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ADVANCED EPOXY RESINS AND COATING
COMPOSITIONS CONTAINING
ADVANCED EPOXY RESINS

The present invention concerns advanced epoxy resins and coatings containing same.

Coatings have heretofore been prepared by reacting diglycidyl ethers of dihydric phenols with dihydric phenols and subsequently curing same with a suitable curing agent or, for the very high molecular weight advanced products, merely applying a solution of such resin and evaporating the solvent therefrom. While such coatings have good physical and chemical properties, they are somewhat lacking in flexibility. There are some applications such as automotive primer surfacers, automotive stone chip resistant coatings, and coil coatings where somewhat reduced physical and/or chemical properties can be accepted for an improvement in flexibility or a reduction in the amount of volatile solvent required to achieve the same application viscosity. Also, because the solution coatings contain solvents which must either be recovered or vented into the atmosphere, the latter of which is not environmentally acceptable, solvent recovery systems are required.

The present invention provides for coatings having improved flexibility and requiring less solvent to achieve desirable application viscosities.

The cured advanced epoxy resins of this invention
05 have increased elongation values when cured with a curing quantity of a suitable curing agent as compared to similarly cured advanced resins prepared by reacting together only component (A-2) with component (B). The advanced epoxy resins of this invention
10 require less solvent to reach desired viscosity values as compared to the quantity of solvent to reach a like viscosity value for advanced resins prepared from component (A-2) and component (B).

According to a first aspect, there is provided an
15 advanced epoxy resin prepared by reacting in the presence of a suitable catalyst

(A) a composition comprising

(1) at least one diglycidyl ether of a
polyoxypropylene glycol or dipropylene
20 glycol; and

(2) at least one aromatic diepoxide;
with

(B) at least one compound having two aromatic
hydroxyl groups per molecule;

25 wherein components (A-1) and (A-2) are employed in quantities such that from 10 to 50 percent of the epoxide equivalents contained in component (A) are contributed by components (A-1), from 50 to 90 percent

of such epoxide equivalents are contributed by component (A-2), and component (A-1) is present as at least 20 weight % and less than 50 mol % of components (A-1) and (A-2), and wherein components (A) and (B) are present in a quantity which results in an advanced epoxy resin having an average epoxide equivalent weight of from 350 to 30,000.

In one preferred embodiment, the resultant epoxy resin has an average epoxide equivalent weight of from 350 to 1500.

The aliphatic diepoxides employed herein are the diglycidyl ethers of polyoxypropylene glycols or dipropylene glycol.

Suitable aliphatic diepoxides include the glycidyl ethers of polyoxypropylene glycols having an average molecular weight of from 200 to 800, preferably from 200 to 400, which polyoxypropylene glycols are prepared by reacting an aliphatic initiator compound with propylene oxide. Preferred aliphatic diepoxides have an average epoxide equivalent weight of from 123 to 400. When component (A-2) is a diglycidyl ether of bisphenol A, it is especially preferred that the average epoxide equivalent weight is from 120 to 260.

Suitable aromatic diepoxides which can be employed herein include the diglycidyl ethers of polyhydric phenols such as, for example, catechol, resorcinol, hydroquinone, bisphenol A, and mixtures thereof.

Particularly suitable diglycidyl ethers of bisphenols and dihydric phenols which can be employed herein include those mentioned by P. H. Martin in U.S. 3,931,109. Preferred aromatic diepoxides are the diglycidyl ethers of bisphenol A having an average epoxide equivalent weight of from 172 to 250.

It is to be understood, that because of the manner in which the commercial epoxy resins prepared from aliphatic dihydric compounds and aromatic dihydric compounds are prepared, these epoxy resins contain minor amounts of monoglycidyl ether products. However, so long as less than 10 percent of the epoxy groups are derived from such monoglycidyl ether products, they are suitable. Suitable such commercially available diglycidyl ethers of aromatic dihydric compounds include D.E.R.[®] 330 epoxy resin, D.E.R.[®] 331 epoxy resin, D.E.R.[®] 332 epoxy resin and D.E.R.[®] 383 epoxy resin commercially available from The Dow Chemical Company as well as EPON[®] 825, EPON[®] 826 and EPON[®] 828 commercially available from Shell Chemical Company. The symbol ® used in this Specification indicates a Trade Mark.

Suitable commercially available diglycidyl ethers of polyoxypropylene glycol include D.E.R.[®] 732 epoxy resin and D.E.R.[®] 736 epoxy resin available from The Dow Chemical Company.

05 The quantities of the aliphatic and aromatic epoxy resins and the compound containing two aromatic hydroxyl groups to be employed are those quantities which will provide the desired average epoxide equivalent weight of the advanced epoxy resin.

10 The percent of aliphatic diepoxide depends within the previously specified parameters upon the particular end use for which the advanced epoxy resin is to be employed.

For example, in automotive primer coatings, the
15 desired percent aliphatic diepoxide is up to 30 percent by weight based upon the combined weight of the aliphatic diepoxide and the aromatic diepoxide and the epoxide equivalent weight of the advanced resin is usually from 350 to 700.

20 For beverage can coating applications, the desired percent of aliphatic diepoxide is up to 25 percent and the epoxide equivalent weight of the advanced resin is from 1400 to 3000.

For coil coating applications, the desired percent of aliphatic diepoxide is up to 50 percent and the epoxide equivalent weight of the advanced epoxy resin is from 1400 to 3000.

5 Suitable solvents which can be employed herein include, for example, ketones such as acetone, methylethyl ketone, methyl n-amyl ketone, methyl isobutyl ketone; glycol ethers such as, for example, the methyl ether of diethylene glycol, the methyl ether of propylene glycol, the n-butyl ether of ethylene glycol; and
10 esters such as, for example, ethyl acetate and butyl acetate.

 Suitable solvents also include aromatic compounds, such as, for example, toluene and xylene.
15 It is also understood that mixtures of such solvents can be employed.

 Suitable catalysts which can be employed herein in preparing the advanced epoxy resins of the present invention, include any such catalyst suitable
20 for catalyzing the reaction between an epoxy group and a phenolic hydroxyl group. Particularly suitable catalysts include those phosphonium catalysts described by W. O. Perry in U.S. 3,948,855 and Dante et al. in U.S. 3,447,990.

25 Suitable curing agents which can be employed in the coating compositions of the present invention include, for example, aminoplast resins such as the reaction products of melamine or urea with formaldehyde. Such adducts can be partially or totally etherified
30 with alcohols such as methanol or butanol. Other amino

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resins would include glycourils, or benzoguanamines. Blocked isocyanates may also be utilized. Typical examples are tolylene diisocyanate, 4,4'-diphenylmethane-isocyanate, a buiret from hexamethylenediisocyanate, a
5 cocyclic trimer of hexamethylenediisocyanate and tolylene diisocyanate blocked with phenols such as phenol, 4-chlorophenol, o-sec-butylphenol, lactams such as caprolactam, and oximes such as acetaldehydeoxime or methylethylketoxime. Also useful are those prepolymers
10 prepared by reacting diols or triols with diisocyanate such as, e.g. tolylene diisocyanate, hexamethylene diisocyanate or isophorone diisocyanate blocked with the aforementioned phenols. Coatings capable of curing at room temperature can be obtained by use of the afore-
15 mentioned isocyanates which contain no blocking agent.

The coating compositions of the present invention may also contain, if desired, colorants, dyes, pigments, fillers, leveling agents, and mixtures thereof.

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

The following components were employed in the examples.

25 ALIPHATIC DIEPOXIDE A was a diglycidyl ether of polyoxypropylene glycol, said glycol having an average molecular weight of 400 and said diglycidyl ether having an average epoxide equivalent weight (EEW) of 311.

ALIPHATIC DIEPOXIDE B was a diglycidyl ether of dipropylene glycol having an average EEW of 195.

- 5 AROMATIC DIEPOXIDE A was a diglycidyl ether of bisphenol A having an average EEW of 189.

DIHYDRIC PHENOL A was bisphenol A.

EXAMPLES 1 THROUGH 6 AND COMPARATIVE RUN A

Preparation of Advanced Epoxy Resin

- 10 A series of advanced epoxy resins were prepared from an aromatic diepoxide with varying quantities of aliphatic diepoxide and bisphenol A (BPA). The catalyst employed was a 70 percent solution of ethyltriphenyl phosphonium acetate-acetic acid complex in methanol.
- 15 In each instance, the mixture of epoxy resins and bisphenol A were heated to between 70°C and 90°C whereupon they formed clear solutions after which the catalyst was added and heating continued to 150°C whereupon the solution was permitted to exotherm. The solutions were
- 20 heated for an additional time and temperature. After cooling, the advanced resin was diluted to 85 percent non-volatiles in toluene. The quantities, reaction conditions and results are given in Table I.

Binder Compositions

- 25 The advanced resins prepared in A above were blended with a sufficient quantity of a solvent composition consisting of 100 parts by weight (pbw) of methyl ethyl ketone, 100 pbw xylene, 200 pbw toluene and 100 pbw 2-(ethoxy)ethylacetate so as to provide a
- 30 viscosity employing a No. 2 Zahn cup of 38 seconds.

(17)

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The percent non-volatiles and percent total solvent (includes solvent employed during preparation of advanced resin) required to provide the 38 seconds viscosity employing a No. 2 Zahn cup are given in Table I.

Preparation of Paints

Binder compositions were made using sufficient quantities of the solutions prepared in (B) above to provide 30 grams of non-volatile resin, 4.5 g of hexamethoxymelamine, commercially available from American Cyanamid Co. as CYMEL[®] 303, 1.5 weight percent of a 40 percent solution of p-toluenesulfonic acid in isopropanol and an additional 3 g of solvent blend. The binder compositions were then blended with a pigment composition consisting of 7.67 weight percent of ferric oxide, 7.67 weight percent of titanium dioxide, 7.67 weight percent of ASP 400 clay, 75 weight percent of barytes and 2 weight percent of zinc chromate in a ratio of 2 parts of pigment to one part by weight of binder. The binder/pigment blend was placed in a steel cylinder and a volume of steel shot equal to the volume of the binder/pigment blend was added and the cylinder was shaken on paint shaker for 15 minutes (900 s). The contents were filtered to remove the steel shot and the paint aged overnight at 140°F (60°C) prior to use.

Films of these paint compositions were applied to polished cold rolled steel panels or unpolished BONDERITE[®] 40 panels with a number 22 wire wound Meyer rod. The panels were baked 30 minutes (1800 s) at 325°F (163°C). Solvent resistance was determined by rubbing the coating with a 2-pound (0.9 kg) ballpeen hammer where the hammer head was covered with gauze and

soaked in methyl ethyl ketone. The number of double rubs, a push-pull motion, observed until a marring of the coating occurred was recorded.

The solids content of the point was determined by heating two grams of the sample at 150°C in a vacuum oven for 2 hours (7200 s).

The salt spray resistance was carried out in a salt fog cabinet employing the procedure of ASTM B117-73.

The results are given in Table I.

EPOXY RESIN PREPARATION

Aliphatic Resin
Type/pbw¹/EE²
% Epoxide Equiv.⁴

Aromatic Resin
Type/pbw/EE
% Epoxide Equiv.⁴

Dihydric Phenol
Type/pbw/OHE³
Advanced Resin EEW

Catalyst, pbw

Exotherm Temp. °C

Post Heat
Temp., °C
Time, Hrs./secs.

Binder composition
% Non-volatiles
% Solvent

Paint Composition
MEK Rubs
Salt Spray
32nds of an inch
mm.

TABLE I

EXAMPLES		
1	2	3
B/80/0.41 19.5	B/120/0.615 29.34	B/200/1.026 49.23
A/320/1.693 80.5	A/280/1.481 70.66	A/200/1.058 50.77
A/104.2/0.915 425-430	A/101.8/0.893 425-430	A/95.8/0.840 425-430
0.4	0.4	0.4
175	175	170
175	175	170
1/3600	1/3600	1/3600
59.4	59	63.7
40.6	40	36.3
35	29	25
2-3 1.6-2.4	1-2 0.8-1.6	---

TABLE I (cont'd)

EPOXY RESIN PREPARATION	EXAMPLES AND COMPARATIVE RUN			
	4	5	6	A
Aliphatic Resin Type/pbw ¹ /EE ² % Epoxide Equiv. ⁴	A/80/0.257 13.18	A/120/0.386 20.67	A/200/0.643 37.8	--- 0
Aromatic Resin Type/pbw/EE % Epoxide Equiv. ⁴	A/320/1.693 86.82	A/280/1.481 79.33	A/200/1.058 62.2	A/400/2.116 100
Dihydric Phenol Type/pbw/OHE ³ Advanced Resin EEW	A/93.6/0821 425-430	A/89.5/0.785 425-430	A/66.8/0.586 425-430	A/106/0.937 425-430
Catalyst, pbw .	0.4	0.4	0.4	0.4
Exotherm Temp. °C	180	170	160	180
Post Heat Temp., °C	175	175	170	175
Time, Hrs./secs.	1/3600	1/3600	1/3600	1/3600
Binder composition % Non-volatiles	59.3	61.3	67.1	56
% Solvent	40.7	38.7	32.9	44
Paint Composition MEK Rubs	15	15	---	---
Salt Spray 32nds of an inch mm.	2-6 1.6-4.8	1-6 0.8-4.8	---	---

TABLE I (cont'd)

- 1 pbw = parts by weight
- 2 EE = epoxide equivalents
- 3 OHE = hydroxide equivalents
- 4 Percent epoxide equivalents contributed by this resin
based upon total epoxide groups.



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CLAIMS

1. An advanced epoxy resin prepared by reacting in the presence of a suitable catalyst

(A) a composition comprising

05 (1) at least one diglycidyl ether of a polyoxypropylene glycol or dipropylene glycol; and

(2) at least one aromatic diepoxide;

with

10 (B) at least one compound having two aromatic hydroxyl groups per molecule;

wherein components (A-1) and (A-2) are employed in quantities such that from 10 to 50 percent of the epoxide equivalents contained in component (A) are

15 contributed by components (A-1), from 50 to 90 percent of such epoxide equivalents are contributed by component (A-2), and component (A-1) is present as at least 20 weight % and less than 50 mol % of components (A-1) and (A-2), and wherein components (A) 20 and (B) are present in a quantity which results in an advanced epoxy resin having an average epoxide equivalent weight of from 350 to 30,000.

2. A resin as claimed in Claim 1, having an average epoxide equivalent weight of from 350 to 15,000.

25 3. A resin as claimed in Claim 2, having an average epoxide equivalent weight of from 350 to 3,000.



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4. A resin as claimed in any one of the preceding Claims, wherein component (A-2) is a diglycidyl ether of a polyhydric phenol.

5. A resin as claimed in any one of the preceding
05 Claims, wherein component (A-2) is a diglycidyl ether of a bisphenol and component (B) is a bisphenol.

6. A resin as claimed in any one of the preceding claims, wherein the said polyoxypropylene glycol has an average molecular weight of from 200 to 400.

10 7. A resin as claimed in any one of the preceding Claims, wherein:-

(a) component (A-1) has an average epoxide equivalent weight of from 123 to 400 and

(b) component (A-2) is a diglycidyl ether of
15 bisphenol A having an average epoxide equivalent weight of from 172 to 250.

8. A resin as claimed in any one of the preceding claims, wherein component (A-1) has an average epoxide equivalent weight of from 120 to 260 and component
20 (A-2) is a diglycidyl ether of bisphenol A.

9. A resin as claimed in any one of the preceding Claims, wherein component (A-1) is present in quantities of up to 30 percent of components

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(A-1) and (A-2) and components (A) and (B) are employed in quantities such that the resultant advanced epoxy resin has an average epoxy equivalent weight of from 350 to 700.

05 10. A resin as claimed in any one of Claims 1 to 8, having an average epoxy equivalent weight of from 1400 to 3000.

11. A resin as claimed in Claim 10, wherein component (A-1) is present in quantities of up to 25 percent of

10 components (A-1) and (A-2).

12. A resin as claimed in Claim 1 and substantially as hereinbefore described in any one of the Examples.
