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A PROCESS FOR HYDROLYZING EPOXY RESINS

The present invention relates to a process for preparing hydrolyzed epoxy resins.

High molecular weight polyepoxide resins have been made more reactive by blending with a hydrolyzed
5 or partially hydrolyzed low molecular weight or high molecular weight epoxy resin as disclosed by Walker in U.S. 3,632,836.

Hydrolyzed and partially hydrolyzed epoxy resins have been prepared by dissolving the epoxy resin
10 to be hydrolyzed in an inert organic solvent, admixing the resultant solution with a dilute aqueous solution of an acid catalyst, heating to a temperature of from 50°C to 374°C, washing to remove the acid catalyst and
15 distilling the solvent to recover the hydrolyzed epoxy resin product. Such process is disclosed by Walker in U.S. 3,405,093, U.S. 3,632,836 and U.S. 3,787,508.

Such process requires the necessity for removing and recovering large quantities of an organic

solvent therefrom. The present invention not only eliminates the need for removing large quantities of organic solvent, but reduces the time required to reach the desired level of hydrolysis.

05 It is known to prepare high molecular weight epoxy resins containing hydrolyzed epoxy groups by reacting, in the absence of an organic solvent, a low molecular weight epoxy resin and a polyhydric alcohol or phenol in the presence of water and a hydrolysis catalyst and,
10 optionally, a catalyst for reaction between the epoxy resin and the polyhydric compound (see WO 82/01878 and US 4340713). The hydrolysis catalyst can be any suitable acid or base catalyst. When the polyhydric compound is a phenol, the optional catalyst preferably
15 is a quaternary phosphonium or ammonium compound. However, when the polyhydric catalyst is an alcohol, the optional catalyst is a Lewis acid.

Surprisingly, we have now found that epoxy resins can be hydrolysed with water in the absence of a
20 polyhydric phenol and an organic solvent by use of a catalyst comprising a dicarboxylic acid and a phosphonium compound within a molar ratio range as specified hereinafter.

The present invention pertains to a process for hydrolyzing an epoxy resin by reacting said epoxy resin with water in the presence of a catalyst, characterized by conducting the reaction in the absence of a polyhydric phenol and of an organic solvent and in the presence of a catalytic quantity of a catalyst comprising

05 (1) at least one dicarboxylic acid, and
(2) at least one phosphonium compound and ..

10 wherein the molar ratio of (1) to (2) is from 1:1 to 20:1, preferably from 3:1 to 10:1, most preferably from 5:1 to 7:1.

Any epoxy resin, preferably a glycidyl ether of a polyhydric aromatic or aliphatic compound type can be hydrolyzed by the process of the present invention.

15 Such resins are fully described in Handbook of Epoxy Resins by Lee and Neville, McGraw-Hill, 1967. Particularly suitable epoxy resins which can be hydrolyzed by the process of the present invention include, for

20 example, the glycidyl ethers of bisphenols and novolac resins.

Suitable dicarboxylic acids which can be employed herein include those having from 2 to 10, preferably from 2 to 6, most preferably from 2 to 4,

25 carbon atoms, such as, for example, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, and

mixtures thereof. Also suitable are the hydrates of the aforementioned acids.

Suitable phosphonium catalysts which can be employed with the dicarboxylic acid in the present invention for hydrolyzing epoxy resins include, for example, those disclosed by Perry in U.S. 3,948,855 or by Dante in U.S. 3,477,990. Particularly suitable phosphonium catalysts include, for example, ethyltriphenylphosphonium chloride, ethyltriphenylphosphonium bromide, ethyltriphenylphosphonium iodide, ethyltriphenylphosphonium acetate, ethyltriphenylphosphonium diacetate (ethyltriphenylphosphonium acetate·acetic acid complex), tetrabutylphosphonium chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium iodide, tetrabutylphosphonium acetate and tetrabutylphosphonium diacetate (tetrabutylphosphonium acetate·acetic acid complex). The total quantity of catalyst varies depending upon the conditions employed, but is advantageously from 0.001 to 0.01, preferably from 0.003 to 0.008 mole of total catalyst per epoxide equivalent contained in the resin or resins to be hydrolyzed. Higher quantities can be employed, but no beneficial results are obtained.

The process of the present invention is conducted at temperatures of from 50°C to 200°C, preferably from 110°C to 150°C for a period of time to reach the desired degree of hydrolysis.

The amount of water employed is dependent upon the desired degree of hydrolysis, but usually from 0 to 100, preferably from 0 to 30, most preferably from 0 to 5 percent in excess of the theoretical amount of water required for hydrolysis is employed.

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

5 The following components were employed in the examples.

CATALYST A is a 70 weight weight solution of ethyltriphenyl phosphonium acetate-acetic acid complex in methanol.

CATALYST B is oxalic acid·2H₂O.

10 EPOXY RESIN A is a diglycidyl ether of bisphenol A having an average epoxide equivalent weight (EEW) of 241.

15 EPOXY RESIN B is a phenol-formaldehyde epoxy novolac resin having an average epoxide functionality of 3.6 and an average EEW of 181.

EPOXY RESIN C is a cresol-formaldehyde epoxy novolac resin having an average epoxide functionality of 5.7 and an average EEW of 228.

20 EPOXY RESIN D is a phenol-formaldehyde epoxy novolac resin having an average epoxide functionality of 2.2 and an average EEW of 180.

EPOXY RESIN E is the triglycidyl ether of tris(4-hydroxyphenyl)methane having an average EEW of 171.

25 CURING AGENT A is a reaction product of a polyfunctional carboxylic acid and a polyalkylenepolyamine with an

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amine hydrogen equivalent weight of 170 commercially available from Henkel Corp. under the tradename VERSAMID 115.

5 CURING AGENT B is a polyalkylenepolyamine with an amine hydrogen equivalent weight of 24.4.

The following components were employed to evaluate coating performance on cold rolled steel panels using the resin examples.

10 COATING FORMULATION A was made up of two parts. Part 1 contained the resin and Part 2 contained the curing agent. Part 1 and 2 were mixed and given an induction time of one hour (3600 s) at 25°C. At the end of one hour (3600 s), the coating was made. Part 1 was composed of 100 parts resin, 72 parts methyl isobutyl ketone, 37
15 parts of the methyl ether of propylene glycol and 1.7 parts of a urea-formaldehyde resin that is 60 percent N.V. in butanol and xylol. Part 2 was composed of 120 parts xylene and 80 parts of curing agent A. All parts were based on mass. This formulation was used to coat
20 steel panels and they were allowed to cure at ambient temperature for 7 days (604,800 s).

COATING FORMULATION B was made up of 100 parts resin, 109 parts of methyl ethyl ketone, 1.7 parts of a urea-formaldehyde resin that is 60 percent N.V. in
25 butanol and xylol and a stoichiometric amount of curing agent B. All parts were based on mass. When all parts were mixed together, a coating was prepared and allowed to cure at ambient temperature for 7 days (604,800 s).

Coatings made from the epoxy resins were evaluated by the following tests.

MEK DOUBLE RUBS

- To the ball end of a 2 lb. (0.9 kg) ball pein hammer was attached a pad of cheese cloth composed of 8 plys. The pad was saturated with methyl ethyl ketone (MEK) and then rubbed across a coated substrate. A constant back and forth motion is used allowing only the weight of the hammer to apply force on the coating. A back and forth movement counts as one double rub. This motion is continued until the coating is mared and/or begins to be removed by the solvent effect.

Pencil Hardness

- This procedure can be found in Paint Testing Manual by H. A. Gardner and G. G. Sward in the 12th edition (1962) pages 131 and 132. One part was modified. When the coating is broken to the metal surface, that constitutes a failure. The results reported here are a pencil hardness that does not break the film but the next harder pencil grade does break film.

Glacial Acetic Acid Spot Test

- A coating that has been applied to a substrate and cured such as cold rolled steel can be tested for chemical resistance. In this test glacial acetic acid (≈ 1 ml) is placed on the coating. A timer is started. When the coating delaminates from the substrate, failure has occurred and the timer stopped. This time that has been recorded is then called time to failure for glacial acetic acid.

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EXAMPLE 1

A 2 liter pressure reactor was charged in order, with 700 g (2.902 epoxy equivalents) of epoxy resin A, 1.18 g (0.002 mole) of catalyst A, 16.85 g (0.936 mole) of water and 1.4 g (0.011 mole) of catalyst B. The molar ratio of catalyst B to catalyst A was 5.5:1. The reactor was sealed, purged with nitrogen and left with a 20 psig (137.9 kPa gage pressure) of nitrogen. The contents were heated to 134°C in 0.58 hour (2088 s) and maintained at 135°C for 2 hours (7200 s). The reactor was then heated to 189°C and the temperature maintained at 190°C under a vacuum for 1 hour (3600 s). The resultant product had 18 percent of the epoxy groups hydrolyzed.

15 Comparative Experiment A

A 2 liter pressure reactor was charged in order, with 700 g (2.902 epoxy equivalents) of epoxy resin A, 7.67 g (0.013 mole) of catalyst A, 12.23 g (0.679 mole) of water. The reactor was sealed, purged with nitrogen and left with a 20 psig (137.9 kPa gage pressure) of nitrogen. The contents were heated to 132°C in 0.58 hour (2088 s) and maintained at 136°C for 1 hour (3600 s). The reactor was then heated to 186°C and the temperature maintained at 190°C under a vacuum for 0.55 hour (1980 s). The resultant product had essentially none of the epoxy groups hydrolyzed.

Comparative Experiment B

A 2 liter pressure reactor was charged in order, with 1000 g (4.145 epoxy equivalents) of epoxy resin A, 16.93 g (0.941 mole) of water and 2.0 g (0.016 mole) of catalyst B. The reactor was sealed, purged with nitrogen and left with a 20 psig (137.9 kPa gage

pressure) of nitrogen. The contents were heated to 134°C in 0.93 hour (3348 s) and maintained at 134°C for 1.48 hour (5328 s). The reactor was then heated to 165°C and the temperature maintained at 163°C under a vacuum for 0.82 hour (2952 s). The resultant product had essentially none of the epoxy groups hydrolyzed.

EXAMPLE 2

A 2 liter pressure reactor was charged in order, with 700 g (3.888 epoxy equivalents) of epoxy resin B, 1.30 g (0.002 mole) of catalyst A, 9.60 g (0.533 mole) of water and 2 g (0.016 mole) of catalyst B. The molar ratio of catalyst B to catalyst A was 8:1. The reactor was sealed, purged with nitrogen and left with a 24 psig (165.5 kPa gage pressure) of nitrogen. The contents were heated to 134°C in 0.57 hour (2052 s) and maintained at 140°C for 1.02 hour (3672 s). The reactor was then heated to 190°C and the temperature maintained at 190°C under a vacuum for 0.5 hour (1800 s). The resultant product had 12 percent of the epoxy groups hydrolyzed.

Coating formulations A and B were prepared from the above prepared hydrolyzed epoxy resin B. For coating formulation A after curing, the pencil hardness was H, the MEK double rubs were more than 200 and the glacial acetic acid spot test required 360 seconds. For coating formulation B after curing, the pencil hardness was F and the MEK double rubs were more than 200. The glacial acetic acid spot test was not run. For the pencil hardness test, the values going from poorest to best are: 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H and 6H.

Comparative Experiment C

A 2 liter pressure reactor was charged in order, with 431 g (2.385 epoxy equivalents) of epoxy resin B, 6.42 g (0.011 mole) of catalyst A, 6.19 g (0.344 mole) of water. The reactor was sealed, purged with nitrogen and left with a 20 psig (137.9 kPa gage pressure) of nitrogen. The contents were heated to 135°C in 0.53 hour (1908 s) and maintained at 139°C for 1 hour (3600 s). The reactor was then heated to 190°C and the temperature maintained at 190°C under a vacuum for 0.52 hour (1872 s). The resultant product had essentially none of the epoxy groups hydrolyzed.

Comparative Experiment D

A 2 liter pressure reactor was charged in order, with 863 g (4.775 epoxy equivalents) of epoxy resin B, 11.6 g (0.644 mole) of water and 2.76 g (0.022 mole) of catalyst B. The reactor was sealed, purged with nitrogen and left with a 22 psig (151.7 kPa gage pressure) of nitrogen. The contents were heated to 132°C in 0.6 hour (2160 s) and maintained at 133°C for 1 hour (3600 s). The reactor was then heated to 190°C and the temperature maintained at 192°C under a vacuum for 0.58 hour (2088 s). The resultant product had essentially none of the epoxy groups hydrolyzed.

25 EXAMPLE 3

A 2 liter pressure reactor was charged in order, with 485 g (2.126 epoxy equivalents) of epoxy resin C, 0.81 g (0.001 mole) of catalyst A, 5.61 g (0.312 mole) of water and 1.10 g (0.009 mole) of catalyst B. The molar ratio of catalyst B to catalyst A was 9:1. The reactor was sealed, purged with nitrogen and left with a 20 psig (137.9 kPa gage pressure) of nitrogen.

The contents were heated to 133°C in 0.72 hour (2592 s) and maintained at 133°C for 1.5 hour (5400 s). The reactor was then heated to 180°C and the temperature maintained at 185°C under a vacuum for 0.33 hour (1188 s). The resultant product had 11 percent of the epoxy groups hydrolyzed.

EXAMPLE 4

A 2 liter pressure reactor was charged in order, with 1000 g (5.563 epoxy equivalents) of epoxy resin D, 2.01 g (0.003 mole) of catalyst A, 9.8 g (0.544 mole) of water and 2.8 g (0.022 mole) of catalyst B. The molar ratio of catalyst B to catalyst A was 7.3:1. The reactor was sealed, purged with nitrogen and left with a 20 psig (137.9 kPa gage pressure) of nitrogen. The contents were heated to 134°C in 1 hour (3600 s) and maintained at 132°C for 1.38 hour (4968 s). The reactor was then heated to 170°C and the temperature maintained at 180°C under a vacuum for 0.5 hour (1800 s). The resultant product had 11 percent of the epoxy groups hydrolyzed.

EXAMPLE 5

A 2 liter pressure reactor was charged in order, with 600 g (3.519 epoxy equivalents) of epoxy resin E, 1.44 g (0.005 mole) of catalyst A, 22.17 g (1.232 mole) of water and 2.66 g (0.021 mole) of catalyst B. The molar ratio of catalyst B to catalyst A is 4.2:1. The reactor was sealed, purged with nitrogen and left with a 20 psig (137.9 kPa gage pressure) of nitrogen. The contents were heated to 150°C in 0.6 hour (2160 s) and maintained at 152°C for 1.8 hour (6480 s). The reactor was then heated to 185°C and the temperature maintained at 185°C under a vacuum for 0.17

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hour (612 s). The resultant product had 38 percent of the epoxy groups hydrolyzed.

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CLAIMS:

1. A process for hydrolyzing an epoxy resin by reacting said epoxy resin with water in the presence of a catalyst wherein the reaction is conducted in the
05 absence of a polyhydric phenol and of an organic solvent and in the presence of a catalytic quantity of a catalyst comprising (1) at least one dicarboxylic acid and (2) at least one phosphonium compound wherein the molar ratio of (1) to (2) is from 1:1 to 20:1.
- 10 2. A process as claimed in Claim 1, wherein the said molar ratio is from 3:1 to 10:1.
3. A process as claimed in Claim 2, wherein the said molar ratio is from 5:1 to 7:1.
4. A process as claimed in any one of the preceding
15 Claims, wherein the epoxy resin is selected from glycidyl ethers of bisphenols and novolac resins.
5. A process as claimed in any one of the preceding Claims, wherein the dicarboxylic acid contains 2 to 10 carbon atoms.
- 20 6. A process as claimed in Claim 5, wherein the dicarboxylic acid contains 2 to 6 carbon atoms.
7. A process as claimed in Claim 6, wherein the dicarboxylic acid contains 2 to 4 carbon atoms.
8. A process as claimed in Claim 5, wherein the
25 dicarboxylic acid is selected from oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, and mixtures thereof.
9. A process as claimed in Claim 8, wherein the
30 dicarboxylic acid is oxalic acid.
10. A process as claimed in any one of the preceding Claims, wherein the phosphonium compound is selected from ethyltriphenylphosphonium chloride, bromide,
35 iodide, acetate and diacetate, and tetrabutylphosphonium chloride, bromide, iodide, acetate and diacetate.



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11. A process as claimed in Claim 10, wherein the phosphonium compound is ethyltriphenylphosphonium diacetate.
 12. A process as claimed in any one of the preceding
05 Claims, wherein the total quantity of catalyst is from 0.001 to 0.01 moles of catalyst per epoxide equivalent.
 13. A process as claimed in any one of the preceding
10 Claims, wherein the total quantity of catalyst is from 0.003 to 0.008 moles of catalyst per epoxide equivalent.
 14. A process as claimed in any one of the preceding
Claims, wherein the reaction is carried out at from 50°C to 200°C.
 - 15 15. A process as claimed in Claim 14, wherein the reaction is carried out at from 110°C to 150°C.
 16. A process as claimed in any one of the preceding
Claims, wherein the amount of water employed is 0 to 100 percent in excess of the theoretical amount
20 required for hydrolysis.
 17. A process as claimed in Claim 16, wherein said amount of water is 0 to 30 percent.
 18. A process as claimed in Claim 17, wherein said amount of water is 0 to 5 percent.
 - 25 19. A process as claimed in Claim 1 and substantially as described in any one of Examples 1 to 5 herein.
 20. A hydrolysed epoxy resin whenever prepared by a process as claimed in any one of the preceding Claims.
 21. A coating composition comprising a hydrolyzed
30 epoxy resin as claimed in Claim 20.
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