control over the physical characteristics of the surface of the cast material.

2. Discussion of the prior art

It has long been known that most polymerizable materials cannot be cast directly onto a casting surface. Unless the casting surface has been treated in some way, the polymerizing material will adhere to it so that it will be difficult if not impossible to remove the polymerized product from the casting surface. A variety of mold release techniques and materials have been developed to overcome this problem; most of which rely on the use of a non-stick casting surface.

The use of such a casting surface solves only half of the problem encountered in casting polymerizable material. Usually some control over the surface characteristics of the cast material is desirable. Unless particular care is taken, a skin will form on the surface of the cast material which renders it either opaque or in some way different from the rest of the cast material.

Acrylic casting processes are a good example of the problems that can be encountered. The primary problem is that acrylic polymerization is sensitive to the presence of oxygen which will affect the polymerization and cause an opaque, chalky appearance on the exposed surface of the material. Furthermore, normal mold release materials are also generally soluble in acrylic monomer and may well affect the polymerization by inhibiting it. Acrylics also shrink a good deal more on polymerization than many other materials, and polymerizable acrylic compositions normally contain a high percentage of monomer which boils at a low temperature, i.e., about 100° C. for methyl methacrylate. These problems are most acute in those polymerization processes which take place at higher temperatures, particularly the rapid polymerization processes such as that disclosed in copending application Ser. No. 197,974, filed Nov. 11, 1971, still pending, but in all cases, unless the polymerizing material is insulated from oxygen and in most cases from the mold release

materials themselves, the effect will be an uneven, chalky surface, often containing bubbles, on the cast material which renders it opaque. While it might be assumed that problems occur only on the exposed areas of the cast material and not on those portions adjacent to the casting surface, such is not the case, because as polymerization occurs, the material shrinks and pulls away from the casting surface, allowing oxygen access to this surface as well. The use of a mold release agent, therefore, though necessary to aid in the removal of the material from the cast surface, can be detrimental to the surface characteristics of the material unless great care is taken in the casting process.

One way in which this problem has been solved is to sandwich the cast acrylic material between two sheets of film which shrink at the same rate as the polymerizable materials shrinks under the polymerization conditions. Such a system is disclosed in U.S. Pat. 3,600,490. There is still some difficulty in maintaining the surface of the cast material ripple free because of the nature of the shrinking film, but with care, an acceptable product can be produced.

The present invention is most useful in acrylic casting processes, particularly those of the high temperature variety, but it can also be used effectively with other polymerization processes such as low temperature acrylic casting processes and polyester casting processes.

The term casting is intended to include conventional casting, molding and any other processes in which a polymerizable material comes into contact with a surface either flat or curved which will define its finished shape. The surface conditioning layer can be applied to one or more of the casting surfaces, depending upon the requirements of the surface of the polymerizable material.

It is the object of this invention to provide an improved surface conditioning and release system and process for use in all casting processes in which a polymerizable material is deposited onto a casting surface.

SUMMARY OF THE INVENTION

According to the broad aspects of the invention, a surface conditioning layer is applied to the casting surface. The surface conditioning layer comprises a water soluble, film forming, material which is essentially insoluble in the polymerizable material and which will remain water soluble under the conditions used to polymerize the polymerizable material. A variety of materials falling within this generic description can be used. These materials include: proteins, such as gelatins and animal glues; starches; and cellulose derivatives such as cellulose gums. Gelatin and carboxymethylcellulose are two particularly useful materials.

In the preferred embodiment, the casting surface is first coated with a surface release layer and the surface conditioning layer is applied over this release layer. The surface release layer can be a permanent or semipermanent part of the casting surface, such as a fluorocarbon or silicone coating, or it can be an applied material such as wax, oil, grease, ethers, esters, or hydrocarbons, such as paraffin, which will not vaporize at the temperature of the reaction.

Additional components can be added to the surface conditioning layer. For example, up to about 70% by weight of the layer can be a film extending agent, added to the material from which the layer is made to impart to it sufficient extensibility to withstand peeling or cracking as the surface conditioning layer dries. In the preferred embodiment, the film extending agent is a mixture of polyvinyl alcohol and polyether glycol such as that sold under the name Carbowax®. The layer also contains up to about 1.0% based on the weight of the layer of a surfactant which will cause the surface conditioning layer

to wet the release layer, and a small amount of an anti-foaming agent to control the level of foam developed by the surfactant. The layer can further contain a suitable amount of a surface flattening agent to control the gloss of the surface of the structure, and a small amount of a preservative to keep the mixture from spoiling. A base or an acid can be added to control the pH of the layer to make it compatible with the polymerizing material in contact with it. A basic polymerization process should be cast on a basic surface conditioning layer. Finally, a dye can be added to the layer so its presence and thickness can be easily discerned.

DISCUSSION OF THE PREFERRED EMBODIMENTS

In practice, the surface conditioning layer is applied to one or more of the casting surfaces by some suitable process such as spraying, wiping or laying the material down with a doctor knife. It forms a film and the polymerizable material is then deposited on the film coated casting surface and polymerized by some suitable process. The thickness of the layer is not critical, but thicknesses between 0.1 to 1.0 mil have been found to be satisfactory. The film is made from a material which is essentially insoluble in the polymerizable material so that it comes into intimate contact with the surface of the polymerizing material and shrinks with it. The film is not a true film, in the sense that it can be stripped from the cast material, so it should be water soluble. Removal of the film is then accomplished by merely washing the film from the cast material.

The essential ingredient of the surface conditioning layer is the water soluble film forming material. The material must be substantially water soluble. This means that it should be easily removable by washing in warm water with a minimum amount of scrubbing. Furthermore, the material must be insoluble in the polymerizable material. Solubility is a matter of degree, most materials being to a certain extent soluble in one another. In this case, the film forming material should be essentially insoluble in the polymerizable material, which means that there should be no appreciable dissolution of the film forming material in the polymerizable material.

The surface conditioning system of the present invention is particularly useful with acrylic casting processes. When used with such a process, then, the film forming material can be selected from the group of materials consisting of proteins, such as gelatins and animal glues; starches; and cellulose derivatives, such as cellulose gums.

The surface conditioning layer is applied to the mold, but its purpose is to protect the surface of the polymerizing material during polymerization. The surface conditioning layer should, therefore, adhere to the surface of the polymerizing material and shrink with it as it polymerizes. The films formed by the film forming material discussed above, however, are generally brittle, so that if they are applied to large casting surfaces or casting surfaces which contain bends or convolutions, the stresses exerted on them as the surface conditioning layer dries are such that the film has a tendency to crack or peel away from the casting surface. The problem is most acute in low humidity conditions. To prevent this, some material, referred to as a film extending agent, is added to the surface conditioning layer. It is believed that the film extending agent acts as a plasticizer for the film forming material and that any material which acts as a plasticizer for the particular film forming material used will function as the film extending agent so long as its presence in the surface conditioning layer does not decrease the solubility of the layer to the point where it cannot be washed off the cast article with a minimum amount of effort. Above about 85% RH, little or no film extending agent is needed.

Polyvinyl alcohol is one material that has been found to be useful as the film extending agent. Polyvinyl alcohol, however, although water soluble under normal conditions, cross links under the polymerization conditions for acrylics. The concentration of polyvinyl alcohol in the surface conditioning layer must, therefore, be kept below 70% by weight of solids. Even at this concentration, the solubility of the surface conditioning layer is decreased to an undesirable level, so that either the concentration of the polyvinyl alcohol in the mixture must be decreased or some material such as polyether glycol must be substituted in part for the polyvinyl alcohol. The polyether glycol may act merely to replace some of the cross-linkable material. Polyethylene glycol is available in the form of several water soluble commercially available mixtures under the trade name Carbowax®, (e.g. polyethylene glycols and polyethylene glycol ethers). Whatever the case, the surface conditioning layer, which must contain at least 30% by weight of solids of the water soluble film forming material, may contain up to 25% by weight of the Carbowax® with the remaining material being polyvinyl alcohol.

Virtually any type of gelatin can be used. The higher the molecular weight of the gelatin, the less polyvinyl alcohol is necessary, but only low concentration of high molecular weight gelatin can be used, at room temperature, because of gelation. Preferably, then, the highest molecular weight gelatin that will not produce a gel is used. Gelatins having a bloom number up to about 200 have been used without producing a gel, but even these materials will gel in time so the preferred gelatins are those with bloom number of about 75. If gelling does occur, the solution can be restored by warming it above room temperature. A composition containing 45% 75 bloom gelatin and 55% polyvinyl alcohol, has been found to be suitable. A 6% solution in water of this material can be applied with ease.

Virtually any type of cellulose gum can be used, but the preferred gums have as low a viscosity as possible so that they will go into solution without forming gels. The higher viscosity materials give poorer surfaces. Preferably, then, the material should be non-thixotropic. A layer containing 60% carboxymethylcellulose and 40% polyvinyl alcohol has been found to be suitable.

In the preferred embodiment, the surface conditioning layer is applied over a surface release layer on the casting surface. The surface release layer can consist of a separate layer applied to the casting surface or it can be part of the casting surface itself. For example, the casting surface can be made from non-stick materials such as "Teflon"* fluorocarbon resin or it can be coated with a more or less permanent coating of silicone. In another embodiment, the casting surface can be made from normal materials, such as stainless steel, aluminum or even plastic, coated with a conventional mold release material which is applied before each casting. Examples of such materials are waxes, oils, greases, ethers, esters, silicones, and hydrocarbons, such as paraffin. The main criterion is that the materials must not vaporize substantially at the temperatures to which they are subjected.

One particularly useful mold release material is Partall® No. 2 wax; another is Mirror Glaze® wax. In some instances, however, this material may not be highly wettable by the surface conditioning layer, which means that a homogeneous surface conditioning layer may be difficult to apply. This difficulty can be overcome by applying a film of Carbowax® 1500 over the Partall® wax layer or even by mixing Carbowax® 1500 with the Partall®. A mixture containing 95% by weight of Carbowax® 1500 and 5% by weight of Partall® has been found to be highly suitable as a mold release material. High temperature appears to adversely affect the wettability of the Partall® coated surface, but once the Partall® containing layer has been applied to the mold, it can be rejuvenated

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many times by merely wiping the layer with Carbowax® 1500.

The surface conditioning layer should not stick to the casting surface, but in some instances, it is not necessary to specifically apply a mold release layer to the mold or casting surface prior to laying down the surface conditioning layer. Residual oil, or dirt on the casting surface will act as a mold release layer. In some instances, then, merely taking care not to clean the casting surface properly will provide sufficient mold release capability.

If a release layer is used, the surface conditioning layer may have to contain up to about 1.0%, preferably about 0.33%, based on the weight of the total solution of a surfactant which will cause the surface conditioning layer to wet the surface release layer. Examples of such materials are Triton® X–100 or other non-ionic water soluble surfactants. Since surfactants foam, as little surfactant as possible should be used. Furthermore, if a surfactant is used, a small amount of a conventional anti-foaming agent or other materials such as "Zonyl"* A fluorochemical surfactant may also be used to control the level of foam produced.

The primary objective of the present invention is to produce a structure with controlled surface characteristics. It has been observed that different thicknesses of the surface conditioning layer will cause different levels of gloss on the surface of the structure. This is a particular problem when the layer is applied by spraying because such an application often leads to an uneven coating. To circumvent this problem, a thick surface conditioning layer is applied so that a high gloss article will be produced and the gloss level is controlled by adding a suitable amount of a conventional surface flattening agent, such as finely divided silica sold under the trade names Cab-O-Sil®, Sil-O-Nox®, and Siloid® silica, to the surface conditioning layer.

Because the film forming materials are generally organic in nature, some preservative such as thymol should be added to them if they are to be stored for any length of time. Any conventional preservative that does not interfere with the polymerization when it is in the surface conditioning layer can be used.

Polymerization processes, particularly acrylic polymerization processes, are generally either acidic or basic in nature. The pH of the surface conditioning layer should be compatible with the polymerization process with which it is to be used. Some material such as NaOH or HCl can be added to the material from which the surface conditioning layer is made to adjust its pH to the desired level.

Finally, a water soluble dye which is not soluble in the polymerizable material, such as Neolan® Blue 2G, can be added to the surface conditioning layer so that its presence and thickness can be discerned.

A mixture containing at least 30%, preferably 30 to 70%, of gelatin or carboxymethylcellulose, 40 to 70% polyvinyl alcohol, and 25% polyether glycol, all based on the weight of the solids, is suitable for use as the surface conditioning layer. To impart shelf-life, the mixture should also contain a small of a preservative. To impart wettability, the mixture should also contain up to about 1.0% based on the weight of the total solution of a surfactant and a small amount of an anti-foaming agent. It can also contain a small amount of a dye, a flattening agent and a pH adjuster, all of which should be water soluble and not affect the polymerization when used in the surface conditioning layer.

EXAMPLE 1

Seventeen grams of gelatin (Knox®, edible, 200 bloom) was dissolved in 1000 cc. of water. This solution was applied with a cheese cloth to an uncleaned stainless steel plate (12" x 12") and allowed to dry.

A sirup of about 23% by weight of methyl methacrylate homopolymer dissolved in methyl methacrylate monomer is prepared by partial polymerization in situ and about 1.25% ethylene glycol dimethacrylate is added to the mixture. The composition is designated Sirup. To a mixture containing 40% by weight of the above Sirup and 60% by weight of alumina trihydrate (Alcoa C–33) are added 0.25% based on the weight of the Sirup (b.o.s.) of water, 0.5% b.o.s. of calcium hydroxide, 0.5% b.o.s. of t-butyl peroxy maleic acid and 0.25% b.o.s. glycol dimercaptoacetate.

This acrylic resin composition was cast in a circular pattern on the gelatin coated plate. After the resin cured, the part (½" thick by 6" in diameter) was easily removed from the plate. The gelatin coating adhered to the acrylic part and was easily washed off with warm water.

The procedure of Example 1 was repeated except that the stainless steel plate was flame treated in a conventional manner to clean the surface and improve its wetting properties, and the gelatin coating was sprayed on the clean plate. After curing, the part was still removed easily, but the gelatin coating remained on the stainless steel plate, indicating the need for a mold release layer.

EXAMPLE 2

The procedure of Example 1 was repeated except that a 6% solution of 75 bloom gelatin (Knox® edible) was used in place of the 200 bloom gelatin. The part again separated easily from the plate and the gelatin layer, adhering to the part, was easily washed off with warm water.

EXAMPLE 3

The process of Example 2 was repeated except that a polyester resin composition was used instead of the acrylic Sirup. The polyester composition contained 40% by weight of polyester resin (Polylite® 32–129), 60% by weight of alumina trihydrate (Alcoa C–33) and 1% based on the weight of the polyester of methyl ethyl ketone peroxide.

After curing, the part separated easily with the gelatin adhering to the part. The gelatin was removed by washing in warm water.

EXAMPLE 4

The process of Example 2 was repeated except that the plate was first wiped with wax (Mirror Glaze® No. MGH–8) before applying the gelatin layer.

The part separated extremely easily from the plate and the gelatin coat, adhering to the part, was easily removed by washing with warm water.

EXAMPLE 5

The process of Example 4 was repeated except that the gelatin was replaced with sodium carboxymethylcellulose (Du Pont R75XL).

The part separated extremely easily from the plate and the coating, adhering to the part, was easily removed by washing with warm water.

EXAMPLE 6

A solution containing the following constituents was made:

Gelatin (Knox®, 75 bloom)	gm.	28
Water	gm.	372
Thymol (4% in ethanol)	cc.	1
Carbowax® 600	gm.	2.8
Triton® X–100	gm.	1.3

This solution was applied by spraying on both surfaces of a prewaxed (Mirror Glaze® No. MGH–8) polyester fiberglass (Gruber Co.) mold. The wettability was excellent.

After the coating was dried, a Sirup having the same composition as in Example 1, was cast in the mold.

The cured part, which had the shape of a bowl, was removed easily from the mold. The gelatin coating adhered to the part and was easily removed by washing with warm water.

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EXAMPLES 7–11

The following solutions were made:

Solution A:		
Gelatin (Knox®, 75 bloom)	g.	144
Water	g.	2316
Tymol (4% solution in ethanol)	cc.	6
Carbowax® 600	g.	14.4
Triton® X–100	g.	7.8
Solution B:		
Polyvinyl alcohol (Du Pont 51–05)	g.	144
Water	g.	2316
Thymol (4% solution in ethanol)	cc.	6
Carbowax® 600	g.	14.4
Triton X–100	g.	7.8
Solution C:		
NaOH	g.	5
Water	g.	95

The solutions were mixed:

	Volume of solution in final mixture (cc.)		
	A	B	C
Example:			
7	60	40	2.5
8	55	45	2.5
9	50	50	2.5
10	45	55	2.5
11	40	60	2.5

The above mixes were sprayed on prewaxed (Partall® No. 2 wax) polyester fiberglass molds (Gruber Co.). The molds were allowed to dry and then they were stored overnight in a dry room (RH 20%). In Examples 7–9, some separation occurred between the film and the mold in one or more corners of the mold. In Examples 10 and 11, no separation at all took place, indicating that the higher percentages of polyvinyl alcohol in the composition are preferred.

The acrylic Sirup of Example 1 was cast in the mold coated with the mixture of Example 10. The cured bowl was removed from the mold very easily. The release film adhered to the acrylic part and was washed off very easily with water.

EXAMPLE 12

The following solution was made:

	Gm.
Sodium carboxymethylcellulose (Du Pont R75XL)	7,560
Polyvinyl Alcohol (Du Pont 51–05)	5,040
Water	131,400
Carbowax® 600	1,134
Triton® X–100	586
Thymol (4% in alcohol)	441
Zonyl® A	187

A hot mold (60–70° C.) which had been previously coated with Partall® wax was wiped with Carbowax® 1500 and a coating of the above solution was applied by spraying. After the mold dried, the acrylic Sirup of Example 1 was cast in it.

After curing, the part was separated from the mold very easily. The film adhered to the part and was very easily washed off with warm water.

What is claimed is:

1. A surface conditioning system for use in a casting process in which a polymerizable material containing acrylic monomer, or a polyester, is deposited onto a casting surface, said surface conditioning system comprising a water soluble surface conditioning layer, applied on said casting surface, said layer comprising about 30–70% by weight of the solids of a water soluble, film forming material which is gelatin or carboxymethyl cellulose and about 40–70% by weight of the solids of a water-soluble film-extending agent which is polyvinyl alcohol or a mixture of polyvinyl alcohol with up to 25% by weight of the solids of a polyether glycol.

2. The surface conditioning system of Claim **1** in which said surface conditioning layer further contains up to about 1.0% based on the weight of the layer of a non-ionic surfactant.

3. The surface conditioning system of Claim **2** in which said surface conditioning layer further contains a small amount of an anti-foaming agent.

4. The surface conditioning system of Claim **1** in which a surface release layer composed of materials selected from the group consisting of silicones and fluoropolymers is applied to the casting surface between the casting surface and surface conditioning layer.

5. The surface conditioning system of Claim **1** wherein a surface release layer composed of materials selected from the group consisting of waxes, oils, greases, esters, ethers, silicones and hydrocarbons which will not vaporize at the temperatures to which they are subjected is applied to the casting surface between the casting surface and surface conditioning layer.

6. In a polymerization process of the type in which a polymerizable material containing acrylic monomer or a polyester is deposited onto a casting surface and cured, the improvement wherein, prior to the deposition of said polymerizable material on said casting surface, a water soluble surface conditioning layer is applied on said casting surface, said surface conditioning layer comprising about 30–70% by weight of the solids of a water-soluble, film-forming material which is gelatin or carboxymethyl cellulose and about 40–70% by weight of the solids of a water-soluble film-extending agent which is polyvinyl alcohol or a mixture of polyvinyl acohol with up to 25% by weight of the solids of a polyether glycol.

7. The process of Claim **6** in which said surface conditioning layer further contains up to about 1.0% based on the weight of the layer of a surfactant.

8. The process of Claim **7** in which said surface conditioning layer further contains a small amount of an anti-foaming agent.

9. The process of Claim **6** in which a surface release layer composed of materials selected from the group consisting of silicones and fluoropolymers is applied to the casting surface between the casting surface and surface conditioning layer.

10. The process of Claim **6** in which a surface release layer composed of materials selected from the group consisting of waxes, oils, greases, esters, ethers, silicones and hydrocarbons which will not vaporize at the temperatures to which they are subjected is applied to the casting surface between the casting surface and surface conditioning layer.

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