

PATENT SPECIFICATION

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(54) COATING COMPOSITION AND PROCESS FOR ITS PREPARATION

(71) We, NIPPON OIL COMPANY LTD., a Japanese Body Corporate organised under the laws of Japan, of 3—12, 1-chome, Nishishintashi, Minato-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a water-soluble curable coating composition, especially a water-soluble curable coating composition suitable for electrodeposition coating of various objects which act as a cathode, and to a process for its production.

Conventional water-soluble paints, especially electrodeposition paints, are based on resins containing an acid group, for example maleinized oils, maleinized polybutadiene, alkyd resins, or acrylic resins containing acrylic acid or methacrylic acid as a copolymer component, which will be rendered water-soluble by neutralization with bases such as ammonia, amines or potassium hydroxide.

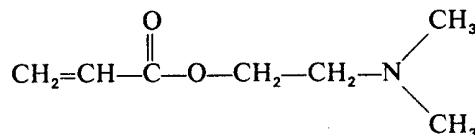
The resins dissociate in water to yield anions, and in electrodeposition, precipitate on an object to be coated which is an anode. Since the metal to be coated becomes an anode in this process, it undergoes oxidation by oxygen generated as a result of electrolysis of water, and partly dissolves in the aqueous solution. A part of the metal that has dissolved remains in the resulting electrodeposited coating to color it. For example, if the object to be coated is made of iron, it changes the color of a white paint to brown; and if it is made of aluminum, it colors the paint yellow. Furthermore, the metal ion remaining in the coating markedly reduces the corrosion resistance of the coating. The paint solution is also contaminated by the dissolved ion, and the stability of the electrodeposition bath is considerably impaired.

The above dissolving and contamination occur similarly when the metal to be coated is treated with a phosphate for rust-proofness. The phosphate coating formed is dissolved and drastically decreases in rust-proofing effect. Furthermore, coatings of a paint of this type do not possess sufficient alkali resistance.

If an object to be coated can be used as a cathode in electrodeposition, the dissolving of the metal from the coated article or the dissolving of its surface coating will not occur, and therefore, a coating having good corrosion resistance will be obtained without the coloration of the coating by the dissolved metal ion. In addition, this electrodeposition process is applicable to metals which because of their tendency to dissolve, cannot be satisfactorily coated by the anode-precipitating electrodeposition method.

In order to perform an electrodeposition method using a coating object as a cathode, it is necessary to use a water-soluble resin which becomes a cationic resin in water and precipitates on the cathode.

Various investigations have been made about the method for producing water-soluble resins that will precipitate on a cathode, and resulted, for example, in modified epoxy resins (Japanese Patent Publications Nos. 23807/74 and 31736/74), and modified acrylic resins obtained by radical-copolymerization of acrylic monomers containing a tertiary amino group such as



with various acrylic monomers or other monomers (Japanese Patent Publication Nos. 37147/73, 12396/70, 12395/70, and 39351/70).

These conventional electrodeposition paints that will precipitate on a cathode have various defects such as a high curing temperature or a low degree of curing, and have not gained commercial acceptance.

Coatings of water-soluble paints are required to be cross-linked by some means because they are readily soluble in water. Usually, this is accomplished by baking the coating at 150 to 200°C for about 30 minutes after coating. To meet this requirement, the conventional practice has relied, for example, on a method involving mixing or pre-condensing water-soluble paints with a melamine-formaldehyde resin or a phenol-formaldehyde resin, or a method involving modifying them with drying oils. These methods, however, are not applicable to cathode-precipitating electrodeposition paint resins because they do not contain an acid group and therefore, cannot be cured sufficiently with the melamine-formaldehyde resin or phenol-formaldehyde resin, or because the composition of the coating varies.

For use in electrodeposition, any such water-soluble basic resin that precipitates on a cathode must afford a good coating having superior properties; otherwise, they would be low in practical value as electrodeposition resins. Furthermore, paints based on such resins must have sufficient stability not only in low concentrations after dilution or in usual paint concentrations before dilution, but also during storage or transportation.

It is an object of this invention therefore to provide a curable water-soluble resin which is free from the defects of the conventional resins described above, has improved curability, and can be readily made water-soluble.

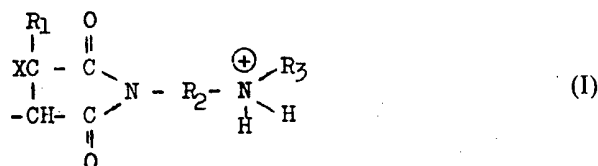
Another object of this invention is to provide a coating composition having high storage stability which can afford a coating having superior resistance to external mechanical forces such as impact or bending, and superior chemical resistance such as resistance to alkali, water or solvent.

We made extensive investigations in an attempt to achieve the above objects, and consequently found that cathode-precipitating resins having superior curability and capable of affording coatings of superior properties can be obtained by reacting certain resins resulting from the introduction of acidic groups into a polymer of a conjugated diolefin containing 4 to 8 carbon atoms e.g., maleinized liquid polybutadiene, with diamines having a primary and a secondary amino group or mixtures of diamines having a primary and a secondary amino group and diamines having a primary and a tertiary amino group.

The above objects can be achieved in accordance with this invention by a coating composition for cathode-precipitating electrodeposition consisting essentially of

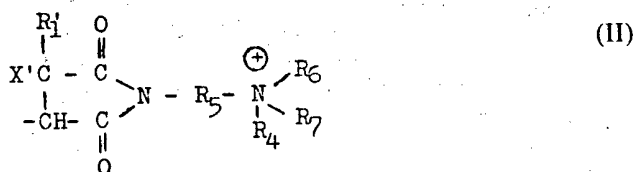
(1) a curable resinous film-forming component rendered water-soluble by neutralization with a water-soluble inorganic or organic acid, and

(2) an aqueous medium or an organic liquid medium;
said component (1) consisting of an ethylenically unsaturated organic compound having a molecular weight of 300 to 30,000 containing carbon-carbon double bonds in an amount corresponding to an iodine value of 50 to 500, which is a polymer of a conjugated diolefin containing 4 to 8 carbon atoms, said unsaturated organic compound having bonded thereto, by carbon-carbon bonding, an organic basic group of the following formula in aqueous solution when rendered water-soluble



wherein R₁ represents a hydrogen atom a halogen atom or an organic group

containing 1 to 3 carbon atoms; R_2 and R_3 each represents an organic group containing 1 to 20 carbon atoms; and X represents a hydrogen atom or a bond, and when X is a bond, the carbon atom to which R_1 is attached and the adjacent carbon atom to which hydrogen is attached may both be attached to carbon atoms which are part of the main chain, or both the organic basic group of formula (I) and an organic basic group of the following formula



wherein R'_1 represents a hydrogen atom, a halogen atom or an organic group containing 1 to 3 carbon atoms; R_5 , and R_6 and R_7 , which may be identical or different, each represents an organic group containing 1 to 20 carbon atoms; R_4 represents a hydrogen atom or an organic group containing 1 to 20 carbon atoms; and X' represents a hydrogen atom or a bond, and when X' is a bond, the carbon atom to which R'_1 is attached and the adjacent carbon atom to which hydrogen is attached may both be attached to carbon atoms which are part of the main chain,

the amount of said organic basic group or groups being 0.05 to 0.5 mole per 100 g of the film-forming component (I).

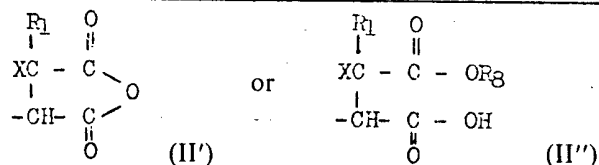
The present inventors previously found that a water-solubilizable polymer obtained by reacting a known anode-precipitating electrodeposition paint resin of the type obtained by introducing an acid group into a skeletal polymer having an unsaturated group, with a diamine having a primary and a tertiary amino group gives a superior cathode-precipitating water-base paint which is free from the defects associated with the conventional water-soluble paints or electrodeposition paints — see Japanese Patent Application No. 44802/75.

The water-solubilizable polymer has such a structure that the acid group bonded to the skeletal polymer reacts with the primary amino group of the diamine to form an imide linkage through which the diamine having a terminal tertiary amino group is suspended from the acid group. In rendering this polymer water-soluble, the pH of the solution must be maintained at a somewhat low level, and therefore, there is some likelihood that the polymer may cause the corrosion of the receptacle.

The water-solubilizable polymer in accordance with this invention which is obtained by reacting a diamine containing a primary and a secondary amino group with the acid group bonded to a skeletal polymer can be rendered water-soluble at a higher pH, and the likelihood of corrosion can be obviated.

Unexpectedly, it was found in accordance with this invention that the diamine having two groups, primary amino and secondary amino, which are reactive with an acid, reacts smoothly with the polymer containing an acid group to afford a water-solubilizable polymer suitable as a cathode-precipitating electrodeposition paint. According to the conventional knowledge of those skilled in the art, it was expected that if a compound containing two groups reactive with an acid is reacted with a polymer containing an acid group, undesirable reactions such as gellation would take place, and it would be difficult to advance the reaction further. The discovery in accordance with this invention which was contrary to such expectation is indeed surprising.

The resin containing a carbon-carbon double bond and the group of formula (I) or both groups of formula (I) and (II), which constitutes the film-forming component of the coating composition of this invention, is a novel high-molecular-weight compound. This compound can be produced by reacting (A) an ethylenically unsaturated organic compound having a molecular weight of 300 to 30,000 containing carbon-carbon double bonds in an amount corresponding to an iodine value of 50 to 500, which is a polymer of a conjugated diolefin containing 4 to 8 carbon atoms, said unsaturated organic compound having bonded thereto, by carbon-carbon bonding, an acidic group of the formula

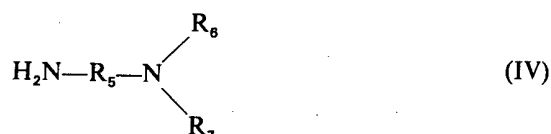


wherein R_1 represents a hydrogen atom, a halogen atom, or an organic group containing 1 to 3 carbon atoms; R_8 represents a hydrogen atom or an organic group containing 1 to 20 carbon atoms; and X represents a hydrogen atom or a bond, and when X is a bond, the carbon atom to which R_1 is attached and the adjacent carbon atom to which hydrogen is attached may both be attached to carbon atoms which are part of the main chain;

with (B) a diamine compound of the formula



wherein R_2 and R_3 each represents an organic group containing 1 to 20 carbon atoms, or a mixture of the diamine compound of formula (III) and a diamine compound of the formula



wherein R_5 , and R_6 and R_7 , which may be identical or different, each represents an organic group containing 1 to 20 carbon atoms, at a temperature of 100 to 200°C to form a resinous substance containing basic groups, adding a water-soluble inorganic or organic acid to the resinous substance to render the resinous substance water-soluble, and if desired mixing the resulting water-soluble resinous substance additionally with an aqueous medium or an organic liquid medium. The above reaction may be carried out in the presence of the liquid medium.

When the diamine compound of formula (III) alone is used, a resin which upon water solubilization can gain the basic group of formula (I) is produced. The use of the mixture of the diamine compounds of formulae (III) and (IV) can lead to the production of a resin which upon water solubilization can gain the basic groups of formulae (I) and (II).

The acid modified resinous substance contains a main chain derived from an ethylenically unsaturated group-containing liquid or solid polymer having a number average molecular weight (to be referred to simply as molecular weight) of 300 to 30,000 and containing carbon-carbon double bonds in an amount corresponding to an iodine number of 50 to 500, preferably 100 to 470.

Examples of the ethylenically unsaturated group-containing liquid or solid polymer are homopolymers having low degrees of polymerization of conjugated diolefins containing 4 to 8 carbon atoms such as butadiene, isoprene or piperylene, copolymers having low degrees of polymerization of two or more of these conjugated dienes, and copolymers having low degrees of polymerization of at least one of these conjugated diolefins and a vinyl monomer containing 2 to 20 carbon atoms, especially, aliphatic or aromatic vinyl monomers such as isobutylene, diisobutylene, acrylic or methacrylic acid or the esters thereof, allyl alcohol or its esters, styrene, α -methylstyrene, vinyltoluene or divinylbenzene. These compounds can be used either alone or as admixtures of two or more.

These polymers with low degrees of polymerization can be produced by known methods. A typical method comprises the anionic polymerization of conjugated diolefins containing 4 or 5 carbon atoms either alone, or as mixtures with each other or with an aromatic vinyl monomer such as styrene, α -methylstyrene,

vinyltoluene or divinylbenzene in an amount of not more than 50 mole% at a temperature of 0 to 100°C in the presence of an alkali metal or organic alkali metal compound as a catalyst. In order to control the molecular weight and obtain a light-colored low polymer with a reduced gel content, it is convenient to employ a chain-transfer polymerization method using an organic alkali metal compound such as benzyl sodium as a catalyst and a compound containing an alkylaryl group such as toluene as a chain-transfer agent (United States Patent 3,789,090), a living polymerization method carried out in a tetrahydrofuran solvent using a polynuclear aromatic compound such as naphthalene as an activator and an alkali metal such as sodium as a catalyst (Japanese Patent Publications Nos. 17485/67 and 27432/68), and a method in which an aromatic hydrocarbon such as toluene or xylene is used as a solvent and a dispersion of a metal such as sodium in an organic solvent is used as a catalyst, and the molecular weight of the polymer is controlled by adding an ether such as dioxane (Japanese Patent Publications Nos. 7446/57, 1245/58, and 10188/59). The polymers having a low degree of polymerization can also be produced by coordination anionic polymerization using an acetylacetonate compound of a metal of Group VIII of the periodic table, such as cobalt or nickel, and an alkylaluminum halogenide as catalysts (Japanese Patent Publications Nos. 597/70 and 30309/71).

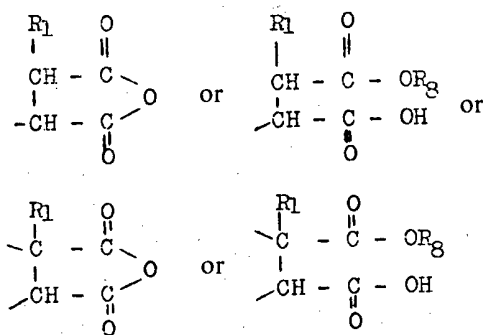
Furthermore, a butadiene/isobutylene copolymer having a low degree of polymerization and prepared by using a Friedel-Crafts catalyst such as aluminum chloride boron trifluoride or a complex of these at 0 to 100°C, can also be used as the main chain portion of the resins used in the present invention.

The low polymers of conjugated dienes have a molecular weight of 300 to 30,000, preferably 1,000 to 5,000. If the molecular weight is larger than 30,000, these compounds have poor solubility in water, and if it is less than 300, coatings obtained from these compounds have too low a strength to be practical.

The above conjugated diolefin polymers or copolymers having low degrees of polymerization have an iodine value of 50 to 500, preferably 100 to 470. If the iodine value is less than 50, the curability of these compounds is poor, and if it exceeds 500, they have poor storage stability.

The "iodine value", as referred to in the present application, is measured by the following method disclosed in A. Kemp and H. Peters, Ind. Eng. Chem., Anal., Ed. 15, 453 (1943). About 0.1 g of a sample is collected in a flask for iodine value measurement, and 100 ml of chloroform and 100 g of p-dichlorobenzene are added to dissolve the sample. Then, 60 ml of a 0.1N carbon tetrachloride solution of iodine monochloride is added, and reacted with the sample by shaking at room temperature for 1 hour. Then, 10 ml of a 10% aqueous solution of potassium iodide is added, and mixture is shaken for 5 minutes. The resulting solution is then titrated with a 0.1N aqueous solution of sodium thiosulfate using starch as an indicator.

Introduction of acid group of the general formula

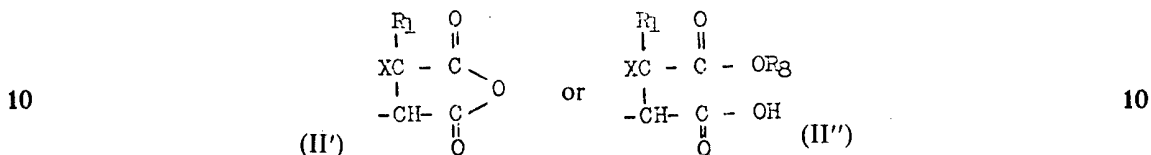


wherein R_1 represents a hydrogen atom or an organic group containing 1 to 3 carbon atoms, and R_8 represents a hydrogen atom or an organic group containing 1 to 20 carbon atoms,

into the conjugated diolefin polymers or copolymers of low degrees of polymerization can be effected by utilizing a known method which comprises causing the addition of a specified acid or anhydride thereof such as maleic acid, maleic anhydride, citraconic acid or citraconic anhydride (Japanese Patent Publication No. 11195/71). A method for preventing gellation by the presence in

the reaction system of phenylenediamines, pyrogallols, naphthols, etc. (German OLS 2,362,534) can be preferably employed in performing this addition reaction. It is also possible to mix at least two of the conjugated diolefin polymers or copolymers of low degrees of polymerization and then introduce the acid group; or to first introduce the acid group into such compounds and then mixing at least two of them. However, when the rates of addition of the acid groups differ markedly, it is preferred to introduce the acid groups first into the above components, and then mix these components.

The amount of the acid group of the formula



is 0.05 to 0.5 mole, preferably 0.1 to 0.25 mole, per 100 g of the acid-modified resinous substance. If the amount of the acid group is less than 0.05 mole per 100 g of the acid-modified resinous substance, a resin obtained by reacting the unsaturated organic compound (A) with the diamine compound of formula (III) or a mixture of it with the diamine compound (IV) has poor water-solubility when solubilized by neutralization with an acid. If the amount of the acid group is larger than 0.5 mole, the water solubility of the resulting resin is too high. Hence, a coated film of the resin has poor water resistance, and cannot be used for practical purposes.

Examples of the diamine compound of formula (III) having a primary and a secondary amino group include β -hydroxyethylaminoethylamine, β -hydroxyethylaminopropylamine, methylaminoethylamine, ethylaminoethylamine, methylaminopropylamine, ethylaminopropylamine, and butylaminopropylamine. Examples of the diamine compound of formula (IV) containing a primary and a tertiary amino group are dimethylaminoethylamine, diethylaminoethylamine, dimethylaminopropylamine, diethylaminopropylamine and dibutylaminopropylamine.

In the present invention, the unsaturated organic compound (A) is reacted with the diamine compound of formula (III) or both the diamine compounds of formula (III) and (IV). The reaction is an imidization reaction between the acid group and the primary amino group. The total amount of the diamine compound (III) or both (III) and (IV) is preferably equimolar to the acid group of component (A). It is also possible to use the diamine compound in excess, and evaporate it off after the reaction. When the mixture of the diamine compound (III) and the diamine compound (IV) is used, the proportion of the diamine (IV) based on the mixture [(III) + (IV)] is usually 0 to 90 mole%, preferably 20 to 80 mole%. Usually, in this reaction, the mole ratio of the diamine used in the reaction is approximately equal to the mole ratio of the diamines introduced.

The imidization reaction between the unsaturated organic compound (A) having an acid group and a carbon-carbon double bond and the diamine compound [(III) or a mixture of (III) and (IV)] is carried out at a temperature of 50 to 300°C, preferably 100 to 200°C.

The imidization reaction can be performed in the presence or absence of a solvent. When the viscosity of the unsaturated organic compound (A) to be imidized is low, it is preferred not to use a solvent. Examples of suitable solvents used in the imidization reaction are hydrocarbons such as benzene, toluene, cyclohexane and xylene, alcohols such as butyl Cellosolve ("Cellosolve" is a registered Trade Mark), and ethers such as diglyme. Preferably, however, a hydrophilic solvent such as butyl Cellosolve is used and the product is directly water-solubilized.

The resulting curable resinous film-forming material containing carbon-carbon double bonds and secondary and tertiary amino groups can be conveniently rendered water-soluble by neutralization with 0.2 to 1.0 mole, per mole of the secondary and tertiary amino groups, of an inorganic acid such as hydrochloric acid or sulfuric acid or a water-soluble acid such as formic acid, acetic acid or propionic acid.

The coating composition of this invention may be obtained by dissolving or dispersing the resulting resinous material having a carbon-carbon double bond and

basic groups as a film-forming component in water or in a water-soluble organic solvent. For example, a water-soluble organic solvent which can dissolve the resinous film-forming component, such as ethyl Cellosolve, propyl Cellosolve, butyl Cellosolve, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, diacetone alcohol or 4-methoxy-4-methyl-pentanone-2, may be added in an amount of 10 to 100 g per 100 g of the resinous material at the time of water-solubilizing the resinous material in order to facilitate the water solubilization, increase the stability of the aqueous solution, improve the flowability of the resinous material, and to improve the smoothness of the coated film.

The dissolving or dispersing the resinous material in the aforesaid medium can be effected by conventional mixing procedures for film-forming components and media used in the production of paints, such as by using a stirrer equipped with stirring vanes.

The amount of the film-forming component in the coating composition of this invention is not particularly critical. Usually, the composition contains 100 parts by weight of the film-forming component, up to 100 parts by weight of a solvent, up to 300 parts by weight of a pigment and up to 2000 parts by weight of water. When the film-forming component is a water-solubilized product, the amount of water is preferably 50 to 1000 parts by weight in the coating composition.

Water-base paints prepared by incorporating a suitable pigment such as titania, red iron oxide or carbon black and a rust-proof pigment such as strontium chromate in an aqueous solution obtained by neutralizing the resin having a carbon-carbon double bond and basic groups in accordance with this invention with a water-soluble acid are self-curable. Hence, they are not likely to become nonuniform in composition in an electrodeposition bath as is often the case with the use of a multi-component resin having heat curability imparted thereto by mixing a curability-imparting component. Furthermore, since these paints can be precipitated on a cathode, the coated films do not undergo coloration, the electrodeposition bath is stable, and the rust proofness of the coated film does not decrease.

The coating composition of this invention may be incorporated with a dryer such as cobalt naphthenate or manganese naphthenate to decrease the baking temperature and shorten the curing time.

The self-curable water-soluble resin in accordance with this invention can be utilized also as water-base paints which can be applied by ordinary methods such as spraying or dipping.

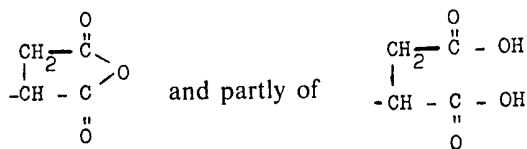
The following Examples and Comparative Examples illustrate the present invention more specifically. The properties of the coated films obtained in these examples were determined in accordance with the methods stipulated in JIS K-5400.

Example 1.

A 30-liter autoclave was charged with 1 mole of benzyl sodium, 15 moles of toluene and 15 liters of n-hexane under a stream of nitrogen. The temperature was raised to 30°C., and then 10 liters of butadiene was charged into the autoclave at 30°C. over the course of 2 hours. Then, 200 ml of methanol was added to stop the polymerization. Terra alba (1 kg) was added, and the mixture was stirred vigorously. The stirred mixture was then filtered to afford a clear polymer solution free from alkali. The unreacted butadiene, toluene, and n-hexane were evaporated off from the polymer solution to afford polybutadiene (A) having an iodine value of 430, a 1,2-bond content of 65% and a number average molecular weight of 1,000.

A 2-liter autoclave was charged with 1,000 g of polybutadiene (A), 212 g of maleic anhydride, 300 g of xylene and 2 g of Antigen 3C (trademark for a product of Sumitomo Chemical Co., Ltd.), and the reaction was performed at 190°C. for 8 hours under a stream of nitrogen. The unreacted maleic anhydride and xylene were evaporated off under reduced pressure to afford maleinized liquid polybutadiene (A') having an acid value of 100.

The structure of the acid group in the maleinized polybutadiene (A') consisted mainly of



resulting from hydrolysis with water in the air.

A 2-liter separable flask was charged with 1,000 g of maleinized polybutadiene (A'), 200 g of butyl Cellosolve, 91.3 g of dimethylaminopropylamine and 92.9 g of β -hydroxyethylaminoethylamine, and they were heated at 140°C. for 3 hours. Under reduced pressure, the generated water, butyl Cellosolve and unreacted amine were evaporated off to afford imidized polybutadiene (A'') having a secondary amino group and a tertiary amino group.

Then, 100 g of the imidized polybutadiene (A'') was dissolved in 20 g of butyl Cellosolve which was water soluble. Then, 32 g of titania and 1.3 g of carbon black were incorporated. The resin was neutralized with 5.0 g of acetic acid, and the entire mixture was dissolved in pure water to prepare an aqueous solution having a solids concentration of 12% by weight.

The aqueous solution was placed in a 1-liter beaker, and electrodeposited on a non-treated mild steel panel (a product of Nippon Test Panel Company) as a cathode using a carbon electrode plate as an anode. The results are shown in Table 1.

Comparative Example 1.

The maleinized polybutadiene (A) synthesized in Example 1 (100 g) was dissolved in 20 g of butyl Cellosolve. Then, 32 g of titania and 1.3 g of carbon black were incorporated, and the resin was neutralized with an aqueous solution of potassium hydroxide. The entire mixture was then dissolved in pure water to prepare an aqueous solution having a solids concentration of 12% by weight.

The aqueous solution was placed in a 1-liter beaker, and electrodeposited on a non-treated mild steel panel (a product of Nippon Test Panel Company) as a cathode using a carbon electrode plate as an anode. The results are shown in Table 1.

A comparison of Example 1 and Comparative Example 1 shows that the electrodeposition characteristics of the coating compositions and the properties of the coated films differ greatly from each other even when the starting resin is the same, and that the coated film obtained in Example 1 is stronger than in Comparative Example 1 and has a markedly improved alkali resistance although its acid resistance is reduced a little.

TABLE 1

	Example 1	Comparative Example 1	Example 2
<u>Coating conditions</u>			
Voltage (V)	50	310	70
Time (minutes)	3	3	3
<u>Baking conditions</u>			
Temperature (°C.)	200	160	200
Time (minutes)	30	30	30
Coating thickness (microns)	20	20	20
<u>Physical tests</u>			
Pencil hardness	H - 2H	2H - 3H	F - H
Sketching	Good	Good	Good
Crosscut test (tape test)	100/100	90/100	100/100
Erichsen \ddagger (mm)	>9	4.5	>9
<u>Impact strength (cm)</u> (500g, 1/2B) (*1)			
Top surface	>50	20	>50
Back surface	>50	10	>50
Flexural resistance (mm) (*2)	<2	6	<2
<u>Chemical tests</u>			
Alkali resistance (hr) (*3)	>100	3.5	>100
Acid resistance (hr) (*4)	60	>100	50
Water resistance (days) (*5)	>30	>30	>30
Solvent resistance (days) (*6)	>30	>30	>30
Corrosion resistance (mm) (*7)	<1	8	2

\ddagger : The maximum diameter of the extruded portion attained before breakage of the coating.

Footnotes to Table 1

- (*1): The maximum height of a ball fall which does not cause the breakage of the coating in the extruded portion (5) g, 1/2B).
- (*2): The minimum bending radius which causes cracks to the coating.
- (*3): The time that elapses until a change, such as blistering, occurs in the coating (when immersed in 5% NaOH).
- (*4): The time that elapses until a change, such as blistering, occurs in the coating (when immersed in 5% H₂SO₄).
- (*5): The time that elapses until a change, such as blistering, occurs in the coating (when immersed in distilled water at 40°C.).
- (*6): The time that elapses until a change, such as blistering, occurs in the coating (when immersed in a 1/1 mixture of toluene and xylene).
- (*7): The maximum rust width from a cut portion provided in the coating (a spray of a 5% aqueous solution of NaCl, 50 hours).

Example 2.

- 5 A 20-liter autoclave was charged with 1.0 mole of benzyl sodium, 18 moles of toluene and 15 liters of benzene under a stream of nitrogen. The temperature was raised to 30°C., and then 10 liters of butadiene was fed into the autoclave over the course of 4 hours while maintaining the temperature at 30°C. The catalyst was decomposed with water, and the catalyst residue was removed by washing with water. The toluene, benzene and unreacted butadiene were evaporated off to afford polybutadiene (B) having an iodine value of 410, a 1,2-bond content of 58% and a number average molecular weight of 900. 10
- A 2-liter separable flask was charged with 1,000 g of the polybutadiene (B), 117 g of maleic anhydride, 10 g of xylene and 2 g of Antigen 3C, and they were reacted at 200°C. for 5 hours. The xylene and unreacted maleic anhydride were evaporated off under reduced pressure to afford maleinized polybutadiene (B') having an acid value of 60 and a viscosity of 8000 poises (25°C). 15
- A 2-liter separable flask equipped with a reflux condenser was charged with 100 g of maleinized polybutadiene (B'), 11.2 g of β -hydroxyethylaminoethylamine and 20 g of butyl Cellosolve, and they were heated at 130°C. for 6 hours to afford polybutadiene (B'') having a secondary amino group. The polybutadiene was neutralized with an aqueous solution of acetic acid, and then 80 g of titania was incorporated to produce a water-thinned paint having a solids concentration of 45%. 20
- The water-base paint was applied to a #280 polished mild steel panel by a 5 mil applicator, and baked at 190°C. for 30 minutes. 25
- The coated film had a thickness of 20 microns. The coated film had a pencil hardness of H, but was very pliable and tough as can be understood from its Erichsen value of 6.5 mm and its good result in a Du Pont impact test (50 cm). The water-base paint had a viscosity of as low as about 80 KU, and thus was found to have superior properties as a water-base baking paint. 30
- Using the resulting imidized polybutadiene (B''), an electrodeposition solution having a solids concentration of 12% was prepared in the same way as in Example 1. An electrodeposition test was performed in the same way as in Example 1 using the resulting electrodeposition solution. The results are shown in Table 1. 35

Example 3.

- 35 (a) Production of pigment paste
- A 2-liter autoclave was charged with 1,000 g of linseed oil having an iodine value of 180 and a molecular weight of about 800, 215 g of maleic anhydride and 50 g of xylene, and the reaction was performed at 190°C. for 8 hours under a stream of nitrogen. Then, the unreacted maleic anhydride and xylene were evaporated off under reduced pressure to afford maleinized linseed oil having an acid value of 100 and a viscosity of 45 poises (25°C.). Then, 700 g of maleinized linseed oil and 130 g of dimethylaminopropylamine were fed into a 2-liter separable flask, and stirred for 1 hour at room temperature. The mixture was heated at 130°C. under reduced 40

pressure for 1 hour to afford linseed oil having an imide group and a tertiary amino group. Four hundred (400) grams of the resulting linseed oil containing an imide group and a tertiary amino group was dissolved in 60 g of diethylene glycol dimethyl ether, and neutralized by adding water and 22.5 g of acetic acid to afford a solution having a solids concentration of 30%. On standing for 3 months, the solution did not change in viscosity, clarity and pH showing very good stability.

A 20-liter stainless beaker was charged with 600 g of the 30% solution prepared, 750 g of titania, 24 g of carbon black, 24 g of strontium chromate and 1000 g of glass beads, and stirred vigorously for 2 hours in a high-speed rotary mixer. The glass beads were removed by filtration to afford a pigment paste (A) having very good water dispersibility.

(b) Production of electrodeposition paint

Polybutadiene (C) having an iodine value of 450, a 1,2-bond content of 65% and a number average molecular weight of 2,000 was synthesized in the same way as in Example 2 except that the amount of toluene was changed to 5 moles. Then, maleinized polybutadiene (C') having an acid value of 100 and a viscosity of 150000 poises was prepared in the same way as in the method of synthesizing maleinized polybutadiene shown in Example 2 except that the amount of maleic anhydride was changed to 212 g.

A 2-liter separable flask equipped with a reflux condenser was charged with 100 g of maleinized polybutadiene (C'), 9.1 g of dimethylaminopropylamine, 9.3 g of β -hydroxyethylaminoethylamine and 20 g of butyl Cellosolve, and the mixture was heated at 150°C. for 3 hours to afford polybutadiene (C'') having a secondary amino group and a tertiary amino group. The polybutadiene (C'') was dissolved in an aqueous solution of acetic acid to afford an aqueous solution having a solids concentration of 20%. To the aqueous solution was added 63.1 g of the pigment paste (A) prepared in section (a) above, and after good mixing, pure water was added to prepare an electrodeposition paint having a solids concentration of 12%.

The electrodeposition paint was placed in a 1-liter beaker, and electrodeposited on a mild steel panel treated with Bonderite (registered Trade Mark) #137 (a product of Nippon Test Panel Co., Ltd.) as a cathode using a carbon electrode plate as an anode. The results are shown in Table 2.

Example 4.

An electrodeposition paint was prepared in the same way as in Example 3 except that polybutadiene B-1000 (1,2-bond content 90%, number average molecular weight 1000; a product of Nippon Soda Co., Ltd.) was used as the polybutadiene. The results are also shown in Table 2.

Example 5.

An electrodepositing solution was prepared in the same way as in Example 3 except that Polyoil Hüls 110 (polybutadiene having a cis-1,4 content of about 80%, a trans-1,4 bond of about 20% and a number average molecular weight of 1700; a product of Hüls Company) was used as the starting material, and the acid value of the maleinized product was changed to 80. Using the resulting electrodepositing solution, electrodeposition on a cathode was carried out in the same way as in Example 3. The results are also shown in Table 2.

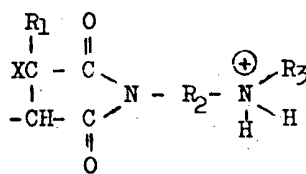
TABLE 2

Example	3	4	5
<u>Coating conditions</u>			
Voltage (V)	150	90	100
Time (minutes)	3	3	3
Baking conditions (°C. × min.)	200 × 30	200 × 3	200 × 30
Coating thickness (microns)	20	20	20
<u>Physical tests</u>			
Pencil hardness	H - 2H	H - 2H	B - HB
Sketching	Good	Good	Good
Crosscut test (tape test)	100 / 100	99 / 100	98 / 100
Erichsen (mm)	> 9	> 9	> 9
Impact strength (cm)			
Top surface	> 50	> 50	> 50
Back surface	> 50	> 50	> 50
Flexural resistance (mm)	< 2	< 2	< 2
<u>Chemical tests</u>			
Alkali resistance (hr)	> 100	25	10
Acid resistance (hr)	50	30	20
Solvent resistance (days)	> 30	> 30	> 30
Water resistance (days)	> 30	> 30	> 30
Corrosion resistance (mm)	1	3	4

WHAT WE CLAIM IS:—

1. A water-soluble curable coating composition comprising essentially
 (1) a curable resinous film-forming component rendered water-soluble by
 neutralization with a water-soluble inorganic or organic acid, and

(2) an aqueous medium or an organic liquid medium;
 said component (1) consisting of an ethylenically unsaturated organic compound
 having a molecular weight of 300 to 30,000 containing carbon-carbon double
 bonds in an amount corresponding to an iodine value of 50 to 500, which is a
 polymer of a conjugated diolefin containing 4 to 8 carbon atoms, said unsaturated
 organic compound having bonded thereto, by carbon-carbon bonding, an organic
 basic group of the following formula in aqueous solutions when rendered water-
 soluble



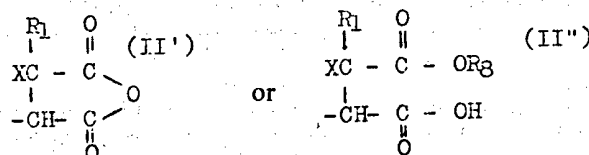
wherein R_1 represents a hydrogen atom, a halogen atom or an organic group containing 1 to 3 carbon atoms; R_2 and R_3 each represents an organic group containing 1 to 20 carbon atoms; and X represents a hydrogen atom or a bond, and when X is a bond, the carbon atom to which R_1 is attached and the adjacent carbon atom to which hydrogen is attached may both be attached to carbon atoms which are part of the main chain, the amount of said organic basic group being 0.05 to 0.5 mole per 100 g of the film-forming component (I).

2. The composition of claim 1 wherein said polymer of a conjugated diolefin is a homopolymer.

3. The composition of claim 1 wherein said polymer of a conjugated diolefin is a copolymer of at least two conjugated diolefins containing 4 to 8 carbon atoms or a copolymer of at least one conjugated diolefin containing 4 to 8 carbon atoms and a vinyl monomer containing 2 to 20 carbon atoms.

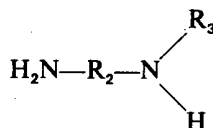
4. A process for producing the composition of any one of claims 1 to 3, which comprises reacting

(A) an ethylenically unsaturated organic compound having a molecular weight of 300 to 30,000 containing carbon-carbon double bonds in an amount corresponding to an iodine value of 50 to 500, which is a polymer of a conjugated diolefin containing 4 to 8 carbon atoms, said unsaturated organic compound having bonded thereto, by carbon-carbon bonding, an acidic group of the formula



wherein R_1 represents a hydrogen atom, a halogen atom, or an organic group containing 1 to 3 carbon atoms, R_3 represents a hydrogen atom or an organic group containing 1 to 20 carbon atoms, and X represents a hydrogen atom or a bond, and when X is a bond, the carbon atom to which R_1 is attached and the adjacent carbon atom to which hydrogen is attached may both be attached to carbon atoms which are part of the main chain,

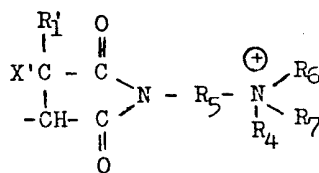
(B) a diamine compound of the formula



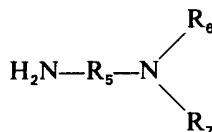
wherein R_2 and R_3 each represents an organic group containing 1 to 20 carbon atoms,

at a temperature of 100 to 200°C. to form a resinous substance containing basic groups, and adding a water-soluble inorganic or organic acid to the resinous substance to render the resinous substance water-soluble.

5. The composition of any one of claims 1 to 3 wherein the unsaturated organic compound contains, in addition to the organic basic group, another organic basic group of the formula



- 5 wherein R'_1 represents a hydrogen atom, a halogen atom or an organic group containing 1 to 3 carbon atoms; R_5 , and R_6 and R_7 which may be identical or different, each represents an organic group containing 1 to 20 carbon atoms; R_4 represents a hydrogen atom or an organic group containing 1 to 20 carbon atoms; and X' represents a hydrogen atom or a bond, and when X' is a bond, the carbon atom to which R'_1 is attached and the adjacent carbon atom to which hydrogen is attached may both be attached to carbon atoms which are part of the main chain,
- 10 the total amount of said organic basic groups being 0.05 to 0.5 mole per 100 g of the film-forming component (I).
- 15 6. The process of claim 4 wherein said diamine compound (B) is selected from β -hydroxyethylaminoethylamine, β -hydroxyethylaminopropylamine, methylaminoethylamine, ethylaminoethylamine, methylaminopropylamine, ethylaminopropylamine and butylaminopropylamine.
7. The process of claim 4 or claim 6 wherein the unsaturated organic compound (A) is reacted with the diamine compound (B) and another diamine compound (C) of the formula



- 20 wherein R_5 , and R_6 and R_7 which may be identical or different, each represents an organic group containing 1 to 20 carbon atoms.
8. The process of claim 7 wherein the diamine compound (C) is selected from dimethylaminoethylamine, diethylaminoethylamine, dimethylaminopropylamine, diethylaminopropylamine and dibutylaminopropylamine.
- 25 9. A water-soluble curable coating composition according to claim 1 substantially as herein described.
10. A water-soluble curable coating composition according to claim 1 substantially as herein described in any of the Examples.

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