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In-mould coating compositions and use thereof.

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Description

This invention relates to in-mould coating compositions, in-mould coating methods, and in one preferred aspect is concerned with providing a fast cure on a substrate such as fibre reinforced polymer (FRP).

US-A-4414173 describes in-mold coating compositions having a similar composition to the present invention as discussed below. Organic free radical peroxide initiators are specified. This document does not mention use of t-butyl-peroxyisobutyrate as an initiator.

JP-A-59065420 describes a varnish containing t-butyl-peroxyisobutyrate, which is hardened by heating at 120 °C for 30 minutes.

Aspects of the present invention are set out in the claims.

In particular, the invention provides the use of t-butyl per oxyisobuty rate as cure initiator or catalyst for an in-mould coating composition. The inventors have found that this particular compound can give a markedly and unexpectedly short cure time compared with other apparently similar cure initiators. Indeed, using from about 1.0 to 1.5 parts by weight of this catalyst per 100 parts by weight of in-mould composition, the inventors were in experiments able to obtain cure times lower than 20 seconds and as low as about 15 seconds without adverse effects on the flow and coverage of the coating composition on the substrate e.g. FRP article.

Cure temperatures of from 140-160 °C and particularly about 150 °C (300 °F) are preferred.

The basic in-mould composition is desirably based on an epoxy- and/or urethane-based oligomer having at least two acrylate groups per molecule, and one or more ethylenically-un saturated monomers copolymerisable therewith. Usually the latter includes unsaturated monomer having -CO- group (e.g. (methy)acrylate) in conjunction with another unsaturated monomer preferably having a vinyl- or allyl-type unsaturation (e.g. a styrene).

The composition for in-mould coating which we find gives good results, and which is used with t-butyl per oxyisobutyrate as initiator, comprises:

(a) 100 parts by weight of at least one polymerisable epoxy based oligomer or urethane based oligomer or mixture thereof having at least two acrylate groups and a weight average molecular weight of from about 250 to 1,500;
(b) from about 80 to 160 parts by weight of at least one polymerisable ethylenically unsaturated monomer;
(c) from about 10 to 120 parts by weight of at least one copolymerizable monoethylenically unsatuated compound having a -CO- group and a -NH₂, -NH and/or -OH group,
(d) from 0 to 90 parts by weight of polyvinyl acetate,
(e) from about 0.2 to 5 parts by weight of at least one zinc salt of a fatty acid having at least 10 carbon atoms,
(f) from about 0.01 to 1.0 part by weight of at least one accelerator for a peroxide initiator,
(g) from about 5 to 30 parts by weight of conductive carbon black,
(h) from about 50 to 155 parts by weight of a filler and
(i) from 0 to 120 parts by weight of at least one copolymerizable polyoxyalkylene glycol based oligomer having two acrylate groups.

Optionally and desirably, there additionally can be added to the foregoing composition (k) at least one calcium salt of a fatty acid having at least 10 carbon atoms in an amount of from about 0.2 to 5 parts by weight.

A t-butyl-peroxyisobutyrate initiator is used in the in-mold coating composition in an amount of up to about 5%, preferably up to 2%, by weight based on the weight of the polymerizable ethylenically unsaturated materials.

The present invention also provides a method which comprises in-mold coating a molded thermostat fiber reinforced polymer substrate with the above composition under pressure, at a temperature and for a time sufficient to cure said in-mold composition to form an adherent thermostat coating on said substrate.

Products of such methods are a further aspect of the invention.

The polymerizable epoxy based oligomer having at least two acrylate (or methacrylate or ethacrylate) groups is prepared by reacting acrylic acid, methacrylic acid or ethacrylic acid and so forth with an epoxy based oligomer or resin such as a Bisphenol A epoxy, a tetrabromo Bisphenol A epoxy, phenolic novolak epoxy, tetraphenylethylene epoxy, dicycloaliphatic epoxy and so forth. Mixtures of these epoxy based oligomers may be used. Of these materials it is preferred to use a diacrylate terminated Bisphenol A epoxy oligomer. They have weight average molecular weights of from about 500 to 1,500. These materials are well known. For more information on these materials see "Heat Resistant Vinyl Ester Resin," M. B. Laukaitis, Technical Bulletin, SC:116-76, Shell Chemical Company, June 1976 and Shell Chemical Company Tech-
The polymerizable urethane based oligomer having at least two acrylate (or methacrylate or ethacrylate) groups include a polysterurethane diacylate, a polyetherurethane diacylate or a polyesteretherurethane diacylate or other polyurethane oligomer having two acrylate groups. These materials may be made by reacting a polyetherdiol (e.g., a polypropylene ether diol), polyesterdiol (e.g., a polyethylene adipate diol) and/or a polyetherester diol (e.g., a polypropylene ether adipate diol) and so forth with a disocyanate like tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene disocyanate and the like in an amount sufficient to form a diisocyanate terminated polyurethane prepolymer which is then reacted with hydroxy propyl acrylate, hydroxy ethyl acrylate, hydroxy ethyl methacrylate and so forth to form the diacrylate terminated polyurethane oligomer or polymer. Mixtures of these acrylate terminated polyurethane oligomers may be used. Acrylate terminated polyurethane oligomers, e.g., curable by light, ultraviolet, electric beam and/or infrared and so forth, are well known, and sometimes are referred to as irradiation or radiation curable materials.

A copolymerizable ethylenically unsaturated monomer is used to copolymerize with and to crosslink the polymerizable oligomers and includes styrene (preferred), alpha methyl styrene, vinyl toluene, t-butyl styrene, chlorostyrene, methyl methacrylate, diallyl phthalate (with styrene or methyl methacrylate and the like) trially cyanurate, trially isocyanurate divinyl benzene, methyl acrylate and so forth and mixtures thereof. The unsaturated monomer is used in an amount of about 80 to 160 parts by weight per 100 parts by weight of the polymerizable oligomer.

For further copolymerization and crosslinking and to improved hardness of the resulting coating there is used in the in-mold coating composition a monoethylenically unsaturated compound having a

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-C-
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and having a -NH₂-, -NH- and/or -OH group. Examples of such monomeric compounds are hydroxyl propyl methacrylate (preferred), hydroxethyl methacrylate, hydroxy ethyl acrylate, hydroxy ethyl crotonate, hydroxypropyl acrylate, hydroxy polyoxyporopylene acrylate, hydroxy polyoxyporopylene methacrylate, hydroxy polyoxetylene methacrylate, acrylamide, methacrylamide, N-hydroxymethyl acrylamide, N-hydroxymethyl methacrylamide and so forth and mixtures of the same. These compounds are used in an amount of from about 10 to 120 parts by weight per 100 parts by weight of the polymerizable oligomer.

Polyvinyl acetate is employed in the in-mold composition to improve paint adhesion of the in-mold coating to the substrate. The polyvinyl acetate is employed in a minor amount by weight as compared to the total weight of the ethylenically unsaturated materials in the in-mold coating composition and sufficient for paint adhesion. The polyvinyl acetate is employed in an amount of from 0 to 90 parts by weight per 100 parts by weight of the polymerizable oligomer.

A zinc salt of a fatty acid having at least 10 carbon atoms, also, is employed in the in-mold coating composition and appears to function as a mold release agent and as a secondary accelerator for the cure. Fatty acids are well known. See "Organic Chemistry," Fieser and Fieser, D. C. Heath and Company, Boston, 1944, pages 88, 381-390, 398 and 401 and "Hackth's Chemical Dictionary," Grant, McGraw Hill Book Company, New York, 1969, page 261. Mixtures of zinc salts of the fatty acids can be used. Examples of some zinc salts are zinc palmitate, zinc stearate, zinc ricinoleate and the like. It is preferred to use the zinc salt of a saturated fatty acid such as zinc stearate. See, also, "Whittington's Dictionary Of Plastics," Whittington, Technomic Publishing Co., Inc., Stamford, Conn., 1968, pages 35, 102 and 261. The zinc salt is used in an amount from about 0.2 to 5 parts by weight per 100 parts by weight of the polymerizable oligomer.

An accelerator is used for the peroxide initiator and is a material such as a drier, e.g., cobalt octoate (preferred). Other materials which may be used are zinc naphthenate, lead naphthenate, cobalt naphthenate and manganese naphthenate. Soluble Co, Mn and Pb salts of linoleic acid, may also be used. Mixtures of accelerators may be used. The accelerator is used in an amount of from about 0.01 to 1 part by weight per 100 parts by weight of the polymerizable oligomer.

Conductive carbon black is used in the in-mold coating composition in an amount of from about 5 to 30 parts by weight per 100 parts by weight of the polymerizable oligomer.
A filler is used in the in-mold coating composition in an amount of from about 50 to 155 parts by weight per 100 parts by weight of the polymerizable oligomer. Examples of fillers are clay, MgO, Mg(OH)_2, CaCO_3, silica, calcium silicate, mica, aluminum hydroxide, barium sulfate, talc, hydrated silica, magnesium carbonate and mixtures of the same. The fillers should be finely divided. Of these fillers it is preferred to use talc. Fillers can afford the desired viscosity and flow to the in-mold composition for molding and contribute to the desired physical properties in the resulting thermostet in-mold coating. Fillers, also, may improve adhesion. However, care should be exercised in the use of high filler contents as this may give high viscosities and result in flow and handling difficulties.

There further can be employed in the in-mold coating composition a copolymerizable polyoxyalkylene glycol diacrylate compound having a weight average molecular weight of from about 250 to 5,000, in an amount of from about 0 to 120 parts by weight per 100 parts by weight of polymerizable oligomer.

Examples of said diacrylate compounds include triethylene glycol diacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol diacrylate, polypropylene glycol diacrylate, ethoxylated Bisphenol A diacrylate, ethoxylated Bisphenol A dimethacrylate, polyethylene glycol dimethacrylate or polyoxyethylene glycol dimethacrylate, polypropylene glycol dimethacrylate, polyethylene propylene glycol diacrylate, and so forth and mixtures thereof. These acrylates are made by reacting polyoxyalkylene glycols such as polyoxyethylene ether glycol with acrylic acid, methacrylic acid and the like. Since some of these reactive difunctional materials may be made by reacting unsaturated acids and alcohols, they may contain some OH and/or COOH groups.

Optionally and desirably also a calcium salt of a fatty acid having at least 10 carbon atoms, from about 0.2 to 5 parts by weight of calcium salt per 100 parts by weight of the polymerizable oligomer, can be used in the in-mold coating composition as a mold release agent and to control the rate of the cure. Fatty acids are well known, see above. Mixtures of calcium salts of the fatty acids can be used. Examples of some calcium salts are calcium stearate, calcium palmitate, calcium oleate and the like. It is preferred to use the calcium salt of a saturated fatty acid like calcium stearate.

The in-mold composition optionally may be additionally compounded with mold release agents, anti-degradants, UV- absorbers, paraffin wax, solid glass or resin micro-spheres, thickening agents, and the like. These compounding ingredients should be used in amounts sufficient to provide satisfactory results.

It is not desirable to use in the in-mold composition of this invention materials like fatty alcohol phosphates.

The ingredients of the in-mold composition should be readily mixed and handled at ambient or room temperature or temperatures below the polymerization temperature so that they may be readily pumped to the mold or injected into the same. The ingredients may be warmed or heated before or during mixing and mixed in steps to facilitate thorough mixing, dispersion and solution of the same. Also, the bulk of the ingredients may be thoroughly mixed and the remainder including the catalyst separately mixed and then both pumped to a mixing head to be mixed together and then injected into the mold.

The initiator is preferably added to the composition and thoroughly mixed therewith just before molding.

All of the ingredients of the in-mold coating composition should be kept dry or have a minimal amount of moisture or the water content should be controlled to obtain reproducible results and to prevent pore formation.

Mixing of the ingredients of the in-mold coating composition should be thorough. Injection or compression, transfer molding, or other molding apparatus or machines can be used for the in-mold coating. The in-mold coating composition may be applied to the substrate and cured e.g. at temperature of about 150 °C and at pressure of about 7000 kPa (about 300 °F and 1000 psi (*F values original)).

The processes and products may be used e.g. in the manufacture of laminates like automobile parts such as grille and headlamp assemblies, deck hoods, fenders, door panels and roofs as well as in the manufacture of food trays, appliance and electrical components, furniture, machine covers and guards, bathroom components, structural panels and so forth. The glass fiber reinforced thermostet plastic (FRP) such as the polyester resin or vinyl ester resin, styrene and glass fiber composition substrate to which the in-mold composition is applied can be a sheet molding compound (SMC) or a bulk molding compound (BMC), or other thermo-setting FRP material as well as a high strength molding compound (HMC) or a thick molding compound (TMC). The FRP substrate can have from about 10 to 75 percent by weight of glass fibers. The SMC compound usually contains from about 25 to 30 percent by weight of glass fibers while the HMC compound may contain from about 55 to 60 percent by weight of glass fibers. The glass fiber reinforced thermostet plastic (FRP) substrate can be rigid or semi-rigid (may contain a flexibilizing moiety such as an adipate group in the polyester). The substrate, also, may contain other flexibilizing polymers, the elastomers and plastomers, such as the styrene-butadiene block copolymers.

For more information on in-mold coating, see U.S. Patent Nos. 4,515,710 and 4,534,888.
The following Example will serve to illustrate the invention to those skilled in the art.

**EXAMPLE**

In-mold compositions were prepared, mixed and molded onto an FRP substrate. The in-mold compositions and results obtained are shown below:

<table>
<thead>
<tr>
<th>Component I (In-Mold Comp.)</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low profile additive LP-90 (40% by wt. of polyvinyl acetate in styrene)</td>
<td>25.00</td>
</tr>
<tr>
<td>Hydroxy propyl methacrylate (ROCRYL 410)</td>
<td>30.00</td>
</tr>
<tr>
<td>Styrene</td>
<td>45.35</td>
</tr>
<tr>
<td>2% benzoquinone in styrene</td>
<td>7.00</td>
</tr>
<tr>
<td>Zinc stearate</td>
<td>1.85</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>0.45</td>
</tr>
<tr>
<td>A dispersion of cobalt octoate in mineral oil, containing 12% cobalt. (Cobalt hex-cem, Hex-cem is a trade mark of Mooney Chemicals.)</td>
<td>0.15</td>
</tr>
<tr>
<td>Acrylate terminated epoxy based oligomer or resin of Bisphenol A (Ebecryl 3790-15S, 15% styrene + 85% Ebecryl)</td>
<td>117.65</td>
</tr>
<tr>
<td>Conductive furnace carbon black (Vulcan XC-72R)</td>
<td>8.50</td>
</tr>
<tr>
<td>Ground talc (WC&amp;D 4404 Talc)</td>
<td>80.00</td>
</tr>
</tbody>
</table>

About 1.5 parts by weight of the various catalyst components listed in the table below per 100 parts of weight of Component I (basic in-mold composition) was used.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Half Life One-Hour</th>
<th>Gel Time</th>
<th>Hot Strength</th>
<th>Molded Performance</th>
<th>Cure Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Butylperoxy Isobutyrate</td>
<td>102</td>
<td>5.6 min</td>
<td>Good</td>
<td>Good</td>
<td>Normal</td>
</tr>
<tr>
<td>t-Butylperoxy Maleic Acid</td>
<td>110</td>
<td>&gt; 30.0 min</td>
<td>None</td>
<td>None</td>
<td>No Cure</td>
</tr>
<tr>
<td>t-Butylperoxy Acetate</td>
<td>123</td>
<td>8.7 min</td>
<td>Good</td>
<td>Good</td>
<td>Normal</td>
</tr>
<tr>
<td>t-Butylperoxy Benzoate</td>
<td>125</td>
<td>9.2 min</td>
<td>Good</td>
<td>Good</td>
<td>Normal</td>
</tr>
<tr>
<td>t-Butylperoxy Neodeconate</td>
<td>66</td>
<td>4.1 min</td>
<td>Poor</td>
<td>None</td>
<td>Blistered</td>
</tr>
<tr>
<td>t-Butylperoxy Pivalate</td>
<td>76</td>
<td>3.4 min</td>
<td>Poor</td>
<td>None</td>
<td>Blistered</td>
</tr>
<tr>
<td>t-Butylperoxy Octoate</td>
<td>95</td>
<td>3.9 min</td>
<td>Poor</td>
<td>Good</td>
<td>Normal</td>
</tr>
</tbody>
</table>

The above Example shows that t-butyl peroxyisobutyrate gave superior properties including a cure time at 300°F of only 15 seconds.

While mixtures of one or more peroxide catalysts with t-butyl peroxyisobutyrate may be used, the advantage of using t-butyl peroxyisobutyrate may be diluted or lost.
weight of from about 250 to 1,500,
(b) from about 80 to 160 parts by weight of at least one copolymerizable ethylenically unsaturated
monomer,
(c) from about 10 to 120 parts by weight of at least one copolymerizable monoethylenically
unsaturated compound having a -CO- group and a -NH₂, -NH- and/or -OH group,
(d) from 0 to 90 parts by weight of polyvinyl acetate,
(e) from about 0.2 to 5 parts by weight of at least one zinc salt of a fatty acid having at least 10
carbon atoms,
(f) from about 0.01 to 1.0 part by weight of at least one accelerator for a peroxide initiator,
(g) from about 5 to 30 parts by weight of conductive carbon black,
(h) from about 50 to 155 parts by weight of a filler,
(i) from 0 to 120 parts by weight of at least one copolymerizable polyoxyalkylene glycol based
oligomer having two acrylate groups and,
(j) a t-butyl peroxysobutyrate initiator in an amount of up to about 5%, preferably not more than 2%,
by weight based on the weight of the polymerizable ethylenically unsaturated materials and
optionally,
(k) at least one calcium salt of a fatty acid having at least 10 carbon atoms in an amount of from
about 0.2 to 5 parts by weight.

2. A method which comprises in-mold coating a molded thermoset fiber reinforced polymer substrate
with the composition of claim 1 under pressure, at a temperature and for a period of time sufficient to cure
said in-mold composition to form an adherent thermoset coating on said substrate.

3. A product produced by the method of claim 2.

4. A composition according to claim 1, comprising:
   I. (basic in-mold composition, all parts by weight, approximately)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>40% by weight of polyvinyl acetate in styrene</td>
<td>25.00</td>
</tr>
<tr>
<td>Hydroxypropyl methacrylate</td>
<td>30.00</td>
</tr>
<tr>
<td>Styrene</td>
<td>45.35</td>
</tr>
<tr>
<td>2% benzoquinone in styrene</td>
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</tr>
<tr>
<td>Calcium stearate</td>
<td>0.45</td>
</tr>
<tr>
<td>A dispersion of cobalt octoate in mineral oil, containing 12% cobalt</td>
<td>0.15</td>
</tr>
<tr>
<td>Acrylate terminated epoxy based oligomer or resin of Bisphenol A (containing 15% styrene)</td>
<td>117.65</td>
</tr>
<tr>
<td>Conductive carbon black</td>
<td>8.50</td>
</tr>
<tr>
<td>Ground talc</td>
<td>80.00</td>
</tr>
</tbody>
</table>

and

II. Ratio of about 1.0 to 1.5 parts by weight of catalyst or initiator (Part II) per 100 parts by weight of
Component I where said catalyst or initiator comprises essentially t-butyl peroxysobutyrate.

5. A method which comprises in-mold coating a molded thermoset or resin-styrene-glass fiber composi-
tion with a thermosetting in-mold coating composition according to claim 4 under pressure, at a
temperature and for a period of time sufficient to cure said in-mold composition to form an adherent
thermoset coating on said molded thermoset or resin glass fiber composition.

6. The product produced by the method of claim 5.

7. A laminate comprising an adherent, thermoset in-mold coating composition according to claim 4 in-
mold coated onto a thermoset polyester-styrene-glass fiber composition.
Patentansprüche

1. Zusammensetzung, die sich als Zusammensetzung für wärmehärtbare Beschichtungen eignet, umfassend:
   (a) 100 Gewichtsteile zumindest eines polymerisierbaren Oligomers auf Epoxid- oder Oligomers auf Urethan-Basis oder eines Gemischs davon mit zumindest zwei Acrylatgruppen und einem durchschnittlichen Molekulargewicht von ungefähr 250 - 1500,
   (b) ungefähr 80 bis 160 Gewichtsteile zumindest eines kopolymerisierbaren, ethylenisch ungesättigten Monomers,
   (c) ungefähr 10 bis 120 Gewichtsteile zumindest einer kopolymerisierbaren, monoethylenisch ungesättigten Verbindung mit einer -CO- Gruppe und einer -NH₂, -NH- und/oder -OH Gruppe,
   (d) 0 bis 90 Gewichtsteile Polyvinylacetat,
   (e) ungefähr 0,2 bis 5 Gewichtsteile zumindest eines Zinksalzes einer Fettsäure mit zumindest 10 Kohlenstoffatomen,
   (f) ungefähr 0,01 bis 1,0 Gewichtsteile zumindest eines Beschleunigers für einen Peroxidinitiator,
   (g) ungefähr 5 bis 30 Gewichtsteile von leitfähigem Ruß,
   (h) ungefähr 50 bis 155 Gewichtsteile eines Füllers,
   (i) 0 bis 120 Gewichtsteile zumindest eines kopolymerisierbaren Oligomers auf Polyoxymethylenglykol-Basis mit zwei Acrylatgruppen, und
   (j) einen t-Butylperoxoctoat-Initiator in einer Menge von bis zu ungefähr 5 Gew.-% bezogen auf das Gewicht des polymerisierbaren, ethylenisch ungesättigten Materials, und wahlweise
   (k) zumindest ein Kalkiumsalz einer Fettsäure mit zumindest 10 Kohlenstoffatomen in einer Menge von ungefähr 0,2 bis 5 Gewichtsteilen.

2. Verfahren, umfassend die in-mold-Beschichtung eines geformten, wärmegehärteten, faserverstärkten Polymersubstrats mit der Zusammensetzung nach Anspruch 1 unter Druck, bei einer Temperatur und über eine Zeitspanne, die ausreichen, um diese in-mold-Zusammensetzung zu einer anhaftenden, wärmegehärteten Beschichtung auf dem Substrat zu härten.


4. Zusammensetzung nach Anspruch 1, umfassend:
   I. (Eine In-mold-Basis-Zusammensetzung, alle Anteile sind Gewichtsteile, näherungsweise)

<table>
<thead>
<tr>
<th>Bestandteil</th>
<th>Anteile</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 Gew.-% Polyvinylacetat in Styrol</td>
<td>25,00</td>
</tr>
<tr>
<td>Hydroxypropylmethacrylat</td>
<td>30,00</td>
</tr>
<tr>
<td>Styrol</td>
<td>45,35</td>
</tr>
<tr>
<td>2% Benzochinon in Styrol</td>
<td>7,00</td>
</tr>
<tr>
<td>Zinkstearat</td>
<td>1,85</td>
</tr>
<tr>
<td>Kalziumstearat</td>
<td>0,45</td>
</tr>
<tr>
<td>Dispersion von Kobaltooctoat in Mineralöl, enthält 12% Kobalt</td>
<td>0,15</td>
</tr>
<tr>
<td>Oligomer oder Harz auf Bisphenol A-Epoxybasis mit Acrylat-Endgruppen (enthält 15% Styrol)</td>
<td>117,65</td>
</tr>
<tr>
<td>Leitfähiger Ruß</td>
<td>8,50</td>
</tr>
<tr>
<td>Gemahlener Talk</td>
<td>80,00</td>
</tr>
</tbody>
</table>

   und

   II. einen Anteil von ungefähr 1,0 bis 1,5 Gewichtsteilen an Katalysator oder Initiator (Anteil II) pro 100 Gewichtsteile an Komponente I, wobei der Katalysator oder Initiator im wesentlichen t-Butylperoxyisobutat umfaßt.

EP 0 504 528 B1


Revendications

1. Composition utilisable comme revêtement thermorécissable, comprenant :

(a) 100 parties en poids d'au moins un oligomère polymérisable à base d'époxy ou un oligomère polymérisable à base d'uréthane, ou un mélange des deux, ayant au moins deux groupes acrylate et un poids moléculaire moyen d'environ 250 à 1500;
(b) d'environ 80 à 160 parties en poids d'au moins un monomère polymérisable éthyléniquement insaturé;
(c) d'environ 10 à 120 parties en poids d'au moins un composé monoéthyléniquement insaturé ayant un groupement -CO- et un groupement -NH₂, -NH- et/ou -OH;
(d) de 0 à 90 parties en poids de polyvinylacétate;
(e) d'environ 0,2 à 5 parties en poids d'au moins un sel de zinc d'un acide gras ayant au moins 10 atomes de carbone;
(f) d'environ 0,01 à 1,0 partie en poids d'au moins un accélérateur pour un initiateur au peroxyde;
(g) d'environ 5 à 30 parties en poids de noir de carbone conducteur;
(h) d'environ 50 à 155 parties en poids d'un matériau de remplissage;
(i) de 0 à 120 parties en poids d'au moins un oligomère copolymérisable à base de polyoxyalkyle glycéol ayant deux groupes acrylate; et
(j) un initiateur au t-butyl-peroxyisobutyrate en une quantité allant jusqu'à environ 5 %, de préférence pas plus de 2 % en poids, sur la base du poids des matières polymérisables éthyléniquement insaturées; et en option
(k) au moins un sel de calcium d'un acide gras ayant au moins 10 atomes de carbone en une quantité d'environ 0,2 à 5 parties en poids.

2. Procédé comprenant l'enduction inverse d'un substrat moulé en polymère thermorécissable renforcé par des fibres avec la composition selon la revendication 1, sous une pression, à une température et pendant une durée suffisantes pour durcir ladite composition d'enduction inverse et former un revêtement thermorécissable adhérant sur ledit substrat.

3. Produit fabriqué selon le procédé de la revendication 2.

4. Composition selon la revendication 1, comprenant

I. (composition de base pour enduction inverse, toutes teneurs en poids, environ)

<table>
<thead>
<tr>
<th>Ingrédient</th>
<th>Parties</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 % en poids de polyvinyl-acétate dans le styrène</td>
<td>25,00</td>
</tr>
<tr>
<td>Hydroxypropyl-méthacrylate</td>
<td>30,00</td>
</tr>
<tr>
<td>Styrène</td>
<td>45,35</td>
</tr>
<tr>
<td>2% de benzoquinone dans le styrène</td>
<td>7,00</td>
</tr>
<tr>
<td>Stéarate de zinc</td>
<td>1,85</td>
</tr>
<tr>
<td>Stéarate de calcium</td>
<td>0,45</td>
</tr>
<tr>
<td>Une dispersion d'octoate de cobalt dans une huile minérale, contenant 12 % de cobalt.</td>
<td>0,15</td>
</tr>
<tr>
<td>Oligomère à base d'époxy à terminaisons acrylate ou résine de type Bisphénol A (contenant 15 % de styrène)</td>
<td>117,65</td>
</tr>
<tr>
<td>Noir de carbone conducteur</td>
<td>8,50</td>
</tr>
<tr>
<td>Talc broyé</td>
<td>80,00</td>
</tr>
</tbody>
</table>

et

II. Un rapport d'environ 1,0 à 1,5 parties en poids de catalyseur ou initiateur (Partie II) pour 100 parties en poids du composant I, ledit catalyseur ou initiateur comprenant essentiellement du t-butyl-
péroxyisobutyrate.

5. Procédé comprenant l'enduction inverse d'une composition moulée thermodurcie ou composition résine-styrène-fibres de verre avec la composition selon la revendication 4, sous une pression, à une température et pendant une durée suffisantes pour durcir ladite composition d'enduction inverse et former un revêtement thermodurci adhérant sur ladite composition moulée thermodurcie ou composition résine-styrène-fibres de verre.

6. Produit fabriqué selon le procédé de la revendication 5.

7. Stratifié comprenant une composition d'enduction inverse thermodurcie adhérante selon la revendication 4, obtenue par enduction inverse sur une composition thermodurcie polyester-styrène-fibres de verre.