

AUSTRALIA

P/00/001
Section 29

Patents Act 1990

PATENT REQUEST: CONVENTION PATENT

We, being the person identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification

Full application details follow:-

Applicant: E.I. DU PONT DE NEMOURS AND COMPANY
Address: 1007 Market Street, Wilmington, Delaware 19898
 United States of America

Nominated Person: E.I. DU PONT DE NEMOURS AND COMPANY
Address: 1007 Market Street, Wilmington, Delaware 19898
 United States of America

Invention Title: METHOD OF INCORPORATING POLYAMINE
 INTO A CATIONIC RESIN

Name(s) of actual Inventor(s): CHUNG, Ding, Yu; DEBROY, Tapan, Kumar
Address for service in Australia: CALLINAN LAWRIE, 278 High Street, Kew 3101,
 Victoria, Australia

Attorney Code: CL

Convention Details

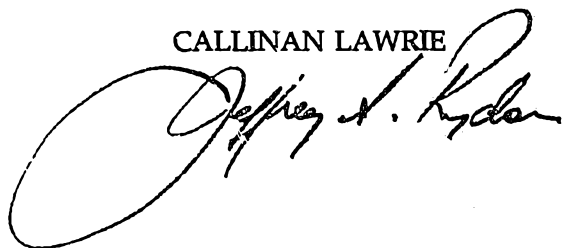
<u>Application Number</u>	<u>Country</u>	<u>Country Code</u>	<u>Date of Application</u>
563,837	USA	US	6 August 1990

D A T E D this 26th day of January 1993.

E.I. DU PONT DE NEMOURS AND COMPANY

By their Patent Attorneys:

CALLINAN LAWRIE



CALLINAN LAWRIE
Private Bag 7, Kew
Victoria 3101, Australia
Facsimile:
61 (3) 853.0062
61 (3) 853.0728

A U S T R A L I A

FA-0469

PATENT

NOTICE OF ENTITLEMENT

We, E.I. DU PONT DE NEMOURS AND COMPANY, of 1007 Market Street, Wilmington, Delaware 19898, United States of America, being the applicant and the person nominated for grant of patent in respect of the Application for an invention entitledMETHOD OF INCORPORATING POLYAMINE INTO A CATIONIC.....
.....RESIN.....
.....

state the following:-

~~(A) STANDARD CONVENTION FILING~~

If (A)
strike out
(B) and
(C)

~~The person nominated for the grant of the patent has entitlement from the actual inventor(s) who is/are the applicant(s) of the basic application(s) listed on the patent request form by virtue of an assignment of the invention and of the priority right from the actual inventor(s).~~

~~The basic application(s) listed on the request form is/are the first application(s) made in a Convention country in respect of the invention.~~

OR

(B) PCT-CONVENTION NATIONAL PHASE FILING

If (B)
strike out
(A) and
(C)

The person nominated for the grant of the patent has entitlement from the inventor(s) and the applicant(s) of the application(s) listed in the declaration under Article 8 of the PCT by virtue of an assignment of the invention from the actual inventor(s).

The basic application(s) listed on the request form and in the declaration made under Article 8 of the PCT is/are the first application(s) made in a Convention country in respect of the invention.

OR

~~(C) STANDARD NON-CONVENTION FILING~~

If (C)
strike out
(A) and
(B)

~~The person nominated for the grant of the patent has entitlement from the actual inventor(s) by virtue of an assignment of the invention from the actual inventor(s).~~

Miriam D. Neerakey

Signature

January 20, 1993

Date

Assistant Secretary of the Patent Board

Executive Position



AU9184200

(12) PATENT ABRIDGMENT (11) Document No. AU-B-84200/91
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 640591

(Modified Examination)

- (54) Title
METHOD OF INCORPORATING POLYAMINE INTO A CATIONIC RESIN
- International Patent Classification(s)
(51)⁵ **C25D 009/02 C09D 005/44**
- (21) Application No. : **84200/91** (22) Application Date : **01.08.91**
- (87) PCT Publication Number : **WO92/02588**
- (30) Priority Data
- | | | |
|---------------|-----------------|------------------------------------|
| (31) Number | (32) Date | (33) Country |
| 563837 | 06.08.90 | US UNITED STATES OF AMERICA |
- (43) Publication Date : **02.03.92**
- (44) Publication Date of Accepted Application : **26.08.93**
- (71) Applicant(s)
E.I. DU PONT DE NEMOURS AND COMPANY
- (72) Inventor(s)
DING YU CHUNG; TAPAN KUMAR DEBROY
- (74) Attorney or Agent
CALLINAN LAWRIE , Private Bag 7, KEW VIC 3101
- (56) Prior Art Documents
AU 91171/91 C09D 5/44 C09D 163/00
AU 629056 64665/90 C09D 5/44 C09D 163/00
AU 623273 58955/90 C09D 5/44 C09D 163/00
- (57) Claim

1. In a method of electrocoating an electrically conductive surface serving as a cathode comprising passing an electric current between said cathode and an anode in electrical contact with an aqueous electrodepositable composition wherein the aqueous electrodepositable composition comprises an epoxy amine adduct which is water solubilized with an acid and a blocked polyisocyanate crosslinker; wherein the improvement comprises the epoxy amine adduct is formed by the following steps:

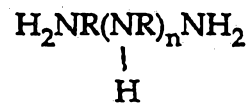
a) reacting an epoxy resin with an amount of secondary amine so that unreacted epoxy functional groups remain; and

b) further reacting the reaction product of a) with a polyamine so that there is a minimum of one equivalent of epoxy for every mole of polyamine;

(11) AU-B-84200/91
(10) 640591

-2-

wherein the polyamine has the formula:



wherein n is a integer of 0 to 4 and R is an alkylene group containing 2 to 6 carbon atoms.

2. The method of claim 1 wherein the polyamine is diethylene triamine, triethylene tetramine, hexamethylene diamine or 1,3-diaminopentane.

OPI DATE 02/03/92

APPLN. ID

84200 / 91



AOJP DATE 09/04/92

PCT NUMBER PCT/US91/05327

INTERN.

I TREATY (PCT)

<p>(51) International Patent Classification ⁵ : C09D 5/44</p>	<p>A1</p>	<p>(11) International Publication Number: WO 92/02588 (43) International Publication Date: 20 February 1992 (20.02.92)</p>
<p>(21) International Application Number: PCT/US91/05327 (22) International Filing Date: 1 August 1991 (01.08.91) (30) Priority data: 563,837 6 August 1990 (06.08.90) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: CHUNG, Ding, Yu ; 2062 Hickory Leaf Drive, Rochester Hills, MI 48309 (US). DEBROY, Tapan, Kumar ; 54727 Blue Cloud Drive, Shelby Township, MI 48315 (US).</p>	<p>(74) Agents: FRICKE, Hilmar, L. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). 640591 Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: METHOD OF INCORPORATING POLYAMINE INTO A CATIONIC RESIN (57) Abstract Disclosed herein is a method of incorporating amine functionality onto a polyepoxy resin to be used for cathodic electrocoat. This method has the following steps: a) reacting an epoxy resin with an amount of secondary amine so that unreacted epoxy functional groups remain; and b) further reacting the reaction product of a) with a polyamine so that there is a minimum of one equivalent of epoxy for every mole of polyamine. This method results in an electrocoat bath with the desired high pH and a stable dispersion.</p>		

TITLE
METHOD OF INCORPORATING POLYAMINE
INTO A CATIONIC RESIN

5

TECHNICAL FIELD

The field of art to which this invention pertains is a method of incorporating polyamine in a cationic resin to be used in cathodic electrocoat.

10

BACKGROUND

The coating of electrically conductive substrates by electrodeposition is a well known and important industrial process. (For instance, electrodeposition is widely used in the automotive industry to apply primers to automotive substrates). In this process, a conductive article is immersed as one electrode in a coating composition made from an aqueous emulsion of film-forming polymer. An electric current is passed between the article and a counter-electrode in electrical contact with the aqueous emulsion, until a desired coating is produced on the article. The article to be coated is the cathode in the electrical circuit with the counter-electrode being the anode.

25

Resin compositions used in cathodic electrodeposition baths are also well known in the art. These resins are typically manufactured from polyepoxide resins which have been chain extended and adducted to include a nitrogen. The nitrogen is typically introduced through reaction with an amine compound. Typically these resins are blended with a crosslinking agent and then neutralized with an acid to form a water emulsion which is usually referred to as a principal emulsion.

35

The principal emulsion is combined with a pigment paste, coalescent solvents, water, and other additives (usually at the coating site) to form the electrodeposition bath. The electrodeposition bath is placed in an insulated tank containing the anode. The article to be coated is made the cathode and is passed through the tank containing the electrodeposition bath. The thickness of the coating is a function of the bath characteristics, the electrical operating characteristics, the immersion time, and so forth.

The coated object is removed from the bath after a set amount of time. The object is rinsed with deionized water and the coating is cured typically in an oven at sufficient temperature to produce crosslinking. It is typically covered with any of a variety of different topcoat systems (e.g. basecoat/clearcoat.)

The prior art of cathodic electrodepositable resin compositions, coating baths, and cathodic electrodeposition processes are disclosed in U.S. Pat. Nos. 3,922,253; 4,419,467; 4,137,140; and 4,468,307 which are incorporated herein by reference.

An important step in the production of the cathodic electrodepositable polymer is the introduction of the amine to the epoxy compound. This is needed in order to make the polymer water soluble through the use of an acid counter-ion. Typically the epoxy is reacted with a secondary amine with or without protected primary amine (e.g. the diketimene of diethylene triamine). It is important to have a high pH and stable dispersion. Current commercial electrocoat systems typically use ketimenes to introduce the amine functionality to the epoxy resins. This well known process is described in U.S. Patent 4,017,438 which is incorporated herein by reference.

However, the ketimene method has some disadvantages. It must be protected from moisture, the ketone must be stripped off (ketone is the reaction product between ketimene and water), and it is time consuming to
5 prepare. There is a need for an alternate method (other than ketimene) for introducing the amine functionality to the epoxy resin.

Summary of the Invention

10 It has been discovered that amine functionality can be introduced into the epoxy resin by reacting an epoxy resin with secondary amine/polyamine. This new method comprises the following steps:

15 a) reacting an epoxy resin with an amount of secondary amine so that unreacted epoxy functional groups remain; and

b) further reacting the reaction product of a) with a polyamine so that there is a minimum of one
20 equivalent of epoxy for every mole of polyamine.

The secondary amine/polyamine method results in the desired high pH and stable dispersion in the electrocoat bath.

Detailed Description of the Invention

25 As previously mentioned, it is well known that most principal emulsions in electrodeposition baths comprise an epoxy amine adduct blended with a cross-linking agent and neutralized with an acid in
30 order to get a water soluble product. Typical crosslinkers which can be used in our invention are aliphatic and aromatic isocyanates such as hexamethylene diisocyanate, toluene diisocyanate, methylene diphenyl diisocyanate and so forth. These
35 isocyanates are pre-reacted with a blocking agent such

as oximes, alcohols, and caprolactams which block the isocyanate functionality (i.e. the crosslinking functionality). Upon heating, the blocking agents separate and crosslinking occurs. The blocked isocyanate crosslinkers which can be used in our invention are well known in the art and are described in detail in numerous patents such as U.S. Patent 4,017,438 and in various other publications.

The polyepoxide resins which are used in the practice of the invention are polymers having a 1,2-epoxy equivalency greater than one and preferably about two, that is, polyepoxides which have on an average basis two epoxy groups per molecule. The preferred polyepoxides are polyglycidyl ethers of cyclic polyols. Particularly preferred are polyglycidyl ethers of polyhydric phenols such as bisphenol A. These polyepoxides can be produced by etherification of polyhydric phenols with epihalohydrin or dihalohydrin such as epichlorohydrin or dichlorohydrin in the presence of alkali. Examples of polyhydric phenols are

2,2-bis-(4-hydroxy-3-tertiarybutylphenyl)propane,
1,1-bis-(4-hydroxyphenyl)ethane,
2-methyl-1,1-bis-(4-hydroxyphenyl) propane,
2,2-bis-(4-hydroxy-3-tertiarybutylphenyl)propane,
bis-(2-hydroxynaphthyl methane, 1,5-dihydroxy-3-naphthalene or the like.

Besides polyhydric phenols, other cyclic polyols can be used in preparing the polyglycidyl ethers of cyclic polyol derivatives. Examples of other cyclic polyols would be alicyclic polyols, particularly cycloaliphatic polyols, such as 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-bis(hydroxymethyl)cyclohexane,

1,3-bis-(hydroxymethyl)cyclohexane and hydrogenated bisphenol A.

The polyepoxides have molecular weights of at least 200 and preferably within the range of 200 to 2000, and more preferably about 340 to 2000.

The polyepoxides are preferably chain extended with a polyether or a polyester polyol which enhances flow and coalescence. Examples of polyether polyols and conditions for chain extension are disclosed in U.S. Pat. No. 4,468,307. Examples of polyester polyols for chain extension are disclosed in U.S. Pat. No. 4,148,772.

The polyepoxide is reacted with a cationic group former, for example, an amine and then neutralized with an acid.

In the prior art, the amines used to adduct the epoxy resin are monoamines. In addition to the amines disclosed above, a portion of the amine which is reacted with the polyepoxide-polyether polyol product can be the ketimine of a polyamine. This is described in U.S. Patent No. 4,104,147 in column 6, line 23, to column 7, line 23, the portions of which are hereby incorporated by reference. The ketimine groups will decompose upon dispersing the amine-epoxy reaction product in water resulting in free primary amine groups which would be reactive with curing agents. Mixtures of the various amines described above have also been used in the prior art.

It has been discovered that amine functionality can be introduced into the epoxy resin by reacting an epoxy resin with secondary amine/polyamine. This new method comprises the following steps:

a) reacting an epoxy resin with an amount of secondary amine so that unreacted epoxy functional

groups remain; and

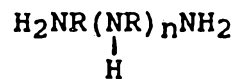
b) further reacting the reaction product of a) with a polyamine so that there is a minimum of one equivalent of epoxy for every mole of polyamine.

5 The reaction between the secondary amine and the epoxy resin (step a) takes place upon mixing the secondary amine with the epoxy resin. The secondary amine is added to the epoxy resin in an amount so that for every equivalent of polyepoxide there is 0.5 to
10 0.95 equivalents of secondary amine. This will generate a reaction product with 0.5 to 0.05 equivalents of polyepoxy. The reaction product of step a) with the remaining 0.5 to 0.05 equivalents of polyepoxy is then reacted with an equal or less number
15 of moles of polyamine (step b). It is possible that residual secondary amine from step a) continues reacting with the epoxy resin during step b).

 The purpose of step a) is to partially defunctionalize the epoxy resin so that when the
20 polyamine is added in step b) there is no gelling. It was previously thought that unprotected polyamine could not be added to polyepoxy without gelling unless there was a large excess of polyamine. (The term
"unprotected polyamine" is defined as an amine with
25 all active hydrogen available for reaction with epoxide). The necessity of an excess of polyamine, as previously believed, is shown in U.S. Patent No. 4,093,594 issued June 6, 1978 which is incorporated
herein by reference. This patent discloses that, at
30 the very least, 1.5 moles of polyamine are required for every equivalent of polyepoxy. Excess polyamine (which would be unreacted) is undesirable because it adversely affects film properties and therefore would have to be removed.

The reaction between the epoxy resin and secondary amine in step a) occurs by adding the secondary amine to the epoxy resin at 50°C to 100°C. The reaction is typically exothermic. When the exotherm stops, the polyamine is then added (step b) and the reaction mixture is then heated to 70°C to 120°C for a sufficient time to assure completion of the reaction.

The preferred polyamines of the invention have the formula:



wherein n is an integer of 0 to 4 and R is an alkylene group containing 2 to 6 carbon atoms. Particularly preferred polyamines are diethylene triamine, triethylene tetramine, hexamethylene diamine, and 1,3-diaminopentane and so forth. Most preferred are diethylene triamine and 1,3-diaminopentane.

The preferred secondary amines of the invention are monoamines with primary hydroxyl groups. Potentially any secondary amine (either with or without primary hydroxyl groups) could work. When reacting the secondary amine containing the primary hydroxyl group with the terminal epoxide groups in the polyepoxide the result is the amine/epoxy adduct in which the amine has become tertiary and contains a primary hydroxyl group. Our most preferred secondary amines are methyl ethanol amine and diethanol amine.

The final polyepoxide-amine adduct attains its cationic character by at least partial neutralization with acid. Examples of suitable acids include organic and inorganic acids such as formic acid, acetic acid, lactic acid, and phosphoric acid. The extent of neutralization will depend upon the particular product involved. It is only necessary

that sufficient acid be used to disperse the product in water. Typically, the amount of acid used will be sufficient to provide at least 30 percent of the total theoretical neutralization. Excess acid beyond that
5 required for 100 percent total theoretical neutralization can also be used.

The extent of cationic group formation of the resin should be selected such that when the resin is mixed with aqueous medium, a stable dispersion will
10 form. A stable dispersion is one which does not settle, or is one which is easily redispersible if some sedimentation occurs. In addition, the resin should be of sufficient cationic character that the dispersed resin particles will migrate towards the
15 cathode when there is an electrical potential between an anode and a cathode immersed in the aqueous dispersion.

In general, most of the cationic resins prepared by the process of the invention contain from
20 about 10 to 300, preferably from about 30 to 100 milliequivalents of cationic group per hundred grams of resin solids.

The cationic resinous binder (the epoxy-amine adduct) should preferably have weight
25 average molecular weights, as determined by gel permeation chromatography using a polystyrene standard, of less than 100,000, more preferably less than 75,000 and most preferably less than 50,000 in order to achieve high flowability.

30 The cationic resin (the epoxy-amine adduct) and the blocked isocyanate are the principal resinous ingredients in the principal emulsion and are usually present in amounts of about 30 to 50 percent by weight of solids.

Besides the resinous ingredients described above, the electrocoating compositions usually contain a pigment which is incorporated into the composition in the form of a paste. The pigment paste is prepared
5 by grinding or dispersing a pigment into a grinding vehicle and optional ingredients such as wetting agents, surfactants, and defoamers. Pigment grinding vehicles are well known in the art. After grinding, the particle size of the pigment should be as small as
10 practical, generally, a Hegman grinding gauge of about 6 to 8 is usually employed.

Pigments which can be employed in the practice of the invention include titanium dioxide, basic lead silicate, strontium chromate, carbon black,
15 iron oxide, clay and so forth. Pigments with high surface areas and oil absorbencies should be used judiciously because they can have an undesirable effect on coalescence and flow.

The pigment-to-resin weight ratio is also
20 fairly important and should be preferably less than 50:100, more preferably less than 40:100, and usually about 20 to 40:100. Higher pigment-to-resin solids weight ratios have also been found to adversely affect coalescence and flow.

25 The coating compositions of the invention can contain optional ingredients such as wetting agents, surfactants, defoamers and so forth. Examples of surfactants and wetting agents include alkyl imidazolines such as those available from Ciba-Geigy
30 Industrial Chemicals as Amine C[®], acetylenic alcohols available from Air Products and Chemicals as Surfynol 104[®]. These optional ingredients, when present, constitute from about 0.1 to 20 percent by weight of resin solids. Plasticizers are optional ingredients
35 because they promote flow. Examples are high boiling

water immiscible materials such as ethylene or propylene oxide adducts of nonyl phenols or bisphenol A. Plasticizers can be used and if so are usually used at levels of about 0.1 to 15 percent by weight resin solids.

Curing catalysts such as tin catalysts are usually present in the composition. Examples are dibutyltin dilaurate and dibutyltin oxide. When used, they are typically present in amounts of about 0.05 to 2 percent by weight tin based on weight of total resin solids.

The electrodepositable coating compositions of the present invention are dispersed in aqueous medium. The term "dispersion" as used within the context of the present invention is believed to be a two-phase translucent or opaque aqueous resinous system in which the resin is in the dispersed phase and water the continuous phase. The average particle size diameter of the resinous phase is about 0.1 to 10 microns, preferably less than 5 microns. The concentration of the resinous products in the aqueous medium is, in general, not critical, but ordinarily the major portion of the aqueous dispersion is water. The aqueous dispersion usually contains from about 3 to 50 percent preferably 5 to 40 percent by weight resin solids. Aqueous resin concentrates which are to be further diluted with water, generally range from 10 to 30 percent by total weight solids.

Besides water, the aqueous medium may also contain a coalescing solvent. Useful coalescing solvents include hydrocarbons, alcohols, esters, ethers and ketones. The preferred coalescing solvents include alcohols, polyols and ketones. Specific coalescing solvents include monobutyl and monohexyl ethers of ethylene glycol, and phenyl ether of

propylene glycol. The amount of coalescing solvent is not unduly critical and is generally between about 0 to 15 percent by weight, preferably about 0.5 to 5 percent by weight based on total weight of the resin solids.

EXAMPLES

Preparation of backbone resins

10

Example A-1

The following components were charged into a suitable reactor vessel: 697 parts Epon 828[®] (diglycidyl ether of Bisphenol A from Shell Chemical Company having an epoxy equivalent weight of 188); 264 parts of polycaprolactone having a hydroxy equivalent weight of 264 (Tone 200[®] from Union Carbide Company); 198 parts of Bisphenol A; and 51 parts of xylene. The charge was heated to 145°C under a dry nitrogen blanket and 1.2 parts of benzyl dimethyl amine were added. The reaction mixture was further heated to 160°C and held for 1 hour. An additional 2.6 parts of benzyl dimethyl amine were added, and the mixture held at 147°C until 1073 weight-per-epoxy (WPE) was achieved. Methyl isobutyl ketone, 359 parts, was added. When the mixture was cooled to 65°C, 59 parts of methyl ethanol amine was added. When the exotherm stopped, DAMP (1,3 diaminopentane from Du Pont) 21 parts, was added. The reaction mixture was brought to 82°C and held at this temperature for 1.5 hours. The reaction mixture was cooled, and decanted.

20

25

30

Example A-2

The following components were charged into a suitable reactor vessel: 1412 parts Epon 828[®] (diglycidyl ether of Bisphenol A from Shell Chemical

35

Company having an epoxy equivalent weight of 188); 634 parts of Bisphenol A; and 51 parts of xylene. The charge was heated to 145°C under a dry nitrogen blanket and 1.2 parts of benzyl dimethyl amine were added. The reaction mixture was further heated to 160°C and held for 1 hour. Methyl isobutyl ketone, 897 parts, was added. When the mixture was cooled to 65°C, 90 parts of methyl ethanol amine was added. When the exotherm stopped, DAMP 82 parts, was added. The reaction mixture was brought to 82°C and held at this temperature for 1.5 hours. The reaction mixture was cooled, and decanted.

Example A-3

The following components were charged into a suitable reactor vessel: 697 parts Epon 828[®] (diglycidyl ether of Bisphenol A from Shell Chemical Company having an epoxy equivalent weight of 188); 264 parts of polycaprolactone having a hydroxy equivalent weight of 264 (Tone 200[®] from Union Carbide Company); 198 parts of Bisphenol A; and 51 parts of xylene. The charge was heated to 145°C under a dry nitrogen blanket and 1.2 parts of benzyl dimethyl amine were added. The reaction mixture was further heated to 160°C and held for 1 hour. An additional 2.6 parts of benzyl dimethyl amine were added, and the mixture held at 147°C until 1109 weight-per-epoxy (WPE) was achieved. Methyl isobutyl ketone, 359 parts, was added. When the mixture was cooled to 65°C, 59 parts of methyl ethanol amine was added. When the exotherm stopped, DETA 21 parts, was added. The reaction mixture was brought to 82°C and held at this temperature for 1.5 hours. The reaction mixture was cooled, and decanted.

Example BPreparation of Quaternizing Agent

		<u>Wt.</u>	<u>NV*</u>
5	2-Ethylhexanol half capped TDI in MIBK	320.0	304.0
	Dimethylethanolamine	87.2	87.2
	Aqueous Lactic Acid Solution	117.6	88.2
	2-Butoxyethanol	<u>39.2</u>	<u> </u>
10	Total	564.0	479.4

* non volatiles

The quaternizing agent was prepared by adding dimethylethanolamine to the ethylhexanol half-capped toluene diisocyanate (TDI) in a suitable reaction vessel at room temperature. The mixture exothermed and was stirred for one hour at 80°C. Lactic acid was then charged followed by the addition of 2-butoxyethanol. The reaction mixture was stirred for about one hour at 65°C to form the desired quaternizing agent.

Example CPreparation of Pigment Grinding Vehicle

		<u>Wt.</u>	<u>NV</u>
25	Epon 829®	710.0	682.0
	Bisphenol A	289.6	289.6
	2-Ethylhexanol half capped TDI in MIBK	406.0	386.1
30	Quaternizing Agent from Ex. B	496.3	421.9
	Deionized Water	71.2	<u> </u>
	2-Butoxyethanol	<u>1095.2</u>	<u> </u>
	Total	3068.3	1779.6

35

To form the pigment grinding vehicle Epon 829[®] (a diglycidyl ether of Bisphenol A from Shell Chemical Co.) and Bisphenol A were charged under a nitrogen atmosphere to a suitable reaction vessel and heated to 150°-160°C to initiate an exothermic reaction. The reaction mixture was permitted to exotherm for one hour at 150°-160°C. The reaction mixture was then cooled to 120°C and the 2-ethylhexanol half-capped toluene diisocyanate was added. The temperature of the reaction mixture was held at 110°-120°C for one hour, followed by the addition of the 2-butoxyethanol. The reaction mixture was then cooled to 85°-90°C, homogenized and then charged with water, followed by the addition of the quaternizing agent (prepared above). The temperature of the reaction mixture was held at 80°-85°C until an acid value of about 1 was obtained. The reaction mixture had a solids content of 58 percent.

20 Preparation of Emulsion: Example 1

	<u>NV</u>	<u>I-A</u>	<u>I-B</u>	<u>I-A</u>
Backbone Resin				
Example A-1	223.4	297.1		
25 Example A-2	223.4		313.8	
Example A-3	223.4			299.5
capped Isocyanate				
Crosslinker ¹	131.3	187.6	187.6	187.6
"Downol PPH" from Dow		3.6	3.6	3.6
30 Surfactant ²		3.6	3.6	3.6
Deionized Water		494.8	474.0	489.0
Lactic Acid		13.3	17.4	16.7
pH		6.3	6.7	6.4

1 Polyurethane crosslinker formed from half-capping
 toluene diisocyanate (80/20 2,4/2,6 isomer mixture)
 with 2- butoxy ethanol and reacting this product with
 tri methylol propane in a 3:1 molar ratio. The
 5 crosslinker is present as a 70 percent solids solution
 in 2-butoxy ethanol.

2 Surfactant is a mixture of 120 parts "Amine C" from
 Ciba-Geigy, 120 parts acetylenic alcohol, commercially
 available as "Surfynol 104", 120 parts of 2-butoxy
 10 ethanol and 221 parts by weight of deionized water and
 19 parts glacial acetic acid.

Thoroughly mix the backbone resin from Example A,
 polyurethane crosslinker, "Downol PPH", lactic acid,
 15 and surfactant. Then add the deionized water under
 agitation. The emulsions are stable.

Preparation of Pigment Paste: Example II

	<u>Wt.</u>	<u>NV</u>
20 Grind Vehicle from Example C	266.20	154.64
Deionized Water	455.30	
Carbon Black	25.98	5.98
Aluminum Silicate	51.85	51.85
25 Lead Silicate	22.24	2.24
Dibutyl Tin Oxide	16.34	16.34
TiO ₂	<u>296.23</u>	<u>296.23</u>
Total	1134.56	567.28

30 The above ingredients were mixed together and ground
 in a mill to a Hegman No. 7 grind.

Preparation of Electrocoat Bath: Example III

	<u>NV</u>	<u>IIIA</u>	<u>IIIB</u>	<u>IIIC</u>
Emulsions:				
5	Example I-A	144	406	
	Example I-B	144	406	
	Example I-C	144		406
Pigment Paste				
	(Example II)	56	112	112
10	Deionized Water		482	482
	pH		6.1	6.3
	Conductivity		2000	2200
	(micro siemens)			1720
	Film thickness (mil)		0.83	0.44
15				0.78

15

A composition was prepared by blending the above ingredients. The zinc phosphate cold-rolled steel panels were cathodically electrocoated in the electrodeposition bath at 250 volts for 2 minutes at a bath temperature of 83°F. The wet films were cured at 20 360°F for 15 minutes. The film appearances are smooth.

25

30

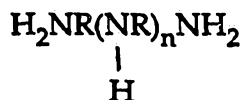
35

The claims defining the invention are as follows:-

1. In a method of electrocoating an electrically conductive surface serving as a cathode comprising passing an electric current between said cathode and an anode in electrical contact with an aqueous electrodepositable composition wherein the aqueous electrodepositable composition comprises an epoxy amine adduct which is water solubilized with an acid and a blocked polyisocyanate crosslinker; wherein the improvement comprises the epoxy amine adduct is formed by the following steps:

a) reacting an epoxy resin with an amount of secondary amine so that unreacted epoxy functional groups remain; and

b) further reacting the reaction product of a) with a polyamine so that there is a minimum of one equivalent of epoxy for every mole of polyamine; wherein the polyamine has the formula:



wherein n is a integer of 0 to 4 and R is an alkylene group containing 2 to 6 carbon atoms.

2. The method of claim 1 wherein the polyamine is diethylene triamine, triethylene tetramine, hexamethylene diamine or 1,3-diaminopentane.

3. The method of claim 2, wherein the secondary amine is added to the epoxy resin in step (a) in an amount so that for every equivalent of polyepoxide there is 0.5 to 0.95 equivalents of secondary amine.

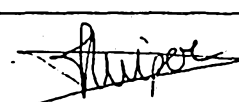
DATED this 20th day of May, 1993.

25 E.I. DU PONT DE NEMOURS AND COMPANY
By their Patent Attorneys:
CALLINAN LAWRIE



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/05327

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁵		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC5: C 09 D 5/44		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	C 09 D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4830722 (DOBDELSTEIN ET AL) 16 May 1989, see column 3, line 1 - line 22; column 11, line 36 - column 12, line 2; claim 1 --	1-5
A	US, A, 4892897 (RICHARD P. REDMAN) 9 January 1990, see abstract, column 6, line 24 - line 64, example 2, column 10 - column 11 --	1-5
A	EP, A2, 0200397 (IMPERIAL CHEMICAL INDUSTRIES PLC) 10 December 1986, see abstract; claims 1-7 --	1-5
<p>[*] Special categories of cited documents:¹⁰</p> <p>^{"A"} document defining the general state of the art which is not considered to be of particular relevance</p> <p>^{"E"} earlier document but published on or after the international filing date</p> <p>^{"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)</p> <p>^{"O"} document referring to an oral disclosure, use, exhibition or other means</p> <p>^{"P"} document published prior to the international filing date but later than the priority date claimed</p> <p>^{"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</p> <p>^{"X"} document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>^{"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.</p> <p>^{"&"} document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
26th November 1991	17 DEC 1991	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	Mme N. KUIPER 	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	EP, A1, 0368459 (IMPFRIAL CHEMICAL INDUSTRIES PLC) 16 May 1990, see abstract; claims 1-4 -- -----	1-5

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/US 91/05327**

SA 50806

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 31/10/91
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
US-A- 4830722	16/05/89	CA-A- 1258740	22/08/89
		DE-A- 3518770	27/11/86
		EP-A-B- 0241476	21/10/87
		JP-T- 62502899	19/11/87
		US-A- 4780524	25/10/88
		WO-A- 86/07083	04/12/86
		-----	-----
US-A- 4892897	09/01/90	AU-B- 596298	26/04/90
		AU-D- 1567488	01/12/88
		EP-A- 0293088	30/11/88
		JP-A- 63309564	16/12/88
-----	-----	-----	-----
EP-A2- 0200397	10/12/86	AU-B- 583608	04/05/89
		AU-D- 5595886	06/11/86
		CA-A- 1261535	26/09/89
		GB-A- 2173802	22/10/86
		JP-A- 61276817	06/12/86
		US-A- 5026743	25/06/91
		US-A- 5034434	23/07/91
		LU-A- 86837	07/12/87
-----	-----	-----	-----
EP-A1- 0368459	16/05/90	AU-D- 4237489	03/05/90
		GB-A- 2228483	29/08/90
		JP-A- 2170818	02/07/90

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