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(54) Title: NON-AQUEOUS DISPERSIONS OF RELATIVELY HIGH MOLECULAR WEIGHT EPOXY RESINS		
(57) Abstract Non-aqueous dispersions which contain (A) an epoxy resin having an average epoxy equivalent weight of at least 475 and a Durrans' softening point of at least 70°C, (B) a non-aqueous dispersion medium, and (C) a dispersant such as a copolymer of (1) at least one polymerizable ethylenically unsaturated monomer containing a group reactive with an epoxy group and (2) at least one polymerizable ethylenically unsaturated monomer free of any groups reactive with an epoxy group. These dispersions are useful in coatings, electrical or structural laminates or composites, body solders, adhesives, caulking compounds, casting compounds, filament winding and the like.		

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NON-AQUEOUS DISPERSIONS OF RELATIVELY
HIGH MOLECULAR WEIGHT EPOXY RESINS

The present invention concerns non-aqueous dispersions of relatively high molecular weight epoxy resins.

Industry is constantly seeking ways to reduce
5 the amount of solvents into the atmosphere from coatings
and the like. Among the epoxy resin coating compositions
presently employed are the solutions of such epoxy
resins in oxygen-containing solvents such as glycol
ethers, ketones and the like. However, in order to
10 attain suitable application viscosities, high levels of
solvents must usually be employed.

The present invention provides for the use of
lower cost hydrocarbon diluents and much lower concentra-
tions of diluents or much higher concentrations of
15 epoxy resin in order to achieve suitable application
viscosities.

The present invention pertains to a non-aqueous
dispersion comprising

- (A) at least one epoxy resin having an average epoxide equivalent weight of at least 475 and Durran's softening point of at least 70°C;
- (B) a non-aqueous dispersion medium; and
- 5 (C) a dispersant composition which is a polymer prepared from
- (1) at least one polymerizable ethylenically unsaturated monomer containing a group reactive with an epoxy group and
- 10 (2) at least one polymerizable ethylenically unsaturated monomer free of groups reactive with an epoxy group; wherein
- (i) component (A) is present in amounts of from 30 to 75, preferably from
- 15 50 to 75, percent by weight of the combined weight of components (A), (B) and (C);
- (ii) component (B) is present in amounts of from 20 to 60, preferably from
- 20 20 to 45, percent by weight of the combined weight of components (A), (B) and (C);
- (iii) component (C) is present in amounts of from 1 to 60, preferably from 5
- 25 to 21, percent by weight of the combined weight of components (A), (B) and (C);
- (iv) component (C-1) is present in an amount which provides from 0.1 to
- 30 100, preferably from 0.5 to 6, percent by weight of the combined weight of components (C-1) and (C-2); and

- (v) component (C-2) is present in an amount which provides from 0 to 99.9, preferably from 94 to 99.5, percent by weight of the combined weight of components (C-1) and (C-2).

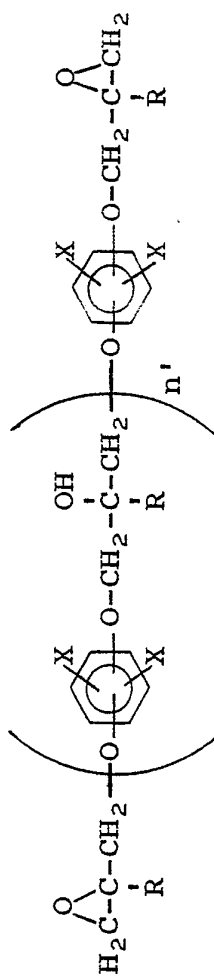
The present invention also pertains to a process for preparing the aforementioned non-aqueous dispersion which process comprises:

- I. reacting
- (A) at least one epoxy resin having an average epoxide equivalent weight of at least 475 and a Durrans softening point of at least 70°C with
- (C-1) at least one polymerizable ethylenically unsaturated monomer containing a group reactive with an epoxy group;
- II. copolymerizing the product resulting from step (I) with
- (C-2) at least one polymerizable ethylenically unsaturated monomer free of groups reactive with an epoxy group; and
- III. dispersing the product from step (II) in
- (B) a non-aqueous dispersion medium; wherein
- (i) component (A) is present in an amount of from 30 to 75 percent by weight of the combined weight of components (A), (C-1), (C-2) and (B);
- (ii) component (C-1) is present in an amount which provides from 0.1 to

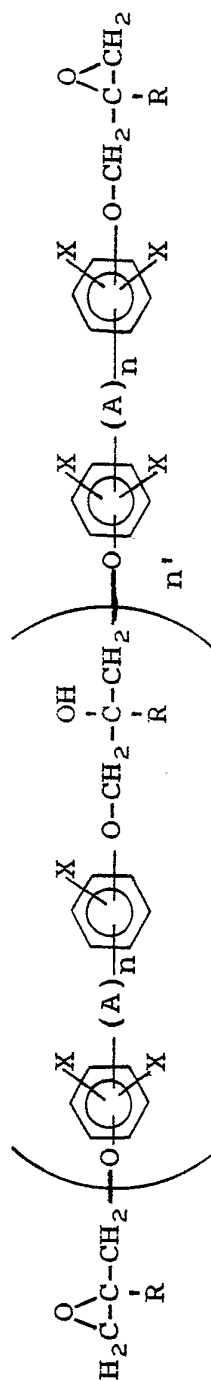
- 100 percent by weight of the combined weight of components (C-1) and (C-2);
- 5 (iii) component (C-2) is presented in an amount which provides from 0 to 99.9 percent by weight of the combined weight of components (C-1) and (C-2); and
- 10 (iv) component (B) is present in an amount of from 20 to 60 percent by weight of combined weight of components (A), (C-1), (C-2) and (B).

Suitable epoxy resins having an average epoxide equivalent weight of at least 475 and Durran's softening point of at least 70°C which can be employed herein include, for example, those represented by the following general formulas

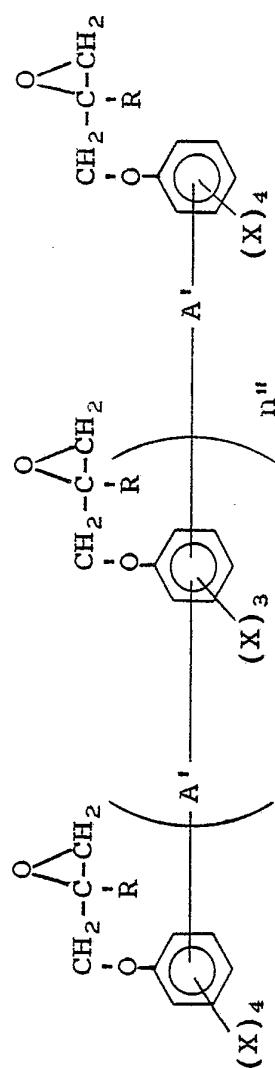
I.



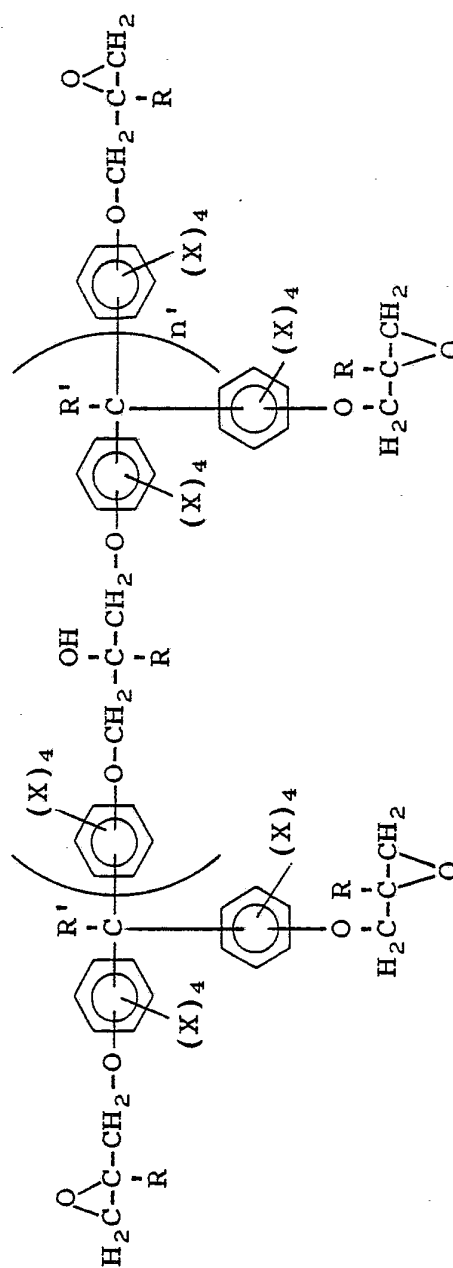
II.



III.



IV.



or mixtures of compounds represented by such formulas wherein each A is independently a divalent hydrocarbon group having from 1 to 8 carbon atoms, -O-, -S-,

5 $-S-S-, -\overset{\overset{O}{\parallel}}{S}-, -\overset{\overset{O}{\parallel}}{S}-, -\overset{\overset{O}{\parallel}}{C}-, -O-\overset{\overset{O}{\parallel}}{C}-O-$; each A' is independently

a divalent hydrocarbon group having from 1 to 8 carbon atoms; each R is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms; R' is hydrogen or a hydrocarbonyl group having from 1 to 8 carbon atoms; each X is independently hydrogen, chlorine, bromine or hydrocarbonyl or hydrocarboxy group having from 1 to 8 carbon atoms; n has an average value of zero or 1; n' has an average value of from 2 to 15 and n'' has an average value of from 1.01 to 8.

Any compound containing a polymerizable ethylenically unsaturated group can be employed herein.

20 Suitable polymerizable ethylenically unsaturated monomers which can be employed herein as either component (C-1) or (C-2) include, for example, those represented by the formulas

$$\begin{array}{ccc}
 \text{(IV)} & & \text{(V)} \\
 25 & & \\
 \text{H}-\text{C}=\text{C} & \begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{O}-\text{R} \end{array} & \text{or} & \begin{array}{c} \text{H} \quad \text{R}^2 \\ | \quad | \\ \text{C}=\text{C} \\ | \quad | \\ \text{H} \quad \text{R}^3 \end{array} \\
 | \quad | & & & \\
 \text{R}^1 \quad \text{R}^1 & & &
 \end{array}$$

30 wherein R is hydrogen or a hydrocarbyl group having
from 1 to 20, preferably from 1 to 10 carbon atoms;
each R¹ is independently hydrogen or a hydrocarbyl
group having from 1 to 20, preferably from 1 to 10
carbon atoms; R² is hydrogen, halogen or a hydrocarbyl
35 group having from 1 to 20, preferably from 1 to 10,

carbon atoms which hydrocarbyl group may be substituted with a $-C\equiv N$ group and R^3 is hydrogen, halogen or a hydrocarbyl group having from 1 to 20, preferably from 1 to 10 carbon atoms, preferably at least one of R^1 and
5 R^2 is hydrogen or a methyl group.

Particularly suitable monomers include, for example, α -methyl styrene, 2-methyl styrene, 4-methyl styrene, t-butyl styrene, 4-methoxystyrene, 4-phenyl styrene, 3-phenyl-1-propene, 2-chloro styrene, 4-chloro
10 styrene, vinyl cyclopentane, vinyl cyclohexane, vinyl naphthalene, vinyl methyl ether, vinyl ethyl ether, vinyl propyl ether, vinyl isopropyl ether, vinyl butyl ether, vinyl isobutyl ether, vinyl sec-butyl ether, vinyl tert. butyl ether, vinyl hexyl ether, vinyl octyl
15 ether, vinyl methyl ketone, methyl isopropenyl ketone, vinyl formate, vinyl acetate, vinyl propionate, vinyl chloroacetate, vinyl trifluoroacetate, vinyl benzoate, 2-vinyl pyridine, vinyl pyrrolidone, vinyl carbazole, methyl acrylate, ethyl acrylate, propyl acrylate,
20 isopropyl acrylate, butyl acrylate, isobutyl acrylate, sec butyl acrylate, tert butyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxy propylacrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate,
25 ate, isobutyl methacrylate, sec butyl methacrylate, tert butyl methacrylate, 2-ethyl butyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, hexyl methacrylate, octyl methacrylate, dodecyl methacrylate, 2-hydroxybutyl methacrylate, octadecyl methacrylate,
30 phenyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, methyl chloro acrylate, acrylonitrile, methacrylonitrile, butadiene, vinyl chloride, vinylidene chloride, ethylene, cinnamic acid derivatives, maleic acid derivatives, mixtures thereof and the like.

Suitable monomers which contain an epoxy group or a group reactive with an epoxy group include, for example, acrylic acid, methacrylic acid, acrylamide, hydroxyethyl or hydroxypropyl acrylate, vinyl phenol, isopropenylphenol, isopropenylphenol glycidyl ether, carboxy terminated butadiene-acrylonitrile copolymers, cinnamic acid, maleic acid, glycidyl methacrylate, or styryl glycidyl ether, diglycidyl ether of bisphenol A mono- or dimethacrylate, mixtures thereof and the like. Particularly suitable as component (C-1) is acrylic acid, methacrylic acid or mixtures thereof.

Particularly suitable monomers which can be employed as component (C-2) are styrene, lauryl methacrylate or mixtures thereof.

Suitable free radical initiators which can be employed to polymerize the monomers include, for example, azo compounds and organic peroxide or hydroperoxide compounds.

Suitable azo compounds include those represented by the formula $R-N=N-R'$ wherein each R and R' is independently hydrogen, alkyl, alkoxy or aryl groups having from 1 to 15 carbon atoms, preferably from 4 to 8 carbon atoms which groups may contain a $-C\equiv N$ moiety. Particularly suitable azo compounds include, for example, 1-t-butylazo-1-cyanocyclohexane, 2-t-butylazo-2-methoxy-4-methyl pentane, 2-t-butylazo-2-cyanopropane, 2-t-butylazo-2-cyanobutane, 2-t-butylazo-2-cyano-4-methyl pentane, 2-t-butylazo-2-cyano-4-methoxy-4-methyl pentane, 2,2'-azobis(2,4-dimethylvaleronitrile), 1,1'-azobis(cyclohexane carbonitrile), 2,2'-azobis(2-methylbutyronitrile),

and 2,2'-azobisisobutyronitrile, mixtures thereof and the like.

Suitable organic peroxide compounds include those represented by the formula $R-O-O-R'$ or $ROO(CO)R'$ wherein each R and R' is independently hydrogen, alkyl or aryl groups having from 1 to 15, preferably from 1 to 8 carbon atoms. Particularly suitable organic peroxides include, for example, cumene hydroperoxide, dicumyl peroxide, t-butyl perbenzoate, t-butyl per-
10 octoate, di-t-butyl peroxide, t-butyl hydroperoxide, lauroyl peroxide, methyl ether ketone peroxide, and chlorobenzoyl peroxide, mixtures thereof and the like.

The quantity of free radical polymerization initiator which is employed depends upon the particular
15 monomer or combination of monomers and initiator being utilized and is usually in the range of from 0.1 to 10, preferably 0.5 to 8 percent by weight based upon the weight of the monomer or combination of monomers.

The polymerization of the monomer is conducted at a temperature of from 80° to 220°C, preferably from 100° to 180°C.
20

Several factors affect the molecular weight of the addition polymer, such as the polymerization temperature and the initiator level. The addition
25 polymer molecular weight can be effectively lowered through the use of chain transfer agents, such as, for example, halogenated solvents, mercaptans and the like without using higher levels of the expensive free radical initiators and without changing the reaction
30 temperature. Ethylene dichloride, ethylene dibromide,

tetrachloroethane, carbon tetrachloride, carbon tetrabromide, bromoform, chloroform, n-butyl mercaptan, dodecyl mercaptan and the like are effective chain transfer agents. Use of volatile chain transfer agents
5 may necessitate the use of a vacuum strip step in the process.

Suitable non-aqueous dispersion media include, any inert material in which the epoxy resin is substantially insoluble such as, for example, any aromatic or
10 aliphatic hydrocarbon materials having from 4 to 28 carbon atoms such as, for example, hexanes, xylene, Isopar[®] E and Isopar[®] M commercially available from Exxon Chemical Company, Super High Flash Naphtha commercially available from Union 76 as SOLV G, cyclo-
15 ketones such as cyclohexanone, methyl amylketone, chlorinated solvents such as perchloroethylene, mixtures thereof and the like.

In the most preferred process an advanced epoxy resin (EEW 575-4000) is melted at a suitable
20 temperature (120°C-160°C). The molten resin is cooled to a suitable temperature and a diluent is added. For solvents with a boiling point below 150°C the preferred temperature for addition is slightly below the boiling point of the solvent (5 to 10 degrees) and for solvents
25 with a boiling point above 150°C the addition is performed at 150°C. After the resin solution is made the temperature is maintained between 120°C-150°C during polymerization. The polymerization is accomplished by continuous addition of the vinyl monomers and the free
30 radical initiator simultaneously. The temperature is maintained at the polymerization temperature 10-60 minutes after addition is complete. The remainder of

the solvent is added and the mixture is cooled to yield a dispersion.

In an equally preferred process for an advanced resin with a lower viscosity (EEW 400-975), the polymer-
5 ization step can be performed in situ in the molten resin alone with no diluent. The resin is heated to 150°C and the monomers and initiator are added dropwise. After complete addition the mixture is allowed to digest for 10 minutes - 60 minutes at 150°C. The
10 mixture is cooled to 70°C-100°C and the dispersion media is added to form a dispersion of a lower molecular weight epoxy resin.

In an alternate process a small portion (.01-.25 equivalent percent) of the epoxy functionality
15 is prereacted with the vinyl acid to give an epoxy acrylate or methacrylate ester. This reaction is either catalyzed by a suitable catalyst such as, for example, ethyltriphenylphosphonium acetate-acetic acid complex or heat catalyzed at 115°C-150°C under an
20 oxygen pad. This epoxy monomer is then copolymerized by simultaneous addition of a comonomer with the free radical initiator and the dispersion is formed as previously described.

In an alternate process the vinyl polymeriza-
25 tion is performed in the liquid epoxy resin which has been heated to 150°C. Simultaneous addition of the vinyl monomers with the free radical initiator to the liquid resin under a N₂ pad results in the polymer formation in a low molecular weight liquid epoxy resin
30 that is advanced by addition of bisphenol A and a suitable catalyst to the desired equivalent weight.

This mixture is then dispersed by adding a suitable non-aqueous dispersion media to the molten mixture slightly below the boiling point of the diluent.

5 The compositions of the present invention are useful in such applications as coatings, structural and electrical laminates or composites, adhesives, caulking compositions, body solders, casting compositions, filament winding and the like.

10 The following examples are illustrative of the invention but are not to be construed as to limiting the scope thereof in any manner.

The following components were employed in the examples.

15 EPOXY RESIN A is a diglycidyl ether of bisphenol A having an average epoxide equivalent weight (EEW) of 475-575 and a Durran's Softening Point of 70°-80°C.

EPOXY RESIN B is a diglycidyl ether of bisphenol A having an average EEW of 1600-2000 and a Durran's Softening Point of 115°-130°C.

20 EPOXY RESIN C is a diglycidyl ether of bisphenol A having an average EEW of 2000-3500 and a Durran's Softening Point of 120°-140°C.

25 EPOXY RESIN D is a diglycidyl ether of bisphenol A having an average EEW of 3500-5500 and a Durran's Softening Point of 135°-155°C.

EPOXY RESIN CURING AGENT A is diethylene triamine.

ISOPAR M is a relatively high boiling, narrow cut isoparaffinic solvent having a flash point of 77°C and a boiling range of from 207° to 260°C commercially available from Exxon Company, U.S.A.

- 5 ISOPAR E is an isoparaffinic hydrocarbon fraction having a boiling range of 116° to 134°C commercially available from Exxon Company, U.S.A.

SAG 100 is a silicone antifoam compound commercially available from Union Carbide Corporation.

- 10 SUPER HIGH FLASH NAPHTHA (SHFN) is a volatile aromatic hydrocarbon solvent having a boiling range of 156° to 180°C commercially available from Union 76 as SOLV G.

DESCRIPTION OF COATINGS TEST METHODS

GLOSS

- 15 Gloss was measured using a Mallinckrodt multi gloss meter following the DIN 67.530. The resin was coated onto a Parker test panel and cured. A beam of light is directed at the coating and the percent reflectance was measured by detecting the amount of light
20 reflected off the coating. The incident beam was angled at 20° and 60°.

CROSS HATCH ADHESION

- The Cross Hatch adhesion test was used to determine the adhesion of the coating to the metal
25 substrate. The coating was etched in a lattice pattern with either six or eleven cuts in each direction. A pressure sensitive tape is applied over the lattice and

then pulled off. The adhesion was evaluated by descriptions and illustrations from ASTM 3359-83 and by determining the amount of coating that was lost or retained. In the water boil cross hatch adhesion test the coating was etched and tested (Preboil test) then it was boiled in test water for one hour and tested (Postboil test) as described above.

MEK DOUBLE RUB TEST (METHYL ETHYL KETONE)

This test was used to evaluate the chemical resistance of the coating. A swatch of cotton gauze was fastened to the rounded end of the hammer and was then dipped into a beaker of methyl ethyl ketone. The excess solvent was shaken off and the hammer moved back and forth over the coating until failure occurred. The only pressure on the coating was from the weight of the hammer head.

GARDNER IMPACT (REVERSE & FORWARD)

Gardner Impact was used to determine the impact resistance (and flexibility) of a coating. A three pound (1.4 kg) weight was dropped onto a coated Parker test panel from a height that corresponds to a certain number of inch-pounds following DIN 53.153 (ASTM D-2794).

If the weight was dropped directly onto the coating itself it is called forward impact and it is called reverse impact if it is dropped onto the metal surface.

EXAMPLE 1

Epoxy Resin A (134.9 g) was charged into a reaction vessel equipped with stirring, a nitrogen

purge, a condenser and a temperature controller. With stirring and N₂ purge on, the resin was melted. When a temperature of 120°-125°C was attained, a monomer feed consisting of lauryl methacrylate (33.73 g), acrylic acid (0.13 g) and tertiary butyl perbenzoate (2.4 g) as an initiator was added dropwise. After complete addition, the vessel was maintained at 120°-125°C for one hour (3600 s). After that time, 110 g of Isopar M was added dropwise. The dispersion was then stirred at 120°C for approximately 1.5 hours (5400 s). The dispersion was then cooled to yield a stable dispersion. The resultant dispersion contained 61 percent solids by weight and had a viscosity at 23°C of 96 cps (0.096 Pa·s).

15 EXAMPLE 2

Epoxy Resin B (134.91 g) was charged into a reaction vessel equipped with stirring, N₂ purge, a condenser and a temperature controller. With stirring and N₂ purge, 107 g of super high flash naphtha (SHFN) was added and the solution stirred for 5 minutes (300 s). A monomer feed of 40 g styrene, 0.5 g acrylic acid and 3.3 g tertiary butyl perbenzoate as an initiator was added at 150°C over approximately 10 minutes (600 s). Heating was continued for one hour (3600 s) at 150°C. SHFN (75 g) was added and the mixture was cooled to 80°C with stirring to yield an iridescent dispersion of Epoxy Resin B in SHFN. The resultant dispersion had an average particle size of less than 1 micron and a viscosity at 23°C of 240 cps (0.24 Pa·s).

30 EXAMPLE 3

Epoxy Resin B (134.9 g) was charged into a reaction vessel equipped with stirring, a nitrogen

purge, a condenser and a temperature controller. With stirring and N² purge on, the resin was melted. When a temperature of 120°-125°C was attained, a monomer feed consisting of lauryl methacrylate (10 g), styrene (10 g), acrylic acid (0.14 g) and tertiary butyl perbenzoate (1.67 g) as an initiator was added dropwise. After complete addition, the vessel was maintained at 120°-125°C for one hour (3600 s). After that time, a mixture of 50 g of xylene and 50 g of hexane was added dropwise. The dispersion was then stirred at 120°C for approximately 1.5 hours (5400 s). The dispersion was then cooled to yield a stable dispersion. The resultant dispersion contained 63 percent solids and had a viscosity at 23°C of 64 cps (0.064 Pa·s).

Example 4

Epoxy Resin B (134.9 g) was charged into a reaction vessel equipped with stirring, a nitrogen purge, a condenser and a temperature controller. With stirring and N² purge on, the resin was melted. When a temperature of 120°-125°C was attained, a monomer feed consisting of styrene (40 g), acrylic acid (0.5 g), and tertiary butyl perbenzoate (3.3 g) as an initiator was added dropwise. After complete addition, the vessel was maintained at 120°-125°C for one hour (3600 s). After that time, a mixture of 92 g of Super High Flash Naphtha and 15 g cyclohexanone was added dropwise. The dispersion was stirred at 120°C for approximately 1.5 hours (5400 s). The dispersion was then cooled to yield a stable dispersion. The resultant dispersion contained 50 percent solids and had a viscosity at 23°C of 960 cps (0.96 Pa·s).

COMPARATIVE EXPERIMENT A

For comparative purposes, a solution of Epoxy Resin B 60.6 percent by weight in the n-butylether of diethylene glycol was prepared. The resulting solution
5 had a viscosity at 23°C of 53,600 cps (53.6 Pa·s).

EXAMPLE 5

Epoxy Resin C (134.91 g) in reaction vessel equipped as in Example 1 was heated to melt the resin at a temperature of approximately 170°C. The resin was
10 cooled to 150°C and stirred for 10 minutes (600 s). Xylene (100 g) was added dropwise. A monomer feed of 12 g styrene, 0.08 g acrylic acid and 1.12 g tertiary butyl perbenzoate as an initiator was begun after addition of xylenes was complete. Addition of monomer
15 mixture was complete in 5-10 minutes (300-600 s). The solution was heated for 5-15 minutes (300-900 s) at 150°C. The solution was then cooled and more xylene (20-50 gms) was added. The product was put in a jar and left on a shaker overnight. A white dispersion of
20 Epoxy Resin C in xylene resulted. The resultant dispersion contained 52 percent solids by weight and had a viscosity at 23°C of 928 cps (0.928 Pa·s).

EXAMPLE 6

Epoxy Resin C (134.91 g) in reaction vessel
25 equipped as in Example 1 was heated to melt the resin at a temperature of approximately 170°C. The resin was cooled to 150°C and stirred for 10 minutes (600 s). Xylene (100 g) was added dropwise. A monomer feed of
10 g laurylmethacrylate, 0.14 g acrylic acid and 1.74 g
30 tertiary butyl perbenzoate as an initiator was begun after addition of xylenes was complete. Addition of monomer mixture was complete in 5-10 minutes (300-600 s).

The solution was heated for 5-15 minutes (300-900 s) at 150°C. The solution was then cooled and more xylene (20-50 gms) was added. The product was put in a jar and left on a shaker overnight. A white dispersion of
5 Epoxy Resin C in xylene resulted. The resultant dispersion contained 52 percent solids by weight and had a viscosity at 23°C of 400 cps (0.4 Pa·s).

COMPARATIVE EXPERIMENT B

For comparative purposes, a solution of 51
10 percent by weight of epoxy resin C in the n-butyl ether of diethylene glycol was prepared. The resultant solution had a viscosity at 23°C for 22,780 cps (22.78 Pa·s).

EXAMPLE 7

15 Epoxy Resin D (79.36 g) was melted in a reaction vessel equipped with stirring, condenser and N₂ purge. With stirring and heating, the resin was mixed with 57.34 g SHFN and heated to 150°C. The solution was stirred for 10 minutes (600 s). A monomer
20 addition of 20 g styrene, 1.65 tertiary butyl perbenzoate as an initiator and 0.14 g acrylic acid was continuously fed into the reactor over a period of 5-15 minutes (300-900 s). Heating was continued for one
hour (3600 s) at 150°C. Heating was discontinued, 50 g
25 of SHFN was added and the solution was put on a shaker overnight. The final result was an iridescent bluish white dispersion of Epoxy Resin D. The resultant dispersion contained 44 percent solids.

EXAMPLE 8A. PREPARATION OF COATING FROM DISPERSION PREPARED
IN EXAMPLE 3

25 g (0.009 equiv.) of the dispersion prepared in Example 3 was mixed with 0.18 g (0.009 equivalent) of epoxy curing agent A. A surfactant SAG 100 (.16 g) and 5-10 gms of a 50-50 mixture by weight Isopar[®] M and Super High Flash Napthta. The mixture was applied to a Bonderite 40 cold rolled steel test panel. The coated panel was then cured at 150°C for 15 minutes (900 s). The coating thickness was .6 to 1 mils (15.24 to 25.4 mm). The coating properties of the dispersion are shown in Table I.

B. PREPARATION OF COATING FROM DISPERSION
PREPARED IN EXAMPLE 5

34.0 g (0.006 equiv.) of the dispersion prepared in Example 5 was mixed with 0.12 g (0.006 equiv.) of epoxy curing agent A, a surfactant S.A.G. 100 (.16 g) and 5-10 g of a 50-50 mixture of xylene-Super High Flash Napthta.

This mixture was coated onto a cold rolled steel Bonderite 40 Parker test panel. (ASTM 4147) The coated panel was cured at 150°C for 15 minutes (900). The coating thickness was .75 to 1 mils (19.05 mm to 25.4 mm). The coating properties of the dispersion are shown in Table I.

COMPARATIVE EXPERIMENT C

A solution coating was prepared from a solution of Epoxy Resin B as follows.

24.6 g (0.009 equiv.) of an epoxy resin solution of epoxy resin B (63 percent by weight) in methyl

amyl ketone (37 percent by weight) was mixed with 0.18 g (0.009 equiv.) of curing agent A. The solution was applied to a Bonderite 40 cold rolled steel test panel. The coated panel was then cured at 150°C for 15 minutes (900 s). The coating thickness was 0.6 to 1 mils (15.24 to 25.4 mm). The coating properties are shown in Table I.

COMPARATIVE EXPERIMENT D

25.06 g (.006 eq) of a solution of epoxy resin C (52 percent by weight) in methyl amyl ketone (48 percent by weight) was mixed with 0.16 g (0.007 equiv.) of curing agent A. The solution was applied to a Bonderite 40 cold rolled steel test panel. The coated panel was cured at 150°C for 15 minutes (900 s). The coating thickness was 0.75 to 1 mils (19.05 to 25.4 mm). The coating properties are shown in Table I.

TABLE I

EXAMPLE OR COMPARATIVE EXPERIMENT

PROPERTY	EXAMPLE 8A	COMP. EXPT. C	EXAMPLE 8B	COMP. EXPT. D
Gloss, 60° 20°	100% 52-54%	100% 56-58%	100% 59%	100% 60-70%
Reverse Impact, in-lbs J	90 10.17	90 10.17	140 15.82	140 15.82
Forward Impact, in-lbs J	160 18.08	150 16.95	140 15.82	140 15.82
Cross-Hatch Adhesion Preboil Postboil	100% adhesion 95% adhesion	100% adhesion 100% adhesion	100% adhesion 0% adhesion	100% adhesion 0% adhesion
MEK Double Rubs	14	50	12	27

1. A non-aqueous dispersion comprising
- (A) at least one epoxy resin having an average
epoxide equivalent weight of at least 475 and
Durrans's softening point of at least 70°C;
- 5 (B) a non-aqueous dispersion medium; and
- (C) a dispersant composition which is a polymer
prepared from
- (1) at least one polymerizable ethylenically
unsaturated monomer containing a group
reactive with an epoxy group and
- 10 (2) at least one polymerizable ethylenically
unsaturated monomer free of groups
reactive with an epoxy group; wherein
- (i) component (A) is present in an
amount of from 30 to 75 percent by
weight of the combined weight of
components (A), (B) and (C);
- 15 (ii) component (B) is present in an
amount of from 20 to 60 percent by
weight of the combined weight of
components (A), (B) and (C);
- 20 (iii) component (C) is present in an
amount of from 1 to 60 percent by
weight of the combined weight of
components (A), (B) and (C);
- 25

- 5 (iv) component (C-1) is present in an amount which provides from 0.1 to 100 percent by weight of the combined weight of components (C-1) and (C-2); and
- 10 (v) component (C-2) is present in an amount which provides from 0 to 99.9 percent by weight of the combined weight of components (C-1) and (C-2).

2. A non-aqueous dispersion of Claim 1
wherein

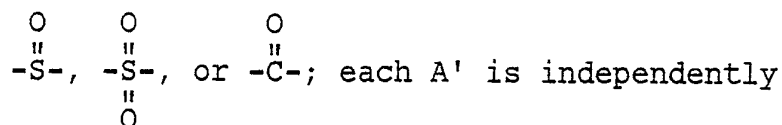
- 15 (i) component (A) is present in an amount of from 50 to 75 percent by weight of the combined weight of components (A), (B) and (C);
- 20 (ii) component (B) is present in an amount of from 20 to 45 percent by weight of the combined weight of components (A), (B) and (C);
- (iii) component (C) is present in an amount of from 5 to 21 percent by weight of the combined weight of components (A), (B) and (C); and
- 25 (iv) component (C-1) is present in an amount which provides from 0.5 to 6 percent by weight of the combined weight of components (C-1) and (C-2).

3. A non-aqueous dispersion of Claim 2
 wherein

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- (i) component (A) is at least one epoxy resin represented by formulas (I), (II) or (III) in the specification wherein each A is independently a divalent hydrocarbon group having from 1 to 8 carbon atoms, -O-, -S-, -S-S-,

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a divalent hydrocarbon group having from 1 to 8 carbon atoms; each R is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms; each X is independently hydrogen, chlorine, bromine or a hydrocarbyl or hydrocarbyloxy group having from 1 to 8 carbon atoms; n has an average value of zero or 1; n' has an average value of from 2 to 15 and n'' has an average value of from 1.01 to 8;

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- (ii) component (B) is an aromatic or aliphatic hydrocarbon material having from 4 to 28 carbon atoms or mixture thereof;

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- (iii) component (C-1) is at least one monomer represented by formula (IV) in the specification wherein R is hydrogen; each R¹ is independently hydrogen or a hydrocarbyl group having from 1 to 20 carbon atoms; R² is hydrogen, halogen or a hydrocarbyl group having from 1 to

20 carbon atoms which hydrocarbyl group may be substituted with a $-C\equiv N$ group and R^3 is hydrogen, halogen, or a hydrocarbyl group having from 1 to 20 carbon atoms;

5 (iv) component (C-2) is at least one monomer represented by formulas (IV) or (V) in the specification wherein R is a hydrocarbyl group having from 1 to 20 carbon atoms; each R^1 is independently hydrogen

10 or a hydrocarbyl group having from 1 to 20 carbon atoms; R^2 is hydrogen, halogen or a hydrocarbyl group having from 1 to 20 carbon atoms which hydrocarbyl groups may or may not be substituted with a

15 $-C\equiv N$ group and R^3 is hydrogen, halogen or a hydrocarbyl group having from 1 to 20 carbon atoms.

4. A non-aqueous dispersion of Claim 3

wherein

20 (i) component (A) is at least one epoxy resin represented by formula (I) wherein each X is hydrogen, and n' has a value from 2 to 15;

25 (ii) component (B) is xylene, hexane, an isoparaffinic hydrocarbon fraction having a boiling range of from 116°C to 134°C , an isoparaffinic hydrocarbon fraction having a boiling range of from 207°C to 260°C , an aromatic hydrocarbon

30 fraction having a boiling range of from 156°C to 180°C or any combination thereof;

- (iii) component (C-1) is acrylic acid, methacrylic acid or a mixture thereof; and
- (iv) component (C-2) is styrene, lauryl methacrylate or a mixture thereof.

5

wherein

5. A non-aqueous dispersion of Claim 1

10

- (i) component (A) is a diglycidyl ether of phenol A having (a) an average epoxy equivalent weight of 475-575 and a Durran's softening point of 70°-80°C, (b) an average epoxy equivalent weight of 1600-2000 and a Durran's softening point of 115°-130°C, (c) an average epoxy equivalent weight of 2000-3500 and Durran's softening point of 120-140°C, and (d) an average epoxy equivalent weight of 3500-5500 and a Durran's softening point at 135°-155°C;

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- (ii) component (B) is xylene, hexane, cyclohexane, isoparaffinic hydrocarbon fraction having a boiling range of from 207°-260°C, an aromatic hydrocarbon fraction having a boiling range of from 150°-180°C, or any mixture thereof;

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- (iii) component (C-1) is acrylic acid; and
- (iv) component (C-2) is styrene, lauryl methacrylate or a mixture thereof.

6. A process for preparing a non-aqueous dispersion which comprises

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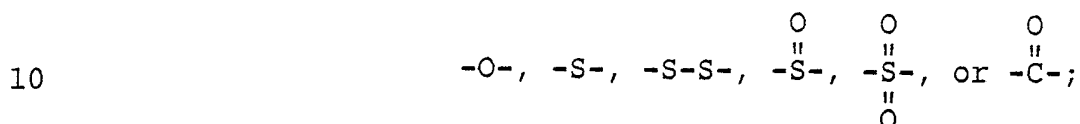
(I) reacting

- (A) at least one epoxy resin having an average epoxide equivalent weight of at

- least 475 and Durran's softening point
of at least 70°C with
- (C-1) at least one polymerizable ethylenically
unsaturated monomer containing a group
reactive with an epoxy group;
- (II) copolymerizing the product resulting from
step (I) with
- (C-2) at least one polymerizable ethylenically
unsaturated monomer free of groups
reactive with an epoxy group; and
- (III) dispersing the product from step (II) in
(B) a non-aqueous dispersion medium wherein;
component (A) is present in an amount
of from 30 to 75 percent by weight of
the combined weight of components
(A), (C-1), (C-2) and (B);
- (i) component (C-1) is present in
an amount which provides from 0.1
to 100 percent by weight
of the combined weight of components
(C-1) and (C-2);
- (ii) component (C-2) is present in an
amount which provides from 0
to 99.9 percent by weight of
the combined weight of components
(C-1) and (C-2); and
- (iii) component (B) is present in an
amount of from 20 to 60
percent by weight of the combined
weight of components (A), (C-1), (C-2)
and (B).

7. A process of Claim 6 wherein

- (i) component (A) is at least one epoxy resin represented by formulas (I), (II) or (III) in the specification wherein each A is independently a divalent hydrocarbon group having from 1 to 8 carbon atoms,



each A' is independently a divalent hydrocarbon group having from 1 to 8 carbon atoms; each R is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms; each X is independently hydrogen, chlorine, bromine or a hydrocarbyl or hydrocarbyloxy group having from 1 to 8 carbon atoms; n has an average value of zero or 1; n' has an average value of from 2 to 15 and n'' has an average value of from 2.01 to 8;

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(ii) component (C-1) is at least one monomer represented by formula (IV) in the specification wherein R is hydrogen; each R¹ is independently hydrogen or a hydrocarbyl group having from 1 to 20 carbon atoms; R² is hydrogen, halogen or a hydrocarbyl group having from 1 to 20 carbon atoms which hydrocarbyl group may be substituted with a -C≡N group and R³ is hydrogen,

halogen or a hydrocarbyl group
having from 1 to 20 carbon atoms;
and

- 5 (iii) component (C-2) is at least one
monomer represented by formulas
(IV) or (V) in the specification
wherein R is a hydrocarbyl group
having from 1 to 20 carbon atoms;
each R¹ is independently hydrogen
10 or a hydrocarbyl group having from
1 to 20 carbon atoms; R² is hydro-
gen, halogen or a hydrocarbyl group
having from 1 to 20 carbon atoms
which hydrocarbyl groups may be
15 substituted with a -C≡N group and
R³ is hydrogen, halogen or a hydro-
carbyl group having from 1 to 20
carbon atoms.

8. A process of Claim 7 wherein

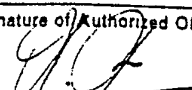
- 20 (i) component (A) is present in an amount of
from 50 to 75 percent by weight of the
combined weight of components (A),
(C-1), (C-2) and (B);
(ii) component (C-1) is present in an amount
25 which provides from 0.5 to 6 percent by
weight of the combined weight of com-
ponents (C-1) and (C-2);
(iii) component (C-2) is present in an amount
which provides from 94 to 99.5 percent
30 by weight of the combined weight of
components (C-1) and (C-2); and

- (iv) component (B) is present in an amount of from 20 to 45 percent by weight of the combined weight of components (A), (C-1), (C-2) and (B).

- 5 9. A process of Claim 8 wherein
- (i) component (A) is at least one epoxy resin represented by formula (I) wherein each X is hydrogen, and n' has a value from 2 to 15;
- 10 (ii) component (C-1) is acrylic acid, methacrylic acid or a mixture thereof;
- (iii) component (C-1) is styrene, lauryl, methacrylate or a mixture thereof; and
- 15 (iv) component (B) is xylene, hexane, an isoparaffinic solvent having a boiling range of from 116°C to 134°C, an isoparaffinic hydrocarbon fraction having a boiling range of from 207°C to 260°C, an aromatic hydrocarbon fraction having a
- 20 boiling range of from 156°C to 180°C or any combination thereof.
10. The product resulting from curing a composition of Claims 1, 2, 3 or 4 with a curing quantity of a suitable curing agent or a catalytic quantity of a
- 25 suitable catalyst or a combination thereof.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 86/00343

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 08 F 283/10; C 08 F 299/02; C 08 F 2/08; C 09 D 3/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 08 F	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	FR, A, 2343009 (HOECHST) 30 September 1977, see claims 1,5 --	
A	US, A, 3810855 (HIDEYOSHI TUGUKUNI et al.) 14 May 1974, see column 5, lines 53-74; column 8, lines 35-75 --	
A	WO, A, 85/00610 (DOW) 14 February 1985 -----	
¹⁰ Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
15th May 1986		19 JUN 1986
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		 L. ROSSI

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 86/00343 (SA 12272)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 02/06/86

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 2343009	30/09/77	DE-A- 2608880	08/09/77
		JP-A- 52107092	08/09/77
		SE-A- 7702358	05/09/77
US-A- 3810855	14/05/74	GB-A- 1410341	15/10/75
		JP-A- 49027584	12/03/74
WO-A- 8500610	14/02/85	AU-A- 3156884	04/03/85
		EP-A- 0152425	28/08/85

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82