

- [54] **METHOD FOR CATHODIC ELECTRODEPOSITION OF COATING COMPOSITIONS CONTAINING DIELS-ALDER ADDUCTS**
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- [64] Patent No.: **4,148,704**
 Issued: **Apr. 10, 1979**
 Appl. No.: **859,296**
 Filed: **Dec. 12, 1977**

- [51] Int. Cl.³ **C25D 13/06**
 [52] U.S. Cl. **204/181 C**
 [58] Field of Search **204/181 C**

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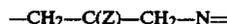
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[57] **ABSTRACT**

Described herein is an organic coating composition particularly useful in cathodic electrodeposition comprising a dispersion, solution or suspension of a coating composition characterized by (a) a reaction product of a conjugated fatty acid ester and an acrylic containing monomer, preferably containing oxirane rings; and (b) Formula A within the molecule, being the reaction product of reacting an oxirane ring and an amine; wherein Formula A is:



wherein Z is hydrogen, hydroxyl, alkoxy of 1 to 6 carbon atoms; acyloxy of from 1 to 6 carbon atoms; (=O, as in a ketone), $\text{-(OR')}_n\text{-H}$; $\text{-(OR')}_n\text{-OH}$, and $\text{-(OR')}_n\text{-(CH}_2\text{OH)-OH}$, wherein R' is a saturated alkyl-ene group of from 2 to 4 carbon atoms and n is a number from 1 to 6.

Also described is a method of electrodepositing coating compositions containing said adducts onto a cathode.

11 Claims, No Drawings

**METHOD FOR CATHODIC
ELECTRODEPOSITION OF COATING
COMPOSITIONS CONTAINING DIELS-ALDER
ADDUCTS**

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

BACKGROUND OF THE INVENTION

It has become commercially of significance to employ cathodic electrodeposition coating compositions for improved corrosion resistance can be obtained employing said compositions.

U.S. Pat. No. 4,001,101 teaches the electrodeposition of epoxy compositions which contain boron in the form of boric acid and like compounds. U.S. Pat. No. 4,001,156 teaches a method of producing epoxy group containing quaternary ammonium salt containing resins.

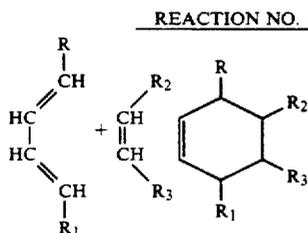
SUMMARY OF THE INVENTION

An object of the present invention is coating compositions of improved corrosion resistance particularly when employed in the cathodic electrodeposition coating process. Additionally the compositions when cured have improved weather durability, particularly on exposure to sunlight and ultraviolet light. There is an improvement over prior art compositions in chaulking resistance, weather exposure and lower bake temperatures.

The coating compositions of the present invention are prepared by reacting through the double bonds of the reactants an acrylic material containing an oxirane ring with a conjugated fatty acid ester. Without being bound to any particular theory, it is believed that this reaction is a Diels-Alder adduct reaction. The product of that reaction is in turn reacted with an amine to introduce the nitrogen moiety into the molecule.

**DESCRIPTION OF PREFERRED
EMBODIMENTS**

In the preparation of the products to be used in the process of the present invention, the first step is the Diels-Alder reaction between the conjugated fatty acid esters and monomeric materials containing oxirane ring. The reaction can be said to proceed along the following lines:



wherein R and R₁ are residue of fatty acid ester molecule; R₂ and R₃ are residue of fatty acid ester molecule; R₂ and R₃ are residue of acrylic containing monomer.

Catalysts may be used to accelerate the adduct reaction such as peroxides.

Reference may be made to applicant's concurrently filed case U.S. Ser. No. 859,295, filed Dec. 12, 1977, CATHODIC ELECTRODEPOSITION COMPOSITIONS EMPLOYING FATTY ACID DERIVATIVES.

TIONS EMPLOYING FATTY ACID DERIVATIVES.

The reactants that are employed for the conjugated fatty acid component may be exemplified by the following materials: alkyl esters wherein the alkyl group ranges from 1 to 12 carbon atoms and the fatty acid that may be employed are long chain fatty acids having from 8 to 24 carbon atoms. A preferred fatty acid is one having high conjugated diene concentration such as products available under the name Pamolyn (trademark of Hercules) especially Pamolyn 380 which has a high concentration of unsaturation at positions 9 and 11 of C₁₈ fatty acid. Suitable fatty acids are caprylic, capric, lauric, myristic, palmitic palmitoleic, stearic, oleic, ricinoleic, linoleic, linolenic, eleostearic, licanic, arachidic, arachidonic, behenic, clupanodonic, lignoceric, nisinic, and the like. A preferred alcohol is an alkanol of from 1 to 8 carbon atoms, such as methanol, butanol, hexanol, and the like.

It is to be appreciated that the esters of the conjugated fatty acids may be employed by using the reaction products resulting from reacting conjugated fatty acids with polyols.

Exemplary among the polyols are the following: ethylene glycol, propylene glycol, butylene glycol, glycerol, trimethylolpropane, hexanetriol, pentaerythritol, neopentylglycol, trimethylolethane and the like. In general the amount of alcohol added is sufficient to react all of the fatty acid so that the number of equivalents of hydroxyl groups exceeds the number of equivalents of carboxyl groups in a range of 1:1-1:1.3—carboxyl:hydroxyl groups.

The monomeric reactants that may be employed for the Diels-Alder reaction may be exemplified by the following materials: acrylic or methacrylic materials alone or together with other monomeric materials.

By "acrylic" is meant a material containing therein the monomer of the formula:



wherein B=hydrogen, methyl or ethyl.

Exemplary acrylic materials that may be employed are acrylic or methacrylic acids, the alkylesters or hydroxyalkylesters thereof where the alkyl group has from one to 18 carbon atoms, such as isobornyl acrylate, methyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl-(meth)acrylate, steryl acrylate, steryl methacrylate, and the like, acrylamides, methacrylamides, and the like. It is to be appreciated that other copolymerizable monomers may also be reacted with the acrylic material. Exemplary ethylenically unsaturated materials are styrene, vinyl toluene; 3,5-dimethyl styrene, p-tertbutyl styrene, alpha methyl styrene, and the like, unsaturated dicarboxylic acids or anhydrides and the alkylesters thereof from 1 to 18 carbon atoms (such as maleic anhydride, fumaric acid and the like).

A preferred class of acrylic reactants are those that contain the acrylic moiety together with an oxirane ring in the same molecule, such as glycidyl acrylate and methacrylate and other similar type materials such as those taught in U.S. Pat. No. 3,773,855, which is hereby incorporated by reference, such as acrylic and methacrylic esters of the monoglycidyl ether of sulfonyl bisphenol, the monoglycidyl ether of a C₁ to C₁₀ alkylene bisphenol, the monoglycidyl ether of oxybisphenol, the monoglycidyl ether of thiobisphenol, the mono-

acted with a polyol as mentioned above. The fatty acid may also be reacted with glycidyl containing materials prior to reaction sequence No. 1, including glycidyl acrylate or methacrylate. Other epoxy or glycidyl containing materials are mono- or polyepoxides, preferably a polyepoxide having an epoxy equivalent greater than 1, such as polyglycidyl ethers of polyphenols, such as bisphenol A. These can be prepared by etherification of a polyphenol with epichlorohydrin in the presence of alkali.

Another quite useful class of polyepoxides are produced similarly from novolak resins or similar polyphenol resins.

Also suitable are the similar polyglycidyl ethers of polyhydric alcohols which may be derived from such polyhydric alcohols as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-propylene glycol, 1,5-pentanediol, 1,2,6-hexanetriol, glycerol, bis(4-hydroxycyclohexyl) 2,2-propane and the like. There can also be used polyglycidyl esters of polycarboxylic acids, which are produced by the reaction of epichlorohydrin or similar epoxy compounds with an aliphatic or aromatic polycarboxylic acid such as oxalic acid, succinic acid, glutaric acid, terephthalic acid, 2,6-naphthylene dicarboxylic acid, dimerized linolenic acid and the like. Examples are glycidyl adipate and glycidyl phthalate. Also useful are polyepoxides derived from the epoxidation of an olefinically unsaturated alicyclic compound. Included are diepoxides comprising in part one or more monoepoxides. These polyepoxides are non-phenolic and are obtained by the epoxidation of alicyclic olefins; for example, by oxygen and selected metal catalysts, by perbenzoic acids, by acetaldehyde monoperacetate, or by peracetic acid, and/or hydrogen peroxide. Among such polyepoxides are the epoxy alicyclic ethers and esters which are well known in the art.

A particularly preferred class of products that may be used in the present case is the reaction product of reacting a fatty acid, conjugated or not conjugated, with compounds containing nitrogen heterocyclic rings of 5 or 6 members, said compounds also containing one or more epoxy rings. The reaction product can be characterized as an epoxy fatty acid ester.

The nitrogen heterocyclic materials are generally available in the trade and have been described in a number of patents as:

U.S. Pat. No. 3,391,097—EPOXY RESINS FROM 1,1'-METHYLENE BIS(5-SUBSTITUTED HYDANTOIN)

U.S. Pat. No. 3,814,775—3-GLYCIDYL-HYDANTOIN ISOCYANATES

U.S. Pat. No. 3,846,442—GLYCIDYL HYDANTOIN COMPOUNDS

U.S. Pat. No. 3,449,353—N,N'-DIGLYCIDYL HYDANTOINS

U.S. Pat. No. 3,542,803—N,N'-DIGLYCIDYL COMPOUNDS

U.S. Pat. No. 3,592,823—N,N'-DIGLYCIDYL COMPOUNDS

U.S. Pat. No. 3,620,983— β -METHYLGlycidylisocyanurates

U.S. Pat. No. 3,679,681—DIGLYCIDYL ETHERS

U.S. Pat. No. 3,726,895—DIGLYCIDYL DERIVATIVES OF COMPOUNDS CONTAINING TWO N-HETEROCYCLIC RINGS

U.S. Pat. No. 3,772,326—DIGLYCIDYL COMPOUNDS OF MONOHYDROXYALKYL HYDANTOINS

U.S. Pat. No. 3,778,439—BINUCLEAR N-HETEROCYCLIC POLYGLYCIDYL COMPOUNDS

U.S. Pat. No. 3,780,057—PYRAZOLONE PIGMENTS

U.S. Pat. No. 3,787,405—DIGLYCIDYL COMPOUNDS CONTAINING A N-DETEROCYCLIC RING

U.S. Pat. No. 3,808,226—POLYACRYLATES OF N-HETEROCYCLIC COMPOUNDS

U.S. Pat. No. 3,809,660—EPOXIDE RESIN MIXTURES OF HETEROCYCLIC N,N'-DIGLYCIDYL COMPOUNTS

U.S. Pat. No. 3,809,696—DIGLYCIDYL COMPOUNDS CONTAINING TWO N-HETEROCYCLIC RINGS

U.S. Pat. No. 3,821,242—DIGLYCIDYL ETHERS

U.S. Pat. No. 3,821,243—HETEROCYCLIC TRIGLYCIDYL COMPOUNDS

U.S. Pat. No. 3,828,045—DIGLYCIDYL ETHERS OF FIVE AND SIX MEMBERED N-HETEROCYCLIC COMPOUNDS

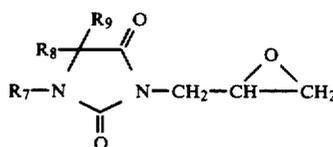
U.S. Pat. No. 3,828,066—DIGLYCIDYLIMIDAZOLIDONES

U.S. Pat. No. 3,843,675—N-HETEROCYCLIC POLYGLYCIDYL COMPOUNDS CONTAINING ESTER GROUPS

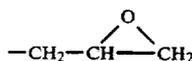
U.S. Pat. No. 3,864,358—EPOXY-ACRYLIC ACID ESTERS

all of which are hereby incorporated by reference.

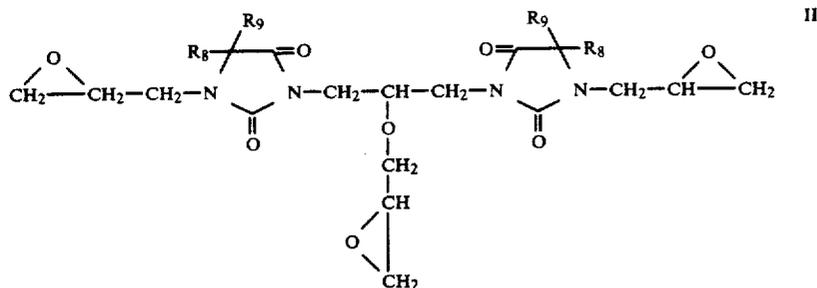
Preferred classes of compounds are:



wherein R₇ is hydrogen or



R₈ and R₉ are independently selected from the group hydrogen, alkyl of 1 to 5 carbon atoms, phenyl, a saturated aliphatic ring of 5 to 7 carbon atoms or together form a 5 to 7 member saturated carbocyclic ring; or



II

Regardless of the manner of introducing the oxirane ring into the coating resin, the amine reactant shown in reaction No. 2 is used in an amount such that all oxirane rings are reacted and that the coating composition as used in the electrodeposition process has no oxirane rings.

In curing the coating composition of the present invention, it has been found highly desirable that nitrogenous containing cross-linking agents be employed in an effective curing amount. Generally the amount of nitrogenous containing material that is employed is sufficient to react with some or all of the hydroxyl groups present on the polymeric material or the number of hydroxyl groups present on Formula A contained in the polymeric material. If desired, the amount of fatty acid containing unsaturation may be increased to produce an air dried composition.

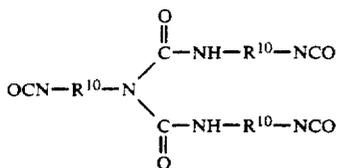
When a cross-linking agent is employed, it is preferred that a blocked isocyanate or a melamine type containing composition be used as the cross-linking agent. Other cross-linking agents may also be used such as urea formaldehyde, phenol formaldehyde, benzoguanamine, amideimide, polyamide, polybenzimidazole, and the like.

Suitable isocyanates that may be used in the present invention are as follows:

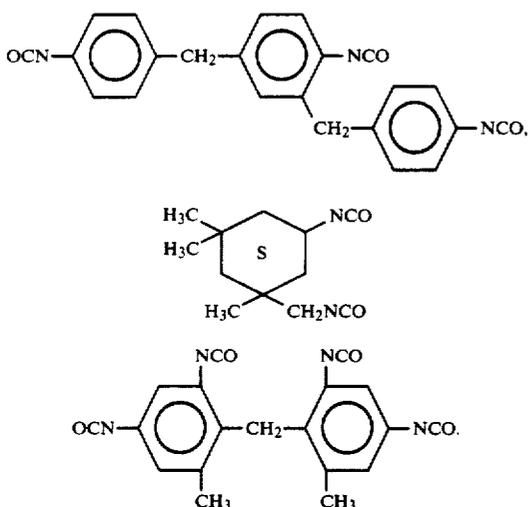
propylene-1,2-diisocyanate,
butylene-1,2-diisocyanate,
butylene-1,3-diisocyanate,
hexamethylene diisocyanate,
octamethylene diisocyanate,
nonamethylene diisocyanate,
decamethylene diisocyanate,
2,11-diisocyno-dodecane and the like,
meta-phenylene diisocyanate,
para-phenylene diisocyanate,
toluene-2,4-diisocyanate,
toluene-2,6-diisocyanate,
xylene-2,4-diisocyanate,
xylene-2,6-diisocyanate,
dialkyl benzene diisocyanate, such as methylpropylbenzene diisocyanate, methylethylbenzene diisocyanate, and the like,
2-2'-biphenylene diisocyanate,
3,3-biphenylene diisocyanate,
4,4'-biphenylene diisocyanate,
3,3'-dimethyl-4,4'-biphenylene diisocyanate, and the like,
methylene-bis-(4-phenyl isocyanate),
ethylene-bis(4-phenyl isocyanate),
isopropylidene-bis-(4-phenyl isocyanate),
butylene-bis-(4-phenyl isocyanate),
hexafluoroisopropylidene-bis-(4-phenyl isocyanate), and the like,

15 2,2'-oxydiphenyl diisocyanate,
3,3'-oxydiphenyl diisocyanate,
4,4'-oxydiphenyl diisocyanate, and the like,
2,2'-ketodiphenyl diisocyanate,
3,3'-ketodiphenyl diisocyanate,
20 4,4'-ketodiphenyl diisocyanate,
2,2'-thiodiphenyl diisocyanate,
3,3'-thiodiphenyl diisocyanate,
4,4'-thiodiphenyl diisocyanate, and the like,
2,2'-sulfonediphenyl diisocyanate,
3,3'-sulfonediphenyl diisocyanate,
25 4,4'-sulfonediphenyl diisocyanate, and the like,
2,2'-methylene-bis-(cyclohexyl isocyanate),
3,3'-methylene-bis-(cyclohexyl isocyanate),
4,4'-methylene-bis-(cyclohexyl isocyanate),
30 4,4'-ethylene-bis-(cyclohexyl isocyanate),
4,4'-propylene-bis-cyclohexyl isocyanate),
bis-(para-isocyno-cyclohexyl) sulfide,
bis-(para-isocyno-cyclohexyl) sulfone,
bis-(para-isocyno-cyclohexyl) ether,
35 bis-(para-isocyno-cyclohexyl)diethyl silane,
bis-(para-isocyno-cyclohexyl) diphenyl silane,
bis-(para-isocyno-cyclohexyl) ethyl phosphine oxide,
bis-(para-isocyno-cyclohexyl)phenyl phosphine oxide,
bis-(para-isocyno-cyclohexyl) N-phenyl amine,
40 bis-(para-isocyno-cyclohexyl) N-methyl amine,
2,6-diisocyno-pyridine,
bis-(4-isocyno-phenyl) diethyl silane,
bis-(4-isocyno-phenyl) diphenyl silane,
dichloro-biphenylene diisocyanate, bis-(4-isocyanophenyl) ethyl phosphine oxide,
45 bis-(4-isocyno-phenyl) phenyl phosphine oxide,
bis-(4-isocyno-phenyl)-N-phenyl amine,
bis-(4-isocyno-phenyl)-N-methyl amine,
3,3'-dimethyl-4,4'-diisocyno biphenyl,
50 3,3'-dimethoxy-biphenylene diisocyanate,
2,4-bis-(β -isocyno-t-butyl) toluene,
bis-(para- β -isocyno-t-butyl-phenyl) ether,
para-bis-(2-methyl-4-isocyno-phenyl) benzene,
para-bis-(1,1-dimethyl-5-amino-pentyl) benzene,
55 3,3'-diisocyno adamantane,
3,3'-diisocyno biadamantane,
3,3''-diisocynoethyl-1,1'-biadamantane,
1,2-bis-(3-isocyno-propoxy) ethane,
1,2-dimethyl propylene diisocyanate,
60 3-methoxy-hexamethylene diisocyanate,
2,5-dimethyl heptamethylene diisocyanate,
5-methyl-nonamethylene diisocyanate,
1,4-diisocyno-cyclohexane,
1,2-diisocyno-octadecane,
65 2,5-diisocyno-1,3,4-oxadiazole,
OCN (CH₂)₃O(CH₂)₂O(CH₂)₃ NCO,
OCN (CH₂)₃ S(CH₂)₃ NCO, OCN (CH₂)₃ N(CH₂)₃ NCO,

polymethylene polyphenyl isocyanate; biurets of the formula



where R¹⁰ is an alkylene group having 1-6 carbon atoms, especially preferred is the biuret of hexamethylene diisocyanate;



A number of blocking agents may also be used to produce a blocked isocyanate which could be used as the cross-linking agent. Such blocking agents as the phenol type, lactone type, active methylene type, alcohol type, mercaptan type, acid amide type, the imide, the amine type, the urea type, carbamate type, oxime type, sulfate type and the like. Most preferably a ketoxime type is preferred, and even more preferably a dialkyl ketoxime of from 1 to 4 carbon atoms per alkyl group. Most preferably the ketoxime would be methyl-ethyl ketoxime, methyl-isobutyl ketoxime, and the like.

Suitable melamine type cross-linking agents are hexamethoxymethyl melamine, alkylated (melamine-formaldehyde), butylated melamines, and the like.

The coating compositions of the present invention are useful in the cathodic electrodeposition of substrates. Generally the bath pH ranges from about 3-9. The substrate may be any conductive substrate, preferably iron, zinc or aluminum containing substrates such as steel, with or without protective coatings, such as phosphate corrosion resistant coatings. Most preferably the coatings of the present invention are applied to metallic substrates such, as steel.

In the electrodeposition process, the conductive metallic substrate would be the cathode in the electrical process and an anode would be placed in the electrodeposition bath, with the electrodeposition coating of the present invention being incorporated in the aqueous electrolyte between the anode and the cathode. The electrodeposition process is one that would be conducted at a temperature ranging from about 50° F. to 150° F., preferably room temperature. The voltage

may vary greatly, although normally it will operate between 50 and 500 volts. The current density ranges from about 1 amp to about 15 amps per square foot.

The nitrogen containing coating compositions of the present invention are solubilized, dispersed or suspended by means of an acid, such as an organic acid, such as acetic acid, lactic acid, citric acid and the like, although any water solubilizing agent may be used as boric or hydrochloric acid, etc.

As has been mentioned above, if a high concentration of unsaturated fatty acids are employed, the composition may be air cured. Preferably, however, the coating compositions are cured by means of subjecting the coated substrate to a high temperature or a bank of infrared lamps having a temperature ranging from about 250° F. (121° C.) to about 500° F. (260° C.), preferably between about 300° F. (149° C.) and about 390° F. (199° C.) from a time ranging from about 1 minute to 1 hour, preferably 10 minutes to 45 minutes.

It is to be appreciated that a curing catalyst may also be added to the coating composition, such as tin compounds as dibutyl tin dilaurate, dibutyl tin diacetate, dibutyl tin oxide, metallic dryers as cobalt and zirconium, naphthenate or octoate.

When a blocked isocyanate is employed as described above, it is to be appreciated that the blocking agent will decompose at temperatures greater than 50° C. which will permit the remaining isocyanate moiety to react with the film forming composition. At less than about 50° C., the blocked isocyanate is substantially stable and is nonreactive with the hydroxyl groups present on the acrylic polymer, or the hydroxyl groups present on Formula A moiety.

In known manner, catalysts, pigments, anti-oxidants, surfactants or fillers may be added to the coating composition to improve the appearance, texture, gloss and other properties of the cured film. Pigments such as carbon black, titanium dioxide, metal oxides, chromates, sulfates and the like may be used.

The components of the coating composition (on a pigment, filler and catalyst free basis) of the present invention are generally present as follows:

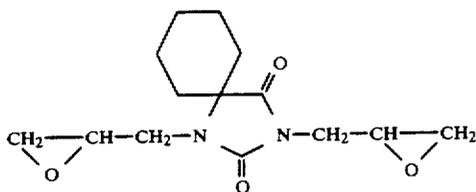
| Resin | Range | Preferred |
|---|----------------------|----------------------|
| Monomer (total) | about 30 to about 60 | 49 |
| acrylic portion | about 10 to about 40 | 20 |
| Fatty acid ester | about 30 to about 50 | 36 |
| Formula A producing amine | balance | 15 |
| TOTAL (parts by weight) | 100 | 100 |
| Cross-linking Agent | about 10 to about 50 | about 20 to about 30 |
| TOTAL (resin + cross-linking agent) (parts by weight) | 100 | 100 |

Having described the invention in general, listed below are embodiments wherein all parts are in parts by weight and all temperatures in degrees centigrade, unless otherwise indicated.

EXAMPLE NO. 1

Into a beaker equipped with a thermometer, stirrer and reflux condenser was placed dehydrated castor oil fatty acid (contains 30% conjugated double bonds; 329.4 parts), n-butyl glycidyl ether (132.6 parts) and zirconium octoate (0.5 parts) and heated under a nitro-

gen environment to 150° and allowed to exotherm. The heat was held at 190° until an acid number of about 33. Then LSU 549 (trademark of Ciba Geigy for a product of the structure



having a melting point of 90°–95° C. and an epoxy equivalent (Kg of 6.8; 55.9 parts) was added and temperature held to an acid number of zero was reached. The mixture was cooled to 165° C. and over 1 7/8 hours was added styrene (413 parts), glycidyl methacrylate (GMA) (287 parts) and dicumene peroxide catalyst (31 parts) and then heated for an additional hour at 180°. The solution was cooked to 140° and di-tert-butyl peroxide (2.7 parts) was added. The product was held to 96% theoretical solids content, cooled to 95° and diethanolamine (202 parts) added. The mixture exothermed to 120° and temperature held there for one hour. Thereafter n-butanol was added (254 parts). The product had an amine value of 75.3 and a viscosity (25° C.; 50% theoretical solids in n-butanol) of P (hereinafter product A).

A coating composition was formulated from the above product as follows:

Into a pebble mill was added carbon black (8 parts), product A (40 parts) and n-butanol (32 parts) and ground for 40 hours until carbon black is dispersed and has a Hegman reading of 7+. (hereinafter product B—pigment dispersion). Product A (311.3 parts), Cymel 1116 (trademark of American Cyanamid for a melamine cross-linking agent)—(71.8 parts) and zirconium octoate (1.8 parts) was placed in a Cowles mixer and mixed with barytes (40 parts) to a reading of Hegman 7+. Thereafter product B (80 parts) and acetic acid (12.3 parts) was mixed with product A and the cross-linking agent and emulsified with deionized water until an inversion occurs.

A zinc phosphate treated panel was used as a cathode and a carbon anode with the coating composition described above (10% solids) as the electrolyte. The voltage employed was 200 volts with the coating thickness on the cathode ranging from 0.50–0.65 mils. The panel was washed and baked at a temperature of 400° F. for 20 minutes. Smooth glossy films with good adherence to the metal substrates were obtained with satisfactory salt spray (5% sodium chloride in water) results. (Scribe pull of 2–6 mm. after 276 hours).

EXAMPLE NO. 2

Into a beaker equipped with a stirrer, thermometer and a reflux condenser was placed Pamolyn 380 (trademark of Hercules for a conjugated fatty acid being characterized as containing 70% conjugated unsaturation of linoleic acid, an acid number of 197, an iodine value of 102 and an oleic acid content of 22%; 224 parts; 0.8 equivalents); n-butanol (59 parts; 0.8 equivalents). The mixture was heated under a nitrogen blanket to a temperature of 130° for about 6 hours, removing water

to produce an acid number of zero to produce the butyl ester of Pamolyn 380.

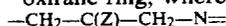
In a separate equivalently equipped beaker was placed butyl ester of Pamolyn 380 (517.9 parts) and heated to 165° C. Over a one-hour-and-forty-five-minute period was added styrene (413 parts), GMA (287 parts) and dicumene peroxide (31 parts). Thereafter the mixture was heated at about 180° C. for another hour. The mixture was cooled to 140° C., and di-tert-butyl peroxide (2.7 parts) was added and mixture held for less than an hour at same temperature until theoretical solids reached 96%. The mixture was cooled to 95° and diethanol amine (202 parts) was added, the temperature heated to 125° C. for 2 hours. Thereafter n-butanol (254 parts) was added. The product had an amine value of 90.0 and a viscosity of m (25° C. in 50% theoretical solids in n-butanol).

What is claimed is:

1. A method of electrocoating a film forming substance onto a substrate by employing an anode, a cathode and an electrolyte therebetween comprising the steps:

(1) Providing an aqueous electrolyte containing an organic coating composition comprising a dispersion, solution or suspension of a coating composition characterized by:

- the reaction product of a conjugated fatty acid ester and an acrylic containing monomer; and
- Formula A within the molecule and being the reaction product of reacting an amine with an oxirane ring; wherein Formula A is:



wherein Z is independently selected from the group consisting of hydrogen, hydroxyl, alkoxy of from one to 6 carbon atoms; acyloxy of from one to 6 carbon atoms; (=O), $-\text{OR}'$, $-\text{H}$, $-\text{OR}'$, $-\text{OH}$, and $-\text{OR}'(\text{CH}_2\text{OH})_n-\text{OH}$; wherein R' is a saturated alkylene of from 2 to 4 carbon atoms and n is a number from 1 to 6;

- Closing the circuit between the anode and the cathode; and
- Depositing the film forming composition onto the cathodic substrate.

2. The method of claim 1 wherein the fatty acid ester is obtained by the reaction between a fatty acid and a polyol.

3. The method of claim 1 wherein the composition is substantially free of oxirane rings.

4. The method of claim 3 wherein Z is hydroxyl.

5. The method of claim 1 further comprising an effective amount of a nitrogenous cross-linking composition.

6. The method of claim 1 wherein the coating composition is comprised of a resin portion characterized as follows:

| Components | Parts by Weight |
|---|----------------------|
| (a) total monomer portion used to produce polymer | about 30 to about 60 |
| (b) fatty acid ester portion | about 30 to about 50 |
| (c) Formula A producing amine portion | balance |

wherein the total resin components equals 100 parts (on a pigment, filler and catalyst free basis).

7. The method of claim 1 wherein the acrylic monomer comprises about 10 to about 40% of the total resin portion of the coating composition.

8. The method of claim 1 wherein Z is hydroxyl.

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9. An article produced according to the process of claim 1.

10. The method of claim 1 wherein the reaction between the fatty acid ester and the acrylic containing monomer is a Diels-Alder reaction as the first step for preparing the coating composition and the second step is reacting said Diels-Alder reaction product with an alkanol amine.

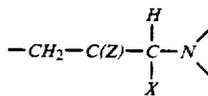
11. A method of electrocoating a film forming substance onto a substrate by employing an anode, a cathode and an electrolyte therebetween comprising the steps:

(1) Providing an aqueous electrolyte containing an organic coating composition comprising a dispersion, solution or suspension of a coating composition characterized by:

(a) the reaction product of a conjugated fatty acid ester and an acrylic containing monomer; and

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(b) Formula A' within the molecule and being the reaction product of reacting an amine with an oxirane ring, wherein Formula A' is:



10 wherein Z is independently selected from the group consisting of hydrogen, hydroxyl, alkoxy of from 1 to 6 carbon atoms; acyloxy of from 1 to 6 carbon atoms; =O), $\text{-(OR')}_n\text{H}$, $\text{-(OR')}_n\text{OH}$, and $\text{-(OR')(CH}_2\text{-OH)}_n\text{OH}$; wherein R' is a saturated alkylene group of 15 from 2 to 4 carbon atoms and n is a number from 1 to 6; and wherein X is H or -C- provided that when X is -C-, then C-X is part of an alicyclic ring structure;

(2) Closing the circuit between the anode and the cathode; and

(3) Depositing the film forming composition onto the cathodic substrate.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : Re. 31,803
DATED : January 15, 1985
INVENTOR(S) : IVAN H. TSOU

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the claims, claim 11:

column 14, line 13:

=0), should read (=0),

column 14, line 16:

H or -C- provided that when X is -C-
should read

H or -Ċ- provided that when X is -Ċ-

Signed and Sealed this

Second **Day of** *July 1985*

[SEAL]

Attest:

DONALD J. QUIGG

Attesting Officer

Acting Commissioner of Patents and Trademarks