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METHODS OF PRODUCING OIL-FREE AND WAX-FREE SURFACES ON POLYURETHANE MOLDINGS

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ABSTRACT OF THE DISCLOSURE

Polyurethane moldings are made by methods using a mold which has been coated with a hydrophobic oily or waxy release agent and overcoated with a film forming water-soluble barrier material (e.g. polyvinyl alcohol) which is reactive with the free isocyanate materials of the molding composition. The moldings are washed to remove the water-soluble barrier material to provide a surface free of oily or waxy residue.

DISCLOSURE

This application is a continuation in part of our copending patent application, Ser. No. 881,926, filed Dec. 3, 1969 and now abandoned.

This invention relates to a method of producing paintable surfaces on polyurethane moldings. Specifically, this invention relates to the method of preparing moldings with release agents so that a molding having surfaces which are clean, blemish-free, and free of adhesion inhibiting mold release agent, suitable for painting, will result.

Polyurethane moldings, especially foamed polyurethane moldings, are useful in a broad variety of applications. For many uses, it is desirable to subsequently coat or paint the surface of the molding with a decorative or protective layer. Conventionally, these layers are applied to a polyurethane molding, by means of brushing, spraying and other methods known in the art, paint-like compositions commonly known to the art. Typically, in the prior art methods, the polyurethane molding is prepared in a mold which is first coated with an oily, waxy fluororganic, or silicone release agent. The release agent serves the purpose of allowing easy removal of the molding from the mold surfaces and providing a smooth and uniform surface to the molding. A problem arises, however, when these polyurethane moldings are subsequently painted because the waxy or oily release agent often leaves a film on the surface of the molding which may be undetectable to the touch or the eye but which will prevent the adhesion of a paint or coating layer. The paint or coating layer may, as a consequence, blister, flake, or peel from the surface of the molded article. To alleviate this problem, it has been common in the art to submit the molding to subsequent steps which were designed to remove from the surface of the molding the oily or waxy residue of the release agent used in the mold. Means such as roughening the surface of the molding with an abrasive material and cleaning the surface of the molding with an abrasive material and cleaning the surface of the molding with a solvent which will solubilize the oily or waxy residue, have been used. These methods have not been generally satisfactory and have the further disadvantage of costliness and often adversely alter the surface of the molding.

Where conventional release agents are used to coat the mold; the problems of poor release, surface blemishes, and undesirable residues of the release agent on the molding are encountered.

The economical manufacture of molded polyurethane especially foamed polyurethane articles having surfaces which are satisfactory for painting, has, therefore, been difficult by methods known in the prior art. The release agents are necessary to allow the removal of moldings from the mold and yet their use causes the aforementioned problems. A method has now been discovered by which polyurethane moldings having surfaces free of adhesion inhibiting mold release agent, and having smooth oil- and wax-free, paintable surfaces are obtained and importantly also, which may be easily released from the mold.

It is, therefore an object of this invention to overcome the disadvantages of the prior art and to provide a method for the manufacture of molded polyurethane articles having a paintable surface to which paint strongly adheres.

Another object of this invention is to produce polyurethane moldings having surfaces that are totally oil- and wax-free.

Still another object of this invention is to accomplish the production of moldings with a paintable surface to which paint strongly adheres, in an economical and efficient manner.

Still other objects of the present invention will be apparent from the following discussion.

Briefly, this invention comprises the treatment of a conventional mold with a waxy or oily material which may be an organic or silicone material and the subsequent coating of this already treated surface with a solid film forming, water-soluble, isocyanate reactive material. When the resultant water-soluble barrier layer is dry, a molding is made with a polyurethane mix in the conventional manner. After molding the article is easily removed from the mold, and is washed with water, aqueous detergent, or slightly alkaline aqueous solution. After drying, the surface may be painted by methods known in the art and said painted surface shows no evidence of poor paint adhesion because of residual oil or wax spots from the release agent.

For purposes of description of this invention, the hydrophobic, oily, or waxy coating layer first applied to the mold is designated the "release agent." The hydrophylic water-soluble layer which is subsequently overcoated onto the mold is designated the "barrier layer."

It has been found, according to this invention, that when a mold is used for consecutive moldings, as it will be in production operations for which this method is intended that the water-soluble barrier layer is advantageously applied every cycle, while the oily or waxy mold release agent need only be applied every three or four cycles. It is noted that the barrier layer adheres more tenaciously to the molded article than to the mold (which is coated with release agent).

The adhesion of the hydrophylic barrier layer to the molded article rather than to the mold surface and the additional use of a barrier layer overcoated hydrophobic release agent on the mold surface provide two important distinctions over the methods known in the prior art. It is recognized that certain of the materials disclosed herein as the "barrier layer" have been used in the prior art as mold "release agents." The use of the same and similar materials herein as "barrier layers" rather than "mold release layers" is no mere semantic distinction. A mold release agent, as is known in the molding art, is designed

to allow easy removal of the molded article from the mold and the release agent advantageously adheres strongly to the mold but not to the molded article. In fact, as those skilled in the art would recognize, an ideal release agent would be one which adhered so strongly to the mold that only single or very infrequent application would be necessary. However, it is commonly known to those skilled in the art, that films of oily or waxy mold release agents adhere to the molded articles and are difficult to remove therefrom. In contradistinction, the materials designated herein as "barrier layers" adhere to the molded article, are applied in each molding operation, and true mold release agents of distinctly different properties are utilized in conjunction therewith. In the absence of the waxy type mold release on the surface of the mold it is known for the barrier layer to adhere strongly to the mold surface as well as to the molded polyurethane foam article thereby making removal of said article from the mold very difficult.

As will be shown in the working examples, the adhesion of the barrier layer to the molded article has been demonstrated by incorporating a dye in the barrier layer. With the barrier layers which have been utilized in the practice of this invention, this adhesion between the barrier layer and the molding is attributed to a chemical reaction at the interface. These barrier layers contain a plurality of moieties which are reactive with the free isocyanate groups of the polyurethane molding composition. Thus various water-soluble, film forming organic compounds containing —OH, —COOH, —NH_2, —$CONH_2$, —NHR, —CONHR where R is a hydrocarbyl radical with 1–12 carbon atoms or other functional groups reactive with isocyanate groups can function as the barrier layer in the practice of this invention. It is theorized for example that when a polyhydroxy material such as polyvinyl alcohol is used as the barrier layer, an interfacial reaction occurs between the hydroxy groups of the barrier layer and the free isocyanate groups in the components of the molding composition. The reaction between free isocyanate groups, which appear in polyurethane molding compositions, and polyhydroxy-containing materials is well-known. It is not surprising, therefore, that this reaction should occur at the surface of the molding. It was, however, totally unexpected that the described isocyanate-reactive barrier layers would function in this invention. It was expected that the entire thickness of the barrier layer would react with the isocyanate in the molding composition to give the same net effect of no barrier layer whatsoever. Other barrier layer materials containing moieties known to react with isocyanate groups and which themselves are known to be reactive with isocyanate groups would be expected to also totally react with the isocyanate groups of the polyurethane molding composition so as to have a net effect of no barrier layer. The contrary was found, and, in fact, barrier layers which are reactive are preferred in the practice of this invention.

Examples of barrier layer materials known to react with isocyanate groups include polyacrylic acid, hydroxy methyl cellulose, polyvinyl pyrrolidone, polymers of hydroxy alkyl acrylates, polymers of hydroxy alkylmethacrylates, sodium silicate, polymethacrylic acid, polyvinyl alcohol and higher molecular weight polyoxyalkylene glycols (e.g. molecular weight about 10,000). Reaction of various of the above compounds with isocyanate groups is known in the chemical art and reported in the chemical and related literature. French Pat. 1,520,222 discloses reaction of polymers and copolymers containing acid groups with isocyanate bearing compounds. K. R. Lange, Chemical Ind. (London) 1968, (14), pp. 441–3, reports the reaction of tolylene diisocyanate with silica. The reaction of polyisocyanates with polyvinyl pyrrolidinone is disclosed in U.S. 3,216,983. Reaction of isocyanates (e.g. tolylene diisocyanate) with polyhydroxy compounds such as copolymers of hydroxylated esters of acrylic or methacrylic acid is described in Belgium Pat. 629,937. Disclosure is made in Belgium Pat. 630,318 as to the reaction of polyisocyanates with polymers and copolymers of hydroxyalkylacrylates or hydroxyalkylmethacrylates. The reaction of primary and secondary amines and amides with isocyanates is disclosed in e.g. *Polyurethane* by Dombrow, Reinhold Publishing Corporation, N.Y. pp. 18, 30.

The consequence of the theorized reaction between for example the hydroxy groups and isocyanate groups is that a portion of the water-soluble barrier layer, e.g., the polyhydroxy layer, is integrated with the surface of the molded article, and in all probability is reacted only at the interface formed between the molding and the barrier layer. The surface of a polyhydroxy barrier layer closest to the oily or waxy release agent apparently does not react with free isocyanate groups because, as shown by the dye test in Example 1, the barrier layer retains its water solubility. Consequently, the polyhydroxy layer adheres strongly to the molded article and is removed therewith when the article is taken from the mold. The entire thickness of the barrier layer adhering to the molding remains water soluble, except possibly for a reacted and insolubilized zone at the interface of the molding and barrier layer. Therefore, the part removed from the mold, in effect, has an outer surface easily removable with water, aqueous detergent, or aqueous alkali. Any of the waxy release agent sticking to the water-soluble outer surfaces of the molding is also easily removed with the aqueous washings.

It is considered necessary, as stated above, that the water-soluble barrier layer be reactive with free isocyanate groups contained in the molding composition so that the tendency of the barrier layer to adhere to the molding itself is much greater than its tendency to adhere to the waxy or oily mold release agent.

Among the materials useful as the barrier layer are any of the water-soluble inorganic or organic materials capable of forming a solid, continuous layer on the release agent-coated mold. Sodium silicate is an example of an inorganic material useful in the method of this invention. Among the organic materials, polymers are particularly preferred. Polyvinyl alcohol and hydrolyzed polyvinyl acetate polymers have been found to be particularly advantageous in this invention. Polyvinyl alcohol is water-soluble and is conventionally prepared by the substantially complete hydrolysis of polyvinyl acetate polymer. Partially hydrolyzed polyvinyl acetate polymers, especially those in which about 90% of the acetate groups are hydrolyzed, are also water-soluble and operative and desirable in the process of this invention. Other polymeric materials which may be used include higher molecular weight polyoxyalkylene glycols, polyvinyl pyrrolidone polymers, polyvinyl methyl ether/maleic anhydride copolymers, hydroxy methyl cellulose and water-soluble hydroxy-substituted acrylate or methacrylate polymers or copolymers, polyacrylic acid, polymethacrylic acid, and natural polymers such as gelatin, albumin, hydrolyzed starch, modified starches, and the like. Non-polymeric organic materials which may be used as barrier layers include sugars, α-methyl glucoside and the like. If desired, a non-ionic hydroxyl-containing surfactant, such as octylphenoxypoly (ethyleneoxy) ethanol containing 9–10 moles ethylene oxide per mole of hydrophobe, may be added to the solution to effect faster wetting of the waxy release agent by the barrier layer composition.

The term "water-soluble" as used herein includes solubility in liquids which are essentially aqueous, such as aqueous alkali and water-solvent systems in which water forms the predominant part. The term does not imply that the barrier layer must be applied from water solvent. In fact, it is preferable if the barrier material can be applied from volatile solvent or aqueous-solvent solutions. Rather, the term "water-soluble" means that the barrier layer is easily removable from the molding by water, i.e. water per se or water containing systems. The advantages of the ability to use water per se or aqueous

solutions for this purpose are obvious in terms of cost, non-toxicity, availability etc.

The mold release agent is applied directly to the mold and is a hydrophobic, oily or waxy organic or silicone material and is selected from those materials which are well-known in the molding art. A number of proprietary compositions exist which contain as their primary ingredient organic oils, organic waxes, silicone oils and waxes, and the like. Common materials such as paraffin, petroleum, carnauba wax, and the like, may also be used. The invention is not dependent on the type of hydrophobic release agent which is used. Rather the invention lies in the conjoint use of a hydrophobic release agent and a water-soluble barrier layer.

In general, the method of this invention may be easily adapted to any polyurethane molding process. The method is, of course, particularly useful where the molded part is to be subsequently painted or where a wax- and oil-free surface is required or desired. In practicing this invention, the following series of steps have been successfully used to produce, in a consecutive fashion, painted moldings from a single mold:

1. Apply mold release;
   A. Apply hydrophobic mold release agent (every three cycles).
   B. Apply (water-soluble) barrier layer over mold release coating (every cycle);
2. Assemble mold;
3. Introduce polyurethane molding ingredients;
4. Allow ingredients to foam and to cure;
5. Disassemble mold;
6. Remove molded article;
7. Wash molded article with mild aqueous detergent solution,
8. Air dry;
9. Apply paint;
10. Repeat process.

The polyurethane molding compositions and methods of their preparation which may be utilized in the practice of this invention are compositions and methods commonly known in the art. Said polyurethane molding compositions contain at least one organic polyisocyanate (i.e. an organic compound containing at least two isocyanate groups per molecule), at least one polyol (i.e. an organic compound having at least two hydroxyl groups per molecule), and optionally one or more surface active agents, one or more catalysts, one or more fire retardants, one or more light stabilizers, one or more pigments and/or fillers or reinforcements. Organic polyisocyanates commonly known to the art which may be employed in the polyurethane molding composition include but are not limited to 2, 4 tolylene diisocyanate, 2,6 tolylene diisocyanate and mixtures thereof, crude tolylene diisocyanate, polyethylene polyphenylisocyanate, 4,4 diphenylmethane diisocyanate, phenylene diisocyanate, xylylene diisocyanate, naphthylene diisocyanate, triphenyl methane triisocyanate, hexamethylene diisocyanate and like aliphatic, cycloaliphatic, aromatic and substituted aromatic polyisocyanates. Isocyanate terminated reaction products obtained by reacting an excess of organic polyisocyanate, such as those described above, with polyhydroxy compounds (e.g. polyether polyols, ethylene glycol, glycerine, trimethylol propane, pentaerylthritol and like monomeric and polymeric polymeric polyhydroxy compounds) may be used in the molding compositions. Polyhydroxy compounds such as, but not limited to, polyols obtained by reacting alkylene oxides (e.g. ethylene oxide, 1,2-propylene oxide, 2,3 butylene oxide and the like) with polyhydric alcohols (e.g. ethylene glycol, glycerol, trimethylol propane, pentaerythritol, sorbitol, sucrose or a-methyl glycoside) or alkylene diamines (e.g. ethylene diamine) may be used in the polyurethane molding compositions employed in the practice of this invention. Hydroxy terminated polyesters such as those obtained by condensation of a polycarboxylic acid (e.g. dicarboxylic acid) with a polyhydric alcohol (e.g. diol or triol) may be used in the said polyurethane compositions. Halogenated and/or phosphorus containing polyols may be employed in the said polyurethane molding compositions. Reaction products obtained by reacting glycols or alkylene oxides with dimethyl siloxane or polydimethyl siloxane are among the more commonly known surfactants which may be used in the polyurethane molding composition. Catalysts usable in the said polyurethane molding compositions include but are not limited to organo tin compounds and tin salts such as dibutyl tin dilaurate and stannous octoate, tertiary amines such triethylene diamine, triethanol amine and N,N,N^1,N^1 tetramethyl-1,3-butane diamine or combinations of said tin and amine compounds.

Blowing agents commonly known to those skilled in the art and which may be used in the polyurethane compositions employed in the practice of this invention include but are not limited to water and low boiling halogenated hydrocarbons such as monofluorotrichloromethane, dichlorodifluoromethane and trichlorotrifluoroethane. Among the fire retardants commonly known to those skilled in the art and which may be used in the said polyurethane molding compositions include halogen and/or phosphorus containing organic compounds (e.g. tris (β-chloroethyl) phosphate), antimony trioxide, ammonium phosphate and the like. Antioxidants and ultraviolet light stabilizers well known to the art may be added to the polyurethane molding composition. Organic and/or inorganic pigments may be included. Fillers such as diatomaceous earth, magnesium silicate, asbestos and the like may be used in the said polyurethane molding compositions.

It is to be recognized that this invention does not lie in the polyurethane molding composition and therefore many variations in the molding composition may be practiced by those skilled in the art without departing from the scope and spirit of this invention.

The invention may be better understood by reference to the following examples in which all parts and percentages are by weight unless otherwise indicated.

These examples are designed to teach those skilled in the art how to practice the invention and to represent the best mode contemplated for carrying out the present invention and are not intended to limit the scope of the invention in any manner.

EXAMPLE 1

This example illustrates the preparation of a foamed polyurethane molding having an oil- and wax-free, paintable surface. This example also illustrates the adhesion of the barrier layer to the molding.

A small aluminum foil dish is coated with a wax-type release agent comprising a paste dispersion of wax in a hydrocarbon solvent in which the wax portion is a mixture of hydrocarbon and ester-type waxes, and overcoated with a proprietary composition comprising polyvinyl alcohol and a surfactant in water/alcohol solution. A small proportion of an alcohol-soluble green dye was added to the polyvinyl alcohol solution. The coating was applied by wetting the inside of the aluminum dish with the polyvinyl alcohol solution, draining off the excess, and drying.

The polyurethane-forming ingredients used in this and subsequent examples are as follows:

A-Component (isocyanate)

A quasi-prepolymer prepared by slowly adding at ambient temperature 56 lbs. of polypropylene glycol of MW about 400 to 444 lbs. of a commercial isocyanate reported to be a polymer of diphenyl methane diisocyanate having 2–5 isocyanate groups per molecule. (The ingredients were mixed and allowed to react and stand for 24 hours before analysis and use.)

B-Component (polyol)

400.0 lbs. of a commercial polyol reported to be a propoxylated mixture of 75% of α-methyl glucoside and 25% glycerol, having a hydroxyl number of about 435.
2.8 lbs. N,N,N¹,N¹-tetramethyl-1,3 butane-diamine
6.9 lbs. silicone dispersing agent
68.6 lbs. monofluorotrichloromethane.

51.6 Grams of the A-component and 48.4 grams of the B-component were mixed with a high speed propellor-agitator, and 10.7 grams of this mix was poured into the prepared aluminum foil dish and allowed to react and expand.

After substantially complete foaming, the dish is placed in a circulating air oven at 120 degrees F. for 20 minutes. Upon removing the dish from the oven, the molded part is removed. The molded article is easily released and has a green coating. None of the green coating is discernible on the mold (dish). The green coating is easily removed by washing the molded article with water.

EXAMPLE 2

This example illustrates the use of this invention in the preparation and painting of a polyurethane molding which has a paintable surface.

A ½" x 4" x 10" cavity aluminum mold is prepared by coating with the wax-type release agent used in Example 1 and overcoating with the commercial solution of polyvinyl alcohol used in Example 1. Immediately after drying, the mold is charged with 106 g. of the polyurethane-forming ingredients used in Example 1, which have been mixed in a commercial foam mixing machine in a ratio of 51.6 parts of A-component to 48.4 parts of B-component. After the foam has expanded, the molding in the mold is placed in a 120 degree F. oven for 20 minutes to cure the molding.

The resulting molding is easily removed from the mold. None of the green dye is noted on the mold. The green-dyed barrier layer is easily removed by washing with water. After drying, the surface of the molding is brush painted with an acrylic latex paint. Good adhesion and a uniform painted surface result.

EXAMPLE 3

This is a control example to illustrate the effect of omission of the mold release agent.

The procedure of Example 2 is repeated except that the mold release agent coating is omitted. Severe sticking of the molded part is noted and removal from the mold is difficult. Surface blemishes are also noted.

EXAMPLE 4

This is a control example to illustrate the effect of omission of the barrier layer in the method of this invention.

The procedure of Example 2 is followed, except that the polyvinyl alcohol coating (barrier layer) is omitted. Non-uniformity and spotty, poor adhesion is noted in the painted article.

EXAMPLE 5

This example illustrates the use of a variety of materials as (1) the mold release agent, and as (2) the barrier layer.

The procedure of Example 2 is repeated with the exception that each of the following materials is substituted for the wax-type mold release agent and the polyvinyl alcohol barrier layer used in Example 2 respectively.

A. Mold Release Agents

1. A suspension in a hydrocarbon solvent of a blend of paraffinic microcrystalline and chemically modified Montan waxes having a melting point of about 140 degrees F.
2. A blend of vegetable, petroleum, and synthetic waxes in a solvent.
3. White petroleum jelly.
4. A commercially available paste wax.
5. A commercially available hydrocarbon wax having the following properties:
   Melting point—190 degrees F.—minimum
   Penetration at 77 degrees F.—8 maximum
   Color ASTM D1500—Brown maximum
   Acid No.—Nil
   Saponification—Nil.
6. Carnauba wax.

B. Barrier Layers

1. α-Methyl glucoside.
2. Sodium silicate.
3. Partially (72.9–77%) hydrolyzed polyvinyl acetate containing 37–42% residual polyvinyl acetate on a weight basis and having a molecular weight of 2000.

In each case, release of the molding from the mold is easy, and the barrier layer is easily removed by washing with water to give moldings comparable in quality to those obtained in Example 2.

EXAMPLE 6

This example demonstrates (a) the interaction between a claimed barrier layer material and a polymerizing urethane composition in contact with said barrier layer applied over a wax (b) the generation of a polyurethane plastic surface to which paint strongly adheres, and (c) the ability to remove from the polyurethane plastic surface substantially all of the barrier layer material with water to leave a wax free and oil free polyurethane plastic surface having high wettability and strong paint adhesion in a practice of this invention.

A. Casting

A solution was prepared as follows:

Materials.—Polyol component:

	Lb.
Poly–G–435–DM [1]	55.58
Poly–G–560–DM [2]	22.96
Niax Catalyst TMBDA [3]	.679
DC–193 Surfactant [4]	1.602
LVT23P [5]	21.18

[1] Poly–G–435–DM—Olin Chemicals Div.—Olin Mathieson Chemicals Corp. described as a propoxylated mixture of 75% α-methyl glucoside and 25% glycerine, having a hydroxyl number of 438. Poly G is a registered trademark of the Olin Mathieson Chemical Corp.

[2] Poly–G–560–DM—Olin Chemicals Div.—Olin Mathieson Chemical Corp. described as a propoxylated mixture of 75% α-methyl glucoside and 25% glycerine, having a hydroxyl number of 556.

[3] Niax Catalyst TMPDA—Union Carbide Chemicals & Plastics Div.—Union Carbide Corp. N,N,N¹N¹-tetramethyl-1,3-butane diamine. Niax is a registered trademark of the Union Carbide Corp.

[4] DC–193—Dow Corning Corp.—a silicone surfactant described in U.S. Pat. No. 3,402,192. DC is a registered trademark of the Dow Corning Corp.

[5] LVT23P—Michigan Chemicals Corp.—tris(2,3-dibromopropyl)phosphate.

Isocyanate component: A quasi-prepolymer having a free NCO content of 25.48%, prepared by reacting a large excess of Mondur MR [1] with Veranol P–400 [2]. The reactants were mixed at room temperature. The temperature of the reaction was thereafter not controlled, and was allowed to follow its natural course resulting from the exothermic reaction in a 22 gallon polyethylene container.

[1] Mondur MR—Mobay Chemical Co.—a polymer of diphenyl methane diisocyanate having 2–5 isocyanate groups per molecule. Mondur is a registered trademark of the Mobay Chemical Co.

[2] Voranol P–400—Dow Chemical Co.—a linear alpha-omega dihydroxy polypropylene oxide having a molecular weight of 400. Voranol is a registered trademark of the Dow Chemical Co.

	Percent	Pounds
Mondur MR	89.13	200.54
Voranol P-400	10.87	24.45
Total	100.00	224.99

The above polyol and isocyanate components at 70° F. and 100° F. respectively were stirred together for 20 seconds, until uniformly blended, in a weight ratio of 47.21 parts polyol to 52.79 parts isocyanate, then immediately cast onto the treated mold surface. The solution was cast in thin (⅛") layers, to give an unexpanded polyurethane formulation, in an open shallow flat aluminum mold of ½" x 4" x 10" dimensions in such a manner that the upper surface of the castings has been exposed only to air. The bottom and side surfaces of these castings were formed against the mold which had previously been prepared in each of the following ways.

(a) wax mold release only (Partall No. 2 Paste Wax Rexco Chemical Co.—a dispersion of solid waxes in an organic solvent).

(b) Polyvinyl alcohol film applied over wax (a) (Partall No. 10—Rexco Chemical Co.—a cold water soluble polyvinyl alcohol dissolved at 4% solids in 190 proof ethanol).

(c) Hydroxy propoxy methyl cellulose film applied over wax (a) [Methocel 60HG, 50 cp.—(Dow Chemical Co.) dissolved in a 50/50 by weight methanol/water mixture, containing 0.1% of a non-ionic surfactant so as to give a 2% solids content].

The wax used is the same in all of these surfaces. The wetting of the bottom surfaces of these castings molded against mold treatments were compared against the top (air contact only) surface of the casting which could not possibly have been contaminated by the mold surface and/or coatings.

The surfaces to be tested were designated as follows:

C_1—cast against a waxed metal mold surface (treatment (a)).

C_2—cast against a polyvinyl alcohol film applied over a waxed metal mold surface (treatment (b)), with the polyvinyl alcohol film subsequently removed from the molding by rinsing with cold (70° F.) water.

C_3—cast against a hydroxypropoxymethyl cellulose film applied over a waxed metal mold surface (treatment (c)), with the hydroxypropoxymethyl cellulose film subsequently removed from the molding by rinsing with cold water.

C_4—cast against air only.

TEST

These castings were tested for wettability by water and energy of wetting surfaces according to the following tests:

Test I—Contact Angle

The theoretical significance of contact angles and methods of measuring them are described in *Surface Active Agents*, Schwartz & Perry, 252–262, (Interscience, 1949). The contact angle is an inverse measure of the wettability of a solid surface by a liquid, with zero degrees representing perfect wetting and 180 degrees no wetting. According to this reference, contact angles of 90 degrees or greater loosely refer to unwettable surfaces. The contact angles in these experiments were measured photographically through a microscope/mirror system.

Test II

Another test developed to further differentiate between the wettability of two surfaces consists of spreading a drop of water into a ⅜" diameter circle and observing whether it remains spread or beads up into a drop again. A green food dye was incorporated into the distilled water and photomicrographs taken.

The results of tests I and II are presented in Table I.

TABLE I

Surface	Contact angle, θ, degrees	Work of wetting (1 plus cos θ)	⅜" circle spread test
C_1 (wax)	95.5	0.904	Beaded up to drop.
C_2 (PVAL)	16	1.96	Remained spread.
C_3 ((Methocel)	31.5	1.85	Do.
C_4 (air)	91	0.980	Beaded up to drop.
PVAL film*	28	1.88	Remained spread.

*For comparison, the contact angle of water on a *film* of the polyvinyl alcohol, (PVAL) dried 20 min. at 180 degrees F., is included in the table.

Test III

The surfaces C_1 to C_4 were then spray coated with a reactive 2-component commercial polyurethane paint (Micothane paint—exemplified by a mixture comprising 1 part by weight resin RS-350, 2 parts by weight pigment mix 7×8123 blue and 1 part by weight solvent S-816—Midland Div. of the Dexter Corp.) Paint adhesion was measured after 24 hours of room temperature drying by the standard ⅛" cross-hatch tape test, and by scraping the paint with a scalpel blade held perpendicular to the surface. The results are shown in Table II. (The ⅛" cross-hatch tape test is a field test commonly used to test adhesion of paint to a substrate; Lines are scribed through the dried paint film with a sharp instrument at ⅛" intervals vertically and horizontally to give a cross-hatched pattern. The number of squares coming off during cross-hatching is a measure of the degree of adhesion. A piece of Scotch tape is then adhered to the cross-hatch pattern and pulled off. Again, the loss of squares of paint is noted. A very similar test, known as the "General Electric test," is described in Principles of Surface Coating Technology, D. H. Parker, 487 (Interscience, 1965).

TABLE II

Surface	Cross hatch/tape test	Scalpel test
C_1 (wax)	Paint came off in sheets while scribing the cross-hatch pattern.	Paint peeled off in large sheets.
C_2 (PVAL)	Perfect adhesion	Perfect adhesion.
C_3 (Methocel)	do	Do.
C_4 (air)	do	Do.

NOTE.—"Perfect adhesion" above is described as follows: Cross-hatch/tape test.—No removal of paint during scratching of ⅛" cross-hatch pattern in paint coating or during subsequent removal of Scotch tape from cross-hatched coating. Scalpel test.—No separation of paint from substrate when scraping through paint into substrate with scalpel blade.

EXAMPLE 7

This example illustrates a practice of this invention with respect to molded, cellular polyurethanes. Additionally, this example demonstrates (a) the interfacial interaction between a claimed barrier layer material and a polyurethane composition in contact with said barrier layer applied over a wax, (b) the generation of a polyurethane plastic surface to which paint strongly adheres and (c) the ability to remove from the polyurethane plastic surface substantially all of the barrier layer material with water to leave a wax-free and oil-free polyurethane plastic surface having high wettability and strong paint adhesion in a practice of this invention.

The formulation described in Example 6 was modified by the addition of monofluorotrichloromethane to the polyol component of Example 6 such that the resulting mixture of the isocyanate component and modified polyol component contained 5.5 parts by weight of monofluorotrichloromethane per 100 parts by weight of the total mixture. This addition (to the polyol component) was accompanied by a change in the weight ratio of polyol to isocyanate components from 47.21/52.79 to 50.12/49.88. The latter weight ratio was used in this example. The addition of monofluorotrichloromethane did not alter the ratios of the other individual ingredients. The mold described in Example 6 was modified by adding a stainless steel liner for the bottom large flat surface and an aluminum plate cover. The stainless steel sheet was degreased with solvent, washed with an alkaline detergent solution,

rinsed with distilled water, and air dried. The heated mold was treated wherein aluminum sides of the mold were waxed, and the aluminum top cover was waxed and overcoated with polyvinyl alcohol (using the wax and polyvinyl alcohol described in Example 6), giving surfaces for comparison with the unaltered surface molded against the stainless steel.

115 gms. of the molding composition, prepared at the conditions described above and in Example 6, was charged to the mold and expanded (foamed) and cured in the closed mold to give the following series of test surfaces:

M_1—Molded against a waxed metal mold surface.
M_2—Molded against a polyvinyl alcohol film coated over the wax release agent, subsequently removed from the molding by rinsing with cold water.
M_3—Molded against thoroughly cleaned stainless steel.

Tests I–II–III

As described in Example 6 tests I and II to measure wettability and test III to measure paint adhesion were conducted on surfaces M_{1-3} and the results are tabulated below. The painted surfaces were prepared with the paint described in Example 6, using the procedure described in Example 6.

Surface	Contact angle, θ	Work of wetting (1 plus cos θ)	¾ circle spread test
M_3	71 degrees	1.33	Partially beaded up into an elongated L-shaped drop.
M_1 (wax)	83 degrees	1.12	Beaded up to drop.
M_2 (PVAL)	17 degrees	1.956	Remained spread.

NOTE.—The stainless steel sheet, upon being separated from the molding, required considerable peel force to separate it from the molding, and an area of the molding ¼" x 3" broke away from the molding and remained adhered to the stainless steel.

Surface	Cross hatch/tape test	Scalpel test
M_1 (wax)	Paint came off in sheets while scribing the cross hatch pattern.	Paint peeled off in large sheets.
M_2 (PVAL)	Perfect adhesion [1]	Perfect adhesion.[1]
M_3 (stainless steel)	do [1]	Do.[1]

[1] As defined in example 6.

EXAMPLE 8

A 2% solution of polyacrylic acid was prepared as follows:

	G.
Acrysol A–1 (containing 25% polyacrylic acid, 75% water) (1)	8.00
Water	42.95
Methanol	48.95
Igepal CA–630 (2)	0.10

[1] Acrysol A–1: Rohm and Haas Co. polyacrylic acid, less than 50,000 molecular wt., 25% in water, pH=2. Viscosity (Brookfield) 15 cp. at 5% conc., 320 cp. at 25% conc. cp.= centipoises. Acrysol is a registered trademark of the Rohm and Haas Co.
[2] Igepal CA–630: General Aniline and Film Co., octyl phenoxy poly (ethyleneoxy) ethanol containing 9–10 moles ethylene oxide per mole of hydrophobe. Igepal is a registered trademark of the General Aniline and Film Co.

The Acrysol A–1 was dissolved in the water at room temperature. The methanol and the Igepal CA–630 were then added and the solution wos stirred, giving a 2% solution of polyacrylic acid in 50/50 water/methanol with .1% wetting agent. A trace of water soluble food coloring was added to impart a deep green color to the solution.

A ½" x 4" x 10" cavity aluminum mold was prepared by coating the mold at 160° F. with a thin layer of Mitchell-Rand 1894EX–5 mold release, which is a paste dispersion of a mixture of hydrocarbon waxes and ester-type waxes in a hydrocarbon solvent, obtainable from the Mitchell Rand Mfg. Corp. Mitchell-Rand is a registered trademark of the Mitchell-Rand Mfg. Corp. The above paste wax was applied to the mold with a paint brush and was subsequently reduced to a thin layer by wiping off excess wax with a cloth. hTe wax layer was then overcoated with a film of the polyvinyl alcohol solution of Example 1, applied to the mold at 150° F. by means of a spray gun. In the same manner and under the same conditions a clean 1/16" x 4¼" x 10¼" steel plate was coated with a thin layer of Mitchell-Rand 1894EX–5 mold release and then overcoated with a film of the 2% polyacrylic acid solution. The polyacrylic acid solution was then allowed to dry to a smooth solid film about ½ mil thick.

A polyurethane foaming mixture was prepared as follows:

A-component (isocyanate)

A quasi-prepolymer was prepared by slowly adding at ambient temperature 56 lbs. of Dow Chemical Co. Voranol P–400 (polypropylene glycol of molecular weight about 400) to 444 lbs. of Moby Chemical Co. Mondur MR (reported to be a polymer of diphenyl methanediisocyanate having 2–5 isocyonate groups per molecule). The ingredients were mixed and allowed to react and stand for 24 hours before analysis and use.

B-component (polyol)

400.0 lbs. of Olin Poly–G–435–DM (reported to be a propoxylated mixture of 75% a-methyl glucoside and 25% glycerol having a hydroxyl number of about 435), obtainable from the Olin Mathieson Chemical Corp.

6.9 lbs. of Dow Corning DC–193, a silicone dispersing agent, obtainable from the Dow Corning Corp. (reported to be a copolymer of polydimethyl siloxane and a glycol).

2.8 lbs. of N,N,N',N'-tetramethyl-1,3-butane diamine.

68.6 lbs. monofluorotrichloromethane.

103.2 g. of the A-component and 96.8 g. of the B-component were mixed at room temperature with a high speed propellor agitator and 115 g. of the mixture was poured into the cavity of the prepared aluminum mold, now at 140° F. The steel plate at 140° F. whose surface had been treated as previously indicated was positioned, treated surface down, over the opening of the mold and then the mold cover placed on top of the steel plate. The mold was closed and clamped shut and the mixture was allowed to react and expand, filling the mold cavity. The mold was then placed in a 180° F. circulating air oven for 20 minutes. After removing the mold from the oven, the mold was opened and the molding was removed from the mold. The molding released easily from the mold and the steel plate and had a green color, indicating the polyacrylic acid coating remained on the molding. None of the green coating was discernible on the cavity surfaces of the mold or the steel plate. The green coating was easily removed by washing the molding with cold running water. Even after prolonged washing of the molding with water, the water wet or "sheeted out" on the surfaces of the molding.

The molding was given a final rinse with a small amount of distilled water (to prevent hard-water spotting) and allowed to dry. (Next, it was wiped with a clean cloth wet with hexane to remove finger prints or other grease films picked up during handling of the molding.) It was then spray-coated with Dexter Corp. (Midland Division) Micothane paint (a two-component reactive polyurethane paint of Example 6). The paint wet the surface of the molding giving a continuous uniform coating about 1 mil thick when dried. After air drying the paint and curing it 24 hours at room temperature, a test was made to determine the degree of adhesion between the paint film and the molding surface formed against the treated steel plate. The test used, the ⅛" cross-Scotch tape test, is described in Example 6. No loss of paint was observed during scoring of the cross-hatch pattern, during peeling of the tape from the cross-hatched film, or during a scraping of the cross-hatch with a scalpel blade held perpendicular to the painted surface.

EXAMPLE 9

The procedure of Example 8 was repeated in every detail, except that the coating of polyacrylic acid was

omitted and the following solution of polyvinyl pyrrolidone was used in its place.

	G.
Antara (General Aniline and Film) polyvinyl pyrrolidone type NP–K30 (40,000 mol. wt.). Antara is a registered trademark of the General Aniline and Film Corp.	2.00
Water	48.95
Methanol	48.95
Igepal CA–630	0.01
Green water soluble food dye	Trace

The behavior of the polyvinyl pyrrolidone film was identical to that of the polyacrylic acid film used in Example 8 in all respects and the paintability and paint adhesion test results obtained in accordance with the procedure described in Example 6 were indistinguishable over those of Example 8 when the molding was painted as described in Example 8.

EXAMPLE 10

The procedure of Example 9 was repeated in every detail except that the 2.00 g. of polyvinyl pyrrolidone in Example 9 was omitted and replaced by 2.00 g. of Mathieson, Coleman and Bell Soluble Starch, Catalog No. SX 930. Upon spraying the wax-coated steel plate with the starch solution, the starch solution wet the waxed surface completely but somewhat non-uniformly, tending to "bead-up" slightly. However, after molding the polyurethane molding and removing it from the mold, the starch coating remained with the molding and not with the steel plate and rinsed easily from the molding with cold running water, leaving a smooth molded surface. As in the case of the polyacrylic acid or polyvinyl pyrrolidone coatings, the washed surface was easily wet by water, which "sheeted out" on the washed molded surface. Upon painting the dried molding, as described in Example 8 a smooth continuous film of paint was obtained. About 8–10% of the cross-hatched paint pattern was removed from the molding during cross-hatching and peeling of the tape in accordance with the test procedure described in Example 6, vs. removal of 100% of the cross hatch pattern from the painted surface of the molding of Example 11. The cross-hatched paint scraped off the molded surface with moderate pressure on the scalpel blade.

EXAMPLE 11

For comparison purposes, the procedure of Example 8 was repeated in every detail except that no water soluble coatings was applied over the wax coated steel plate before filling the mold with polyurethane-foaming mixture (i.e. the use of the water soluble barrier layer was omitted). The polyurethane molding was thus molded directly against the waxed steel surface. The cured molding released easily from the mold, but it was noted that water beaded up into tight discrete droplets on the surface, formed against the wax coated steel, even after attempting to wash the wax from the molded surface with a clean cloth wet with hexane. A uniform coating of paint could not be applied to the molding surface formed against the wax coated steel, in accordance with the painting procedure described in Example 8 because the paint did not completely wet the molded surface. Instead, a bubbly, leather-grain painted surface was obtained. In the cross-hatch test conducted in accordance with the procedure of Example 6, 100% of the paint was removed during cross-hatching and peeling of the tape, and the paint flaked off easily with only slight pressure while being scraped with a scalpel. This example demonstrates the disadvantages of prior art procedure for molding polyurethane plastics which require subsequent painting or other treatments involving adherence to the molded surface.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described above and as defined in the appended claims.

What is claimed is:

1. A process for producing polyurethane moldings having surfaces free of adhesion inhibiting mold release agent comprising the steps of:
   (a) overcoating a mold, which has been coated with a hydrophobic mold-release agent, with a continuous, solid barrier layer of a water-soluble film forming material reactive with isocyanate groups;
   (b) passing into the mold a polyurethane molding composition containing reactive isocyanate groups;
   (c) polymerizing said polyurethane molding composition in contact with said barrier layer material containing a plurality of moieties reactive with isocyanate groups;
   (d) removing the resultant molding; and
   (e) washing the surface of said molding with water to substantially remove said water-soluble barrier layer.

2. The process of claim 1 in which said water-soluble film forming material contains hydroxy groups.

3. The process of claim 1 in which said water-soluble film forming material is polyvinyl alcohol.

4. The process of claim 1 in which said water-soluble film forming material is a partially hydrolyzed vinyl acetate polymer containing alcohol groups.

5. The process of claim 1 in which said polyurethane molding composition contains a blowing agent.

6. The process of claim 1 wherein said water-soluble, film forming material is polyacrylic acid or polymethacrylic acid.

7. The process of claim 1 wherein said water-soluble, film forming material is polyvinyl pyrrolidone.

8. The process of claim 1 wherein said water-soluble, film forming material is hydroxypropylmethyl cellulose.

9. The process of claim 1 wherein said moieties are selected from the group consisting of OH, COOH, NH_2, NHR, $CONH_2$, CONHR and mixtures thereof wherein R is a hydrocarbon radical with 1–12 carbon atoms.

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