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COATING COMPOSITIONS CONTAINING  
ADVANCED EPOXY RESINS

The present invention concerns coating compositions containing advanced epoxy resins.

05       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  
10 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,  
15 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  
20 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  
25 having improved flexibility and requiring less solvent to achieve desirable application viscosities.

The present invention is directed to a coating

composition comprising:-

(I) an advanced epoxy resin prepared by reacting in the presence of a suitable catalyst

(A) a composition comprising

05 (1) at least one aliphatic diepoxide and, optionally

(2) at least one aromatic diepoxide; with

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

wherein components (A-1) and (A-2) are employed in quantities such that from 10 to 100 percent of the epoxide equivalents contained in component (A) are contributed by components (A-1), from 0 to 90 percent  
15 of such epoxide equivalents are contributed by component (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,

20 (II) a curing quantity of a blocked isocyanate agent for component (I); and

(III) at least one solvent in a sufficient quantity such that the coating composition including components (I), (II), (III) and any other  
25 desirable component has a suitable application viscosity.

Preferably, the components (A) and (B) are

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employed in a ratio such that the advanced epoxy resin has an average epoxide equivalent weight of from 350 to 15,000, especially 350 to 3,000.

Suitable aliphatic diepoxides which can be employed herein include the diglycidyl ethers of dihydric aliphatic compounds such as, for example, propylene glycol, tripropylene glycol, butylene glycol, dibutylene glycol, tributylene glycol, 1,4-butane diol, 1,6-hexane diol, and mixtures thereof.

Also suitable are the glycidyl ethers of polyoxyalkylene glycols having an average molecular weight of from 200 to 800, preferably from 200 to 400, which polyoxyalkylene glycols are prepared by reacting an aliphatic initiator compound with propylene oxide, butylene oxide or mixtures thereof. Preferred aliphatic diepoxides have an average epoxide equivalent weight of from 123 to 400.

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.

In one preferred embodiment, component (A-1) is a diglycidyl ether of a polyoxypropylene glycol or  
05 dipropylene glycol, component (A-2), if present, is a diglycidyl ether of a bisphenol and component (B) is a bisphenol. Suitably, the component (A-1) has an average epoxide weight of from 120 to 260 and component (A-2) is a diglycidyl ether of bisphenol A.

10 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.  
15 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,  
20 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  
25 this Specification indicates a Trade Mark.

Suitable commercially available diglycidyl ethers of aliphatic dihydric compounds include D.E.R.<sup>®</sup> 732 epoxy resin and D.E.R.<sup>®</sup> 736 epoxy resin available from The Dow Chemical Company, and ARALDITE<sup>®</sup> RD-2 commercially available from Ciba-Geigy.

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.

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

For example, in automotive primer coatings, the desired percent aliphatic diepoxide is from 10 percent 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.

For applications as automotive chip resistant coatings, the desired percent aliphatic diepoxide is from 70 percent to 100 percent and the epoxide equivalent weight of the advanced epoxy resin is from 1200 to 3000.

For beverage can coating applications, the desired percent of aliphatic diepoxide is from 10 percent to 25 percent and the epoxide equivalent weight of the advanced resin is from 1400 to 3000.

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For coil coating applications, the desired percent of aliphatic diepoxide is from 10 percent 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  
10 glycol, the n-butyl ether of ethylene glycol; and 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.

The curing agents which are employed in the coating compositions of the present invention are blocked isocyanates. Typical examples are tolylene diisocyanate, 4,4'-diphenylmethane-isocyanate, a  
05 buiret from hexamethylenediisocyanate, a 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  
10 methylethylketoxime. Also useful are those prepolymers prepared by reacting diols or triols with diisocyanate such as, e.g. tolylene diisocyanate, hexamethylene diisocyanate or isophorone diisocyanate blocked with the aforementioned phenols.

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

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

In the following examples, ALIPHATIC DIEPOXIDE C was a diglycidyl ether of dipropylene glycol having an average EEW of 176; AROMATIC DIEPOXIDE A was a  
25 diglycidyl ether of bisphenol A having an average EEW of 189; and DIHYDRIC PHENOL A was biphenol A.

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#### EXAMPLE 1

An advanced resin having an average EEW of 1800 was prepared by reacting 324.8 grams (1.845 epoxide equivalents) of aliphatic diepoxide C and 175.2 grams (1.537 phenolic OH equivalents) of bisphenol A in the presence 0.461 grams of a 70 percent solution of ethyltriphenyl phosphonium acetate-acetic acid complex in methanol. The peak exotherm was 200°C and heating was continued thereafter at 175°C for 1.5 hours (5400 s). The resultant product was diluted to 80 percent solids by weight with the monomethyl ether of propylene glycol. A 408 g sample of the 80 percent solids solution was diluted to 70 percent solids by the addition of 63.6 g of 2-methoxypropanol acetate. The resultant solution had a Gardner viscosity of Z<sup>+</sup> (~2300 cps. or ~2.3 Pa·s) at 25°C.

#### EXAMPLES 2 AND 3 AND COMPARATIVE RUN B

Example 1 was repeated employing 243.6 grams (1.38 epoxide equivalents) of aliphatic diepoxide C (75 weight percent), 81.2 grams (0.43 epoxide equivalents) of aromatic diepoxide A (25 weight percent) and 175.2 grams (1.537 phenolic hydroxyl equivalents) of bisphenol A and 0.464 grams of catalyst solution. The peak exotherm was observed to be 204°C. A sample of the resin at 80 percent solids was diluted further with 2-methoxypropanol acetate to give a 60 percent solids solution. This solution had a Gardner viscosity of X-Y at 25°C.

A similar product designated Example 3, was prepared using a blend of 50 percent of aliphatic diepoxide C and 50 percent of aromatic diepoxide A.

Example 4

Preparation of Methyl Ethyl Ketoxime Blocked  
Prepolymer

A one-liter five-necked flask was charged with 174.2 g (2.0 eq.) of 80/20, 2,4-,2,6-tolylene diisocyanate. The flask was heated to 50°C and 205 g (1.0 eq.) of a polyoxypropylene glycol having an average molecular weight of 425 containing 0.87 g of dibutyl tin dilaurate solution (10 percent solids in methyl ethyl ketone) was added during 35 minutes (2100 s) while maintaining the temperature between 65° and 73°C. Fifty grams of methyl ethyl ketone was added to facilitate stirring. Heating was continued an additional 40 minutes (2400 s) at 55°C. Methyl ethyl ketoxime (87.1 g, 1.0 eq.) was added over a 20 minute (1200 s) period while applying cooling to keep the temperature below 55°C. An additional 25 g of methyl ethyl ketone and 25 g of 2-methoxypropanol was added to give a total of 100 g of solvent or 82.3 percent solids. The product was a deep yellow liquid which partially crystallized on standing. A 410 g sample at 82.3 percent solids was diluted further with 79.5 g methyl ethyl ketone and 18 g of 2-methoxypropanol to give a 77.5 percent solids solution.

The products of Examples 1, 2 and 3 were compared to an epoxy resin of 1800 epoxide equivalent weight prepared only from aromatic diepoxide A and bisphenol A. It is sold commercially by The Dow Chemical Company as D.E.R.<sup>®</sup> 667 epoxy resin. The epoxy resins were blended at the ratio of 100 parts of epoxy resin to 50 parts of the blocked isocyanate of Example 4 (solids basis) and 1 part of dibutyl tin dilaurate (T12 catalyst) to 100 parts of blocked isocyanate.

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Films were drawn down on unpolished cold rolled steel panels using a number 40 wire wound rod and baked for 30 minutes (1800 s) at 300°F (149°C) or 275°F (135°C). The films were evaluated for MEK double  
5 rubs, reverse impact and X-adhesion. Reverse impact resistance was measured according to ASTM D-2794. The letter "P" signifies pass and the letter "F" signifies fail. The latter test was performed by scribing an X on a panel with a razor blade and pulling with Scotch  
10 Brand 610 tape. A pass represents no loss of adhesion where as a fail indicates removal of film from all four quadrants of the X-batch. The results are tabulated in Table II.

TABLE II - EVALUATION OF 1800 EEW RESINS WITH BLOCKED ISOCYANATE

| <u>EPOXY RESIN</u>                         | <u>EXAMPLE 1</u> | <u>EXAMPLE 2</u> | <u>EXAMPLE 3</u> | <u>COMPARATIVE<br/>RUN B</u> |
|--------------------------------------------|------------------|------------------|------------------|------------------------------|
| ALIPHATIC DIEPOXIDE C, %                   | 100              | 75               | 50               | 0                            |
| AROMATIC DIEPOXIDE A, %                    | 0                | 25               | 50               | 100                          |
| EEW OF ADVANCED RESIN                      | 1765             | 1900             | 1765             | 1775                         |
| EPOXY SOLIDS, pbw                          | 80.0             | 72.9             | 73.3             | 70.0                         |
| EPOXY SOLUTION, pbw                        | 114.3            | 121.5            | 122.2            | 140.0                        |
| BLOCKED NCO SOLIDS, pbw                    | 40.0             | 36.5             | 36.6             | 35.0                         |
| BLOCKED NCO SOLUTION, pbw                  | 51.6             | 47.1             | 47.2             | 45.1                         |
| T-12 CATALYST, pbw,<br>10% solution in MEK | 4.0              | 3.6              | 3.7              | 3.5                          |
| % SOLIDS OF BLEND                          | 70.8             | 64.4             | 64.3             | 57.9                         |
| GARDNER VISCOSITY OF BLEND                 | Y-Z              | X-Y              | Z                | Z-1                          |
| VISCOSITY, CPS OF BLEND<br>(Pa·s)          | ~1900<br>(~1.9)  | ~1500<br>(~1.5)  | ~2300<br>(~2.3)  | ~2700<br>(~2.7)              |

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TABLE II (cont'd)

| <u>EPOXY RESIN</u>                                                | <u>EXAMPLE 1</u>             | <u>EXAMPLE 2</u>             | <u>EXAMPLE 3</u>                        | <u>COMPARATIVE<br/>RUN B</u>                |
|-------------------------------------------------------------------|------------------------------|------------------------------|-----------------------------------------|---------------------------------------------|
| CURE 1800 s @ 300°F (149°C)<br>REVERSE IMPACT, in.-lbs.<br>(m-kg) | P160<br>(1.84)<br>15<br>PASS | P160<br>(1.84)<br>17<br>PASS | P160<br>(1.84)<br>45<br>PASS            | P80, F100<br>(0.92, 1.15)<br>75<br>FAIL 25% |
| MEK RUBS<br>ADHESION                                              |                              |                              |                                         |                                             |
| CURE 1800 s @ 275°F (135°C)<br>REVERSE IMPACT, in.-lbs.<br>(m-kg) | P160<br>(1.84)<br>15<br>PASS | P160<br>(1.84)<br>13<br>FAIL | P80, F100<br>(0.92, 1.15)<br>25<br>FAIL | F40<br>(0.46)<br>65<br>FAIL                 |
| MEK RUBS<br>ADHESION                                              |                              |                              |                                         |                                             |

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CLAIMS

1. A coating composition comprising:-

(I) an advanced epoxy resin prepared by reacting  
in the presence of a suitable catalyst

05 (A) a composition comprising

(1) at least one aliphatic diepoxide and,  
optionally

(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 100 percent of the  
epoxide equivalents contained in component (A) are  
15 contributed by components (A-1), from 0 to 90 percent  
of such epoxide equivalents are contributed by  
component (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  
20 weight of from 350 to 30,000;

(II) a curing quantity of a blocked isocyanate  
curing agent for component (I); and

(III) at least one solvent in a sufficient quantity  
such that the coating composition including  
25 components (I), (II), (III) and any other  
desirable component has a suitable  
application viscosity.



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2. A composition as claimed in Claim 1, wherein components (A) and (B) are employed in a ratio such that the resultant epoxy resin has an average epoxide equivalent weight of from 350 to 15,000.
- 05 3. A composition as claimed in Claim 2, wherein components (A) and (B) are employed in a ratio such that the resultant epoxy resin has an average epoxide equivalent weight of from 350 to 3,000.
4. A composition as claimed in any one of the  
10 preceding Claims, wherein component (A-1) is a diglycidyl ether of a dihydric aliphatic compound.
5. A composition as claimed in any one of the preceding Claims, wherein component (A-2) is present and is a diglycidyl ether of a polyhydric phenol.
- 15 6. A composition as claimed in any one of the preceding Claims, wherein component (A-1) is a diglycidyl ether of a polyoxypropylene glycol or dipropylene glycol; component (A-2), if present, is a diglycidyl ether of a bisphenol and component (B) is  
20 a bisphenol.
7. A composition as claimed in Claim 6, wherein the said polyoxypropylene glycol has an average molecular weight of from 200 to 400.
8. A composition as claimed in any one of the  
25 preceding Claims, wherein:-



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(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 bisphenol A having an average epoxide

05 equivalent weight of from 172 to 250.

9. A composition as claimed in Claim 7, wherein component (A-1) has an average epoxide equivalent weight of from 120 to 260 and component (A-2) is a diglycidyl ether of bisphenol A.

10 10. A composition as claimed in any one of the preceding Claims, wherein component (A-1) is present in quantities of from 10 to 30 percent by weight of components (A-1) and (A-2) and components (A) and (B) are employed in quantities such that the resultant  
15 advanced epoxy resin has an average epoxy equivalent weight of from 350 to 700.

11. A composition as claimed in Claim 10, which is an automotive primer coating composition.

12. A composition as claimed in any one of Claims 1  
20 to 9, wherein component (A-1) is present in quantities of from 70 to 100 percent by weight of components (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 weight of  
25 from 1200 to 3000.



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13. A composition as claimed in Claim 12, which is an automotive chip resistant coating composition.
14. A composition as claimed in any one of Claims 1 to 9, wherein component (A-1) is present in quantities of from 10 to 50 by weight percent of components (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 1400 to 3000.
15. A composition as claimed in Claim 14, which is a coil coating composition.
16. A composition as claimed in Claim 14, wherein component (A-1) is present in quantities of from 10 to 25 percent of components (A-1) and (A-2).
17. A composition as claimed in Claim 16, which is a beverage can coating composition.
18. A composition as claimed in any one of the preceding claims, wherein the isocyanate is blocked with a phenol, lactam, or oxime.
19. A composition as claimed in Claim 18, wherein the blocked isocyanate is selected from tolylene diisocyanate, 4,4'-diphenyl-methane isocyanate, a biuret from hexamethylenediisocyanate, a cocyclic trimer of hexamethylenediisocyanate and tolylene diisocyanate blocked with phenols, lactams or oximes.



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20. A composition as claimed in Claim 19, wherein the isocyanate is blocked with 4-chlorophenol, o-sec-butylphenol, caprolactam, acetaldehydeoxime, or methylethylketoxime.

05 21. A composition as claimed in Claim 18, wherein the blocked isocyanate is in the form of a prepolymer formed by reaction with a diol or triol with a diisocyanate.

22. A composition as claimed in Claim 20 or in Claim 10 21 wherein the blocked isocyanate is tolylene diisocyanate blocked with methylethylketoxime.

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

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