PATENT SPECIFICATION (11) 1 590 512

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(21) Application No. 8738/78 (22) Filed 6 Mar. 1978 (19)

(31) Convention Application No. 7706758 (32) Filed 8 Mar. 1977 in

(33) France (FR)

(44) Complete Specification Published 3 Jun. 1981

(51) INT. CL.[3] C10M 3/22 //
C08G 65/26

(52) Index at Acceptance
C5F 101 129 353 362 401 630 672 759 B KG
C3R 27K8D 27K8E 27K8F 27K9D 27K9E 27K9F
C3Y B230 B262 B263 B284 F510

(54) ARTICLES OF PLASTICS MATERIAL

(71) We, SAINT-GOBAIN INDUSTRIES, a Body Corporate organised under the laws of the French Republic, of 62 Boulevard Victor Hugo, 92209 Neuilly Sur Seine, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The invention relates to a method for making films, sheets or plates of plastics material, which may be transparent and of high optical quality, in which a smooth support such as silicate glass, plastics material or polished metal is coated with an appropriate separation agent (i.e. a demoulding agent) and there is fed to the coated support a fluid reaction medium or solution which is allowed to solidify on the support before being detached.

In U.K. Patent Specification No. 1457686 there is described a process of this type in which there is used as a support an endless glass ribbon. As separating agent there may be used in this process stearates, silicones, fluorinated hydrocarbons, paraffins and waxes. Instead of an endless glass ribbon there also may be used as a support a ribbon of polished metal or plates of glass or plastics material of finite dimensions or further a train of aligned plates.

These separation agents have to be applied on the support in a separate operation after passage of the support through a washing machine.

The present invention is intended to provide separation agents which are soluble in water and which may be applied on the support by spraying, casting or any other method, for example in the last stage of machine washing of the support. The separation agents further should wet the surface of the support adequately and uniformly and allow to remain after drying a thin regular film of separation agent which, in its turn, should be wetted by the transparent material which is fed to the coated support. Further, the separation agent should neither produce surface faults in the film, sheet or plate of plastics material, nor compromise the intended use of the film, sheet or plate. Finally, the separation agent should fulfill its principal role, that is to say facilitating the separation of the plastics material from the support on which it is formed without this sheet being stretched or altered by an unsticking force which is too great.

United States Patent 3,803,068 describes the use as a separating agent, especially in the paper industry, of a copolymer of vinylether maleic anhydride which is added to a surfactant, that is to say a surface active agent or wetting agent of the general formula $R\text{-}O\text{-}(CH_2CH_2O)_n\text{-}X$ in which R is an alkyl, an isoalkyl, a phenyl-alkyl or an isoalkyl phenyl groups, n being from 0 to 5 and X being a sulphate ester or phosphate ester in the form of free acid, an ammonium salt or a salt of an alkali metal.

According to the present invention there is provided a method of making a film, sheet or plate of a plastics material in which a smooth support surface is coated with a separating agent and a fluid reaction medium or solution is applied to the coated surface and allowed to solidify to form the plastics material, the separating agent comprising an addition product of ethylene oxide having the general formula:

$$R_1\text{-}X\text{-}(C_2H_4O)_n\text{-}R_2$$

in which:

R_1 represents an alkyl group containing 8 to 18 carbon atoms or an alkyl-aryl group

containing 6 to 12 carbon atoms in the alkyl part,

R_2 represents one of the following groups:

SO_3M

PO_3M_2

$CO-CH(SO_3M)-CH_2COOM$

$CO-C_6H_4-COOM$

M being an alkali metal,

X represents one of the following atom or groups:

O, NH, CO–O or CO–NH

and n represents a whole number from 1 to 100.

The surface may be optically flat and the plastics material may be transparent.

The addition product of ethylene oxide may be the product resulting from the fixing of ethylene oxide on fatty acids, amides of fatty acids, alkanol amides of fatty acids, fatty amines or fatty alcohols, said products being esterified and neutralised in suitable manner by acids such as sulphuric acids, phosphoric acid or the dicarboxylic acids such as phthalic acid or further by maleic acid which is finally transformed to sulpho-succinic acid.

The fact that the derivatives of ethylene oxide are suitable as separating agents is surprising as similar combinations may be used for a purpose which is exactly oposite, that is to favour adherence between glass fibres and plastics material in articles of plastics material reinforced with glass fibres (see for example German Auslegeschrift No. 1,158,219).

In a preferred embodiment of the invention the separating agent is deposited on a glass sheet in an amount of 100 mg to 2.5 g per m^2. Advantageously it is used in the form of an aqueous solution of 0.1 – 1% by weight concentration.

The separating agents defined above are suitable for manufacture of sheets, films or plates made of a large variety of plastics materials.

In particular, they are highly suitable as separating agents when they are used in the manufacture of films or sheets of transparent polyurethane formed on supports of silicate glass. It is believed that owing to the use of separating agents according to the invention, the properties of the transparent plastics material film on the surface in contact with the casting support are influenced favourably, that is to say the casting surface is in certain respects improved. Thus for example the coefficient of friction is reduced and the creation of undesirable electrostatic charges is diminished or suppressed which reduces contamination by dust.

Methods according to the invention will be described in the following Examples, given by way of illustration.

Example 1

On a sheet of glass having an optically flat surface without faults, as obtained from the float process, heated to a temperature of about 80°C, there is deposited 10 cm^3/m^2 an aqueous solution containing 0.5% by weight of disodium dodecyl-polyglycol-ether-sulphosuccinate having on average 3 to 4 ethoxy groups per molecule and of formula:

$$C_{12}H_{25}-O-(C_2H_4O)_{(3-4)}-CO-CH(SO_3Na)-CH_2-COONa$$

The application may be carried out in a regular manner by spraying from a nozzle. The layer deposited is dried after about 30 seconds. On the glass sheet thus treated there is fed by means of an appropriate device a polyurethane film of a liquid composition comprising the following constituents:

- 1000 g of a polyether prepared by condensation of propylene oxide with a triol, having a molecular weight of about 450 and a content of free OH groups of 10.5 to 12%,
- 1000 g of a biuret of 1.6 hexamethylene-diisocyanate having a content of 21 to 22% of free N CO groups, and
- 0.5 g of dibutyltin dilaurate.

The polyurethane film thus applied is heated with the support to a temperature of about 80°C and maintained for about 6 minutes at this temperature, which leads to polymerisation to a solid sheet without modification of the geometrical shape of the film in the fluid state. Finally the support and the film of plastics material which covers it are returned to ambient temperature. After cooling the film may be easily separated from the support.

The force required to carry out this separation is about 0.3 to 0.6 kg/cm of sheet width, the force being exerted at a right angle to the support surface. If separation of such a sheet of plastics material was carried out without interposition of a separating agent to the glass sheet, the force necessary to obtain unsticking would reach about ten times this value, this is to say 2 to 5 kg/cm of sheet width, which would damage the sheet.

Example 2

The procedure of Example 1 is carried out but there is used as a separating agent an aqueous solution of disodium nonyl-phenyl-polyglycol-ether-sulphosuccinate of 0.5% by weight concentration having about 50 ethoxy groups per molecule and of formula:

$$C_9H_{19}-C_6H_4-O-(C_2H_4O)_{50}-CO-CH(SO_3Na)-CH_2-COONa$$

This solution is applied by spraying through a nozzle at 10 cm3/m2. The glass sheet may also be coated by immersion in the 0.5% solution and withdrawing it vertically before allowing it to dry.

Example 3

The procedure of Example 1 is carried out, but there is used as a separating agent a 0.5% by weight aqueous solution of disodium decyl-polyglycol-ether-phosphate containing about 20 ethoxy groups per molecule of formula:

$$C_{10}H_{21}-O(C_2H_4O)_{20}-PO_3Na_2$$

Example 4

The procedure of Example 1 is carried out but there is used as separating agent an aqueous solution of 0.5% by weight of sodium dodecyl-polyglycol-ether-sulphate containing on average 3 to 4 ethoxy groups per molecule of formula:

$$C_{12}H_{25}-O-(C_2H_4O)_{(3-4)}-SO_3Na$$

Example 5

The procedure of Example 1 is carried out but there is used as separating agent an aqueous solution of 0.5% by weight of sodium octadecyl-polyglycol-ether-phthalate containing about 25 ethoxy groups per molecule of formula:

$$C_{18}H_{37}-O-(C_2H_4O)_{25}-CO-C_6H_4-COONa$$

As in Example 1 the forces allowing, in the case of Examples 2 to 5, unsticking by vertical drawing of the sheet are of the order of 0.3 to 0.6 kg/cm sheet width. The sheet, after separation from its support, has an optical surface free from faults.

Example 6

A glass sheet serving as a support is prepared and coated with a separated agent as described in Example 1. On the glass sheet thus prepared there is deposited a film of UP 630 polyester resin of FARBWERKE HOECHST to which there is added 2% by weight of dibutylperoxide (BUTANOX of the firm AZKO) and 2% of an accelerator based on vanadium (VN2 of the OXYDO firm). After polymerisation, the film of plastics material formed is easily separated from the support.

Example 7

On a glass sheet provided with a separating agent according to Example 1 there is deposited a film having as a component Silicon 1200 of the GENERAL ELECTRIC Company. After hardening the film of silicone resin formed is easily separated from the support.

Example 8

There is used as a support a flat plate having parallel faces of polymethyl-methacrylate e.g. the product '('PLEXIGLAS" of ROHM UND HAAS). "PLEXIGLAS" is a Registered Trade Mark. On this support there is applied a separating agent as described in Example 3. On the support thus prepared there is fed a layer of epoxy resin having 2 components comprising 100 parts by weight of LEKUTHERM X 50 of BAYER and 18 parts by weight of hardener T 3 of BAYER. The layer is allowed to harden and it is then easily removed from the support in the form of a film.

Example 9

There is used as a support a sheet of 18-8 nickel-chrome steel, optically polished, on which there is applied one of the separating agents described in Example 1 and Example 3. On the support thus prepared there is fed the polyurethane film described in Example 1. When the layer has hardened by polymerisation, it is easy to separate the film from the support.

WHAT WE CLAIM IS:-

1. A method of making a film, sheet or plate of a plastics material in which a smooth support surface is coated with a separating agent and a fluid reaction medium or solution is applied to the coated surface and allowed to solidify to form the plastics material, the separating agent comprising an addition product of ethylene oxide having the general formula:

$$R_1-X-(C_2H_4O)_n-R_2$$

in which:

R_1 represents an alkyl group containing 8 to 18 carbon atoms or an alkyl-aryl group containing 6 to 12 carbon atoms in the alkyl part,

R_2 represents one of the following groups:

SO_3M

PO_3M_2

$CO-CH(SO_3M)-CH_2COOM$

$CO-C_6H_4-COOM$

M being an alkali metal,

X represents one of the following atom or groups:

O, NH, CO–O or CO–NH,

and n represents a whole number from 1 to 100.

2. A method according to Claim 1, in which the surface is optically flat and the plastics material is transparent.

3. A method according to Claim 1 or 2, in which the support surface is a surface of silicate glass, polished metal or a plastics material.

4. A method according to Claim 1, 2 or 3, in which the separating agent is applied to the surface in the form of an aqueous solution containing 100 mg to 2.5 g of separating agent per m^2 of the coated surface.

5. A method according to any preceding claim, in which the separating agent is applied to the surface in aqueous solution having a concentration from 0.1 to 1% by weight.

6. A method according to any preceding claim, in which the separating agent is disodium dodecyl-polyglycol-ether-sylphosuccinate containing an average 3 to 4 ethoxy groups per molecule.

7. A method according to any one of Claims 1 to 5, in which the separating agent is disodium nonyl-phenyl-polyglycol-ether-sulphosuccinate containing about 50 ethoxy groups per molecule.

8. A method according to any one of Claims 1 to 5, in which the separating agent is disodium decylpolyglycol-ether-phosphate containing about 20 ethoxy groups per molecule.

9. A method according to any one of Claims 1 to 5, in which the separating agent is sodium dodecyl-polyglycol-ether-sulphate containing on average 3 to 4 ethoxy groups per molecule.

10. A method according to any one of Claims 1 to 5, in which the separating agent is sodium octadecyl-polyglycol-ether-phthalate containing about 25 ethoxy groups per molecule.

11. A method according to any preceding claim, in which the film, sheet or plate is of a transparent polyurethane.

12. A method according to Claim 11, in which the support surface is of silicate glass and the fluid reaction medium comprises:

- 1000 parts by weight of a polyether resulting frm condensation of propylene oxide with a triol, having a molecular weight of about 450 and a content of OH groups of 10.5 to 12%,
- 1000 parts by weight of biuret of 1.6-hexamethylene diisocyanate having a content of 21 to 22% of free NCO groups,
- 0.5 parts by weight of dibutyltin dilaurate, which gives a film of polyurethane.

13. A method of making a film, sheet or plate of a plastics material, substantially as hereinbefore described with reference to the Examples.

14. Films, sheets and plates of plastics material, when made by a method according to any preceding claim.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1981.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.