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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4:
C08F 283/000, 285/00
C08K 3/20, C08L 51/08

A1

(11) International Publication Number: WO 89/05316

(43) International Publication Date: 15 June 1989 (15.06.89)

(21) International Application Number: PCT/US87/05224

(22) International Filing Date: 10 December 1987 (10.12.87)


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(81) Designated States: BE (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent), SE (European patent).

(54) Title: EPOXY ESTER URETHANE GRAFT ACRYLIC WATER-BASED PRIMER SURFACES

(57) Abstract

Dispersion of an epoxy ester urethane graft acrylic in water with a total of no more than 5% of organic volatiles and amines. These dispersions can be used in primer compositions for metal substrates having a minimum of organic solvent emissions and which can crosslink at temperatures from 140-200°C, giving a good balance of hardness, flexibility, humidity, corrosion resistance and anti-chipping properties.
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TITLE
Epoxy Ester Urethane Graft Acrylic
Water-Based Primer Surfaces

CROSS REFERENCE TO RELATED APPLICATIONS
This application is a continuation-in-part
application of Serial No. 901,567, filed August 29,
1986.

BACKGROUND
This invention relates to epoxy ester
urethane polymers having acrylic portions grafted
thereunto. More particularly, it relates to coating
compositions containing such polymers.

U.S. Patent 4,302,373 - Steinmetz (Nov. 24,
1981) describes water-borne coating compositions of
epoxy resin, polymeric acid and tertiary amine,
wherein the epoxy functionality is partially capped
with a carboxylic acid polymer to form a hydrogel.
Coating compositions made therefrom are taught for use
in can coatings and for automotive and paper coatings.

An acetic acid-neutralized aqueous
polyaminoamido resin made using dimeric fatty acids is
disclosed in European Patent Application Publication
60581 of September 22, 1982 - Guenter et al. (Akzo).

Epoxy graft acrylic water-based primer
surfacers are claimed in U.S. 4,564,648, of
January 14, 1986 - Huybrechts and Vleminckx, but they
do not include urethane grafts. The present invention
is an improvement over this one in giving better chip
resistance over well cured electrocoats, for
instance. This requires a careful balance of
flexibility and hardness in different portions of the
polymer.

Other aqueous epoxy coating compositions also
outside the present invention are disclosed in U.S.
Patents
SUMMARY OF THE INVENTION

The present invention provides a dispersion in water, in percentages by weight based on the total dispersion, of:

(a) 10-60% of an epoxy ester urethane graft acrylic polymer formed by reacting 5-30% of an epoxy ester urethane polymer formed by reaction of n moles of a difunctional epoxy resin with terminal oxirane groups and a number average molecular weight (Mn) of 300-5000, n-1 moles of a diacid-functional linear urethane ester, and 2 moles of a monofunctional acid to form a reaction product, onto which is grafted 5-30% of an acrylic monomer by using a peroxide or azo initiator, to produce said epoxy ester urethane acrylic polymer with a Mn = 1000-50,000 and an acid number of 30-150,

(b) tertiary amines being added to an extent equivalent to neutralizing 50-200% of the moles of acid functionality,

(c) organic solvents, such dispersion having not more than 10% volatile organic solvents plus amines, and

(d) balance water.

The epoxy ester graft acrylic polymers of (a) above, and methods of making them, are different aspects of the invention.

DETAILED DESCRIPTION

The present invention is made possible by a new method of synthesis of an epoxy ester urethane
graft acrylic polymer. The process involves the synthesis of a linear epoxy ester formed by reaction at 80-190°C of an oxirane terminated bisphenol A epoxy resin with aliphatic diacid-functional linear urethane esters and monoacids in approximately stoichiometric proportions so that all the oxirane groups and acid groups have reacted. The reaction is done in a minimum amount of an organic solvent, preferably aromatic for ease of stripping, preferably using a small percentage of a tertiary amine as catalyst. In a second stage an acid functional acrylic is grafted onto the epoxy ester urethane using a peroxide or azo initiator. Grafting onto the epoxy ester urethane is believed to go via hydrogen abstraction of activated carbon-hydrogen bonds. In a third stage the acid functionality on the epoxy ester urethane is neutralized with a tertiary amine (50-200% neutralization), the polymer is dispersed in deionized water and the excess organic solvents are distilled off.

These epoxy ester urethane acrylic dispersions then contain a minimum of organic solvents, so as to be able to formulate primer compositions, preferably with no more than 5% organic volatiles, including amines.

When combined with water soluble or dispersible crosslinkers, like hexamethoxymethylmelamine, pigments and extenders, primer surfacers can be formulated which show good corrosion resistance over bare steel, an excellent balance of hardness, flexibility, improved anti-chipping properties, good topcoat hold-out and appearance.

These primer surfacers can be baked for 30 min at from 160°C to 200°C, still retaining their
basic properties. The primers can be applied by conventional or electrostatic spraying. To further improve application and flow properties, rheology control agents and flow agents can be used. Silica or clay pastes are quite successful for rheology control to prevent pinholing and sagging, and water soluble or dispersible linear or branched polyethylene glycols or polypropylene glycols are efficient for flow properties. The primer surfacers show excellent initial and wet adhesion over bare steel and cathodic electrodeposited primers. Adhesion and hold-out of conventional topcoats (polyester, alkyd, acrylic) is very good over broad temperature ranges. Hold-out is the resistance to interpenetration at the interface between the layers of primer surfacer and topcoat applied in organic solvents.

In the scope of the invention and the teachings of the examples, more or less equivalent substitutions for various ingredients can be made as follows. The lists are illustrative and not complete.

Alternatives for isocyanate:

- hexamethylene diisocyanate
- isophorone diisocyanate
- hydrogenated bisphenyl methane diisocyanate
- trimethyl hexane diisocyanate
- toluene diisocyanate
- bisphenyl methane diisocyanate
- m or p xylylenediisocyanate

Alternatives for glycols:

- ethylene glycol
- propylene glycol
- 1,4 or 1,3 butane diol
- neopentyl glycol
- hexanediol

HDI
IPDI
HPMIDI
TMHIDI
TDI
PMDI
m or p XDI
EG
DG
1,4 or 1,3 BD
NPG
HD
trimethyl pentane diol
polyethylene glycols (various MW)
polypropylene glycols (various MW)
cyclohexane dimethanol
hydrogenated bisphenol A
hydrogenated bishphenol F

Alternatives for anhydrides:
succinic anhydride
maleic anhydride
phthalic anhydride
tetrahydro phthalic anhydride
hexahydro phthalic anhydride
methyl hexahydro phthalic anhydride

Alternative for graft monomers:
reaction product of acrylic acid with equimolar Cardura E (glycidoxy ester of versatic acid product of Shell)
methyl, ethyl, butyl, isobutyl, ethylhexyl and lauryl methacrylates and acrylates

styrene
vinyl toluene
hydroxy ethyl, hydroxy propyl, and hydroxy butyl methacrylates and acrylates

Acrylic acid, metacrylic acid, B-carboxyethyl acrylate

maleic acid
fumaric acid
2-acylamido 2-methypropane sulfonic acid
methacryloxyethyl phosphate
N-methylolacrylamide, N-butoxy methylolacrylamide and N-methoxy methylolacrylamide (MAAM, BMAAM and MMAM)

acrylamide and methacrylamide (AM and MAM)

The following are examples describing manufacture of epoxy ester urethane graft acrylic dispersions. Parts, proportions and percentages are by weight except where indicated otherwise.

**EXAMPLE 1**

**Epoxy Ester Urethane Propolymer**

Into a 6L flask equipped with a thermometer, stirrer, condenser, nitrogen inlet and dropping funnel, are introduced in parts by weight:

- toluene (T) 150
- NPG 832

Water is removed azeotropically by refluxing 60 min. with a water separator, then switch to direct reflux in a nitrogen atmosphere, and add:

- HDI 1176
- T 52

over 30 min. refluxing until free isocyanate has disappeared, as determined by infrared (IR) techniques. Then add:

- SA 200
- dimethylcyclohexylamine (DMCA) 4.4
- T 17.8

Reflux until anhydride IR absorption has disappeared and the acid number (AN) is about 50.

Then add:

- diethyleneglycolmonobutyl ether (DEBPE) 385
- Epon 1001 epoxy resin from Shell 1800
- Dimethylolpropionic acid DMPA 268
DMCA 6.8
DEBE 355
Reflux until AN < 2
Then add:
Isopropanol (IP) 210
to thin the product down to the desired level

Example 2

Acrylic Graft on Epoxy Ester Urethane

Thinned epoxyester urethane prepolymer, product of Ex. 1 1040
Heat at slight reflux to 120°C
Then add
Di-t-butylperoxide (DTBP) 2
IP 8
and start feeding over 3 hours at 120°C
S 81
MMA 81
BA 445.5
HEA 81
AA 121.5

20 t-butyl peroxy 2-ethylhexanoate (BPEH) 12
mercaptoethanol (ME) 3
IP 25
Then add solvent, rinsing to clean the lines
DEBE 20
Hold 15 min. at reflux.
Then add over 30 min.
BPEH 3
DEBE 27

30 Rinse the lines with DEBE 10
and hold at reflux. Then strip off volatiles under vacuum.
Then add
DMEA 127.7

Then add neutralized
deionized water (DW) 3473.3
over 20 min. and disperse to produce a product with
31.1% solids and pH of 8.04.

**Example 3**

**Epoxy Ester Urethane Propolymer**

Add as indicated to reaction flask as in Ex. 1

NPG 416
T 75

Reflux to remove water azeotropically, then
add with nitrogen atmosphere
dibutyltin dilaurate (DBTDL) 1.15
Then add over 30 min and hold at reflux until
the isocyanate IR indication has disappeared.
HDI 588
T 26

Then add and hold at a slight reflux until AN
is about 50.
SA 100
DMCA 2.2
T 8.9

Then add and hold at reflux until AN < 2
xylene(X) 192
Epon 1001 900
DMPA 120
DMCA 3.4
X 178

**Example 4**

**Epoxy Ester Urethane Graft Acrylic**

Add as in Ex. 2:

Epoxy ester urethane of Ex. 3 1110
Heat at reflux to 140 - 145°C
Then feed over 2 hours at reflux
S 180
MMA 180
BA 360
HEA 72
AA 108
\(t\)-butylperbenzoate (BPB) 18
X 25
ME 5

Then add solvent, rinsing to clean the lines
X 5
and hold for 15 min.

Then feed over 45 min.
BPB 3
X 7

rinsing step
X 5
and hold for 45 min.

Cool to 110°C, then add and mix for 15 min.
DMEA 133.5

Add over 20 min and disperse
DW 3200

Strip off all X and T azeotropically to give
a product of 39.3% solids and pH 8.34

Example 5

**Epoxy Ester Urethane Prepolymer**

Thinned epoxy urethane
prepolymer Ex.1 1157

Heat to 120-125°C

Add and heat to 135-140°C

Cardura E from Shell 522.5

Feed over 3 hrs.

S 182.2
MMA 182.2
AA 328.1
BPB 24.3
DEBE 25.7

Rinse lines with
DEBE 20

Hold 60 min at 135-140°C to strip
Low-boiling volatiles, T and IP
Add over 15 min
DMEA 197.6.
Add over 30 min while dispersing
DW 4,965.4
to give a product of 24.8% solids and pH 8.

Example 6
Epoxy ester urethane of Ex. 1 142.7
Heat to 120°C and add over 3 hrs.
S 160
MMA 160
BA 280
AA 120
HEA 80
15

b-butyl peroxy 2 ethyl hexanoate 
(BPEH) 16
ME 5
IP 20
Rinse lines with
(DEGMBE) 20

diethylene glycol 
monobutylether
Feed over 30 min
BPEH 4
DEGMBE 26
20

Hold for 30 min. Then strip off low boiling
volatiles under vacuum
Add and mix 10 min.
DMEA 141
Add over 20 min. and disperse
DW 4,140
to obtain a product of 29.8% solids and pH 7.7

Following are examples describing manufacture 
of paints (with no more than 5% organic volatiles), 
application and properties:
EXAMPLE 7

Resin dispersion of Example 2

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>DW</td>
<td>6.08</td>
</tr>
<tr>
<td>DMEA</td>
<td>0.29</td>
</tr>
<tr>
<td>Surfynol 104 E anti-foam anti-cratering agent</td>
<td>1.84</td>
</tr>
<tr>
<td>Pluriol P 900 polypropylene oxide mol. weight 900 (reactive diluent)</td>
<td>2.26</td>
</tr>
<tr>
<td>Cymel 303 hexamethoxyxymethyl-melamine</td>
<td>4.20</td>
</tr>
<tr>
<td>Aerosil 200 fumed silica</td>
<td>0.87</td>
</tr>
<tr>
<td>Blanc Fixe barium sulfate</td>
<td>10.13</td>
</tr>
<tr>
<td>30 Aluminum silicate</td>
<td>2.56</td>
</tr>
<tr>
<td>Titanium dioxide pigment</td>
<td>6.73</td>
</tr>
<tr>
<td>Carbon black</td>
<td>0.034</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>0.145</td>
</tr>
<tr>
<td>Deionized water</td>
<td>3.941</td>
</tr>
</tbody>
</table>

Pigment to binder ratio (P/B) = 74.3 / 100
Binder ratio: 76.5/15.3/8.2: Resin of Example 2/Cymel 303/Pluriol P 900.

The above mixture is ground to a fineness smaller than 15μm. Next there is added deionized water to obtain a package viscosity of 100 to 150 sec DIN cup 4 at 20°C.

EXAMPLE 8

The procedure of Example 7 was repeated with the exception that the resin dispersion of Example 2 was replaced by resin dispersion of Example 4.

EXAMPLE 9

The procedure of Example 7 was repeated with the exception that the resin dispersion of Example 2 was replaced by the resin dispersion of Example 6.

PANEL PREPARATION

The products of Examples 7-9 were reduced with deionized water to a spray viscosity of 20
seconds DIN cup 4 at 20°C. The coating composition obtained was sprayed over a cataphoretic electrocoated panel at a thickness of 35 μm dry film thickness and cured at a temperature of 170°C for 25 minutes.

The obtained primer film was coated with different topcoats including alkyd/melamine//acrylic//melamine color coat - clear coat resulting in excellent adhesion gloss, flow and DOI. Test results on the coating properties are given in Table I in terms of:

- Buchholz hardness: DIN 53153
- Erichson flexibility: DIN 53156
- Salt spray: DIN 50021. The rust creepage from the scribeline is measured in mm.

- Chip resistance: According to test procedure described in Recommended Practice SAE-J-400 of the Society of Automotive Engineers.

All Examples were submitted to the humidity cabinet according to DIN 50017 for 240 hours over bare steel and 480 hours over electrocoated panels. In neither of the tests did any blistering occur.

**TABLE I**

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Buchholz Hardness</th>
<th>Erichson Flexibility</th>
<th>Salt spray over electrocoated panel 500 hrs</th>
<th>Salt spray over bare steel 144 hrs</th>
<th>Chip Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>83</td>
<td>6.1 mm</td>
<td>0 mm</td>
<td>5 mm</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>95</td>
<td>6.0 mm</td>
<td>0 mm</td>
<td>2 mm</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
<td>117</td>
<td>4.8 mm</td>
<td>0 mm</td>
<td>4 mm</td>
<td>7-8</td>
</tr>
</tbody>
</table>
CLAIMS

1. A dispersion in water in percentages by weight based on the total dispersion of:
   
   (a) 10-60% of an epoxy ester urethane graft acrylic polymer formed by reacting 5-30% of an epoxy ester urethane polymer formed by reaction of n moles of a difunctional epoxy resin with terminal oxirane groups and a number average molecular weight (Mn) of 30-5,000, n-1 moles of a linear, acid terminated urethane ester prepolymer of 300-5,000 Mn, and 2 moles of a monomer having a single acid functionality to form a reaction product, onto which is grafted 5-30% of an acrylic styrenic, fumeric or maleic monomer by using a peroxide or azo initiator, to produce said epoxy ester acrylic polymer with a Mn = 1000-50,000 and an acid number of 30-150,
   
   (b) tertiary amines being added to an extent equivalent to neutralizing 50-200% of the moles of acid functionality,
   
   (c) organic solvents,
   
   such dispersion having not more than 10% volatile organic solvents plus amines, and
   
   (d) balance water.

2. The dispersion of Claim 1 with 5-20% epoxy ester urethane and 10-30% of an acrylic polymer with acid number 60-140 in 50-80% deionized water, said dispersion having been azeotropically distilled to leave not more than 5% organic volatiles.

3. The dispersion of Claim 1 with the epoxy ester urethane formed by reaction of n moles of a difunctional bisphenol A-based epoxy with Mn = 300-2000, and 2 moles of monofunctional acid having 2-25 carbon atoms, wherein the urethane ester prepolymer has a Mn of 1500-2000.

4. The dispersion of Claim 1 with the acrylic graft formed by reaction of alkyl acrylate, alkyl methacrylate, styrene, hydroxyfunctional...
acrylates and/or methacrylates, acid functional acrylates and/or methacrylates, alkylmaleates and/or fumarates, using 0.01-10% by weight of initiator based on the acrylic content, at 60-180°C, with the acrylic having an acid number of 40-120.

5. The dispersion of claim 1 with the epoxy ester-graft acrylic having been neutralized with a tertiary amine which has a boiling point of 60-220°C.

6. The dispersion of claim 1 containing 0-10% of a water soluble organic solvent.

7. The dispersion of claim 1 of which at least 5-15% is epoxy ester, 5-15% is acrylic graft, up to 5% is neutralizing amine plus organic solvent, and 60-80% is deionized water.

8. The dispersion of claim 1 with the epoxy ester and acrylic graft being formed in an aromatic solvent, neutralizing with the amine and the aromatic solvent distilling off.

9. The coating composition comprising (a) 10-40% of the epoxy ester graft acrylic polymer described in claim 1, including up to 5% neutralizing amines plus organic solvents, and 30-80% of deionized water,
  (b) 0-40% of pigments and extenders,
  (c) 0-20% of additives and/or reactive diluents, and
  (d) 0-30% of a water soluble or dispersible crosslinker.

10. The coating composition of claim 9 wherein the epoxy ester urethane graft acrylic polymer has at least 5-15% epoxy ester, 5-15% acrylic graft, up to 5% is neutralizing amine plus organic solvent, and 60-80% deionized water.
11. The coating composition of Claim 9 wherein the additives are water soluble or dispersible linear or branched polyethylene oxides or polypropylene oxides with a $M_n = 100-2500$.

12. The coating composition of Claim 9 wherein the water soluble or dispersible crosslinker is a methylated melamine formaldehyde resin.

13. An epoxy ester urethane graft acrylic polymer made by reacting 5-30% of an epoxy ester urethane polymer formed by reaction of n moles of a difunctional epoxy resin with terminal oxirane groups and a number average molecular weight ($M_n$) of 300-5,000, n-1 moles of a linear, acid terminated urethane ester prepolymer of 300-5,000 $M_n$, and 2 moles of a monomer having a single acid functionality to form a reaction product, onto which is grafted 5-30% of an acrylic styrenic, fumaric or maleic monomer by using a peroxide or azo initiator, to produce said epoxy ester acrylic polymer with a $M_n = 1000-50,000$ and an acid number of 30-150.

14. A process of making an epoxy ester urethane graft acrylic polymer comprising reacting 5-30% of an epoxy ester urethane polymer formed by reaction of n moles of a difunctional epoxy resin with terminal oxirane groups and a number average molecular weight ($M_n$) of 300-5,000, n-1 moles of a linear, acid terminated urethane ester prepolymer of 300-5,000 $M_n$, and 2 moles of a monomer having a single acid functionality to form a reaction product, onto which is grafted 5-30% of an acrylic styrenic, fumaric or maleic monomer by using a peroxide or azo initiator, to produce said epoxy ester acrylic polymer with a $M_n = 1000-5,000$ and an acid number of 30-150.
INTERNATIONAL SEARCH REPORT

International Application No. PCT/US87/03224

I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC4 C08F 283/000, 285/00; C08K 3/20; C08L 51/08

II. FIELDS SEARCHED

Classification System : Classification Symbols

US 523/407, 414, 415
525/528

Documentation Search other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of Document, 14 with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US, A, 4,665,128 (CLUFF) 12 MAY 1987 SEE THE ENTIRE DOCUMENT.</td>
<td>1-14</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 4,564,648 (HUYBRECHTS) 24 JANUARY 1986 SEE THE ENTIRE DOCUMENT.</td>
<td>1-14</td>
</tr>
<tr>
<td>A</td>
<td>EP, A, 0,060,581 (AKZO) 22 SEPTEMBER 1982 SEE THE ENTIRE DOCUMENT.</td>
<td>1-14</td>
</tr>
</tbody>
</table>

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IV. CERTIFICATION

Date of the Actual Completion of the International Search 1
25 JANUARY 1988

Date of Mailing of this International Search Report 1
29 MAY 1988

International Searching Authority 1
ISA/US

Signature of Authorized Officer 29
C. W. IVY

Form PCT/ISA/210 (second sheet) (May 1986)