

PATENT SPECIFICATION

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(54) AQUEOUS EPOXY RESIN PAINT COMPOSITIONS

(71) We, DAI NIPPON TORYO CO, LTD., of No. 38, Nishinoshimono-cho, Konohana-ku, Osaka-shi, Japan, a Japanese corporation, 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 aqueous epoxy resin paint compositions.

According to the invention, there is provided an aqueous epoxy resin paint composition comprising an epoxy resin emulsion formed by emulsifying, in water containing a non-ionic surface active agent, a diglycidyl ether of a bisphenol, there being incorporated into the epoxy resin emulsion a curing agent comprising (i) a polyamine resin derived from a dimer acid and an ether diamine, (ii) a polyamide resin derived from a dimer acid, an ether diamine and an aliphatic amine, (ii) a polyamide resin derived from a dimer acid, an ether diamine and a chain extender, or (iv) a polyamide resin derived from a dimer acid, an ether diamine, an aliphatic amine and a chain extender.

The diglycidyl ether of a bisphenol (A) used in this invention can be, for example, an epoxy resin obtained by condensation between bisphenol A [2,2-bis(4'-hydroxyphenyl)propane] and epichlorohydrin, and is commercially available. Commercially available diglycidyl ethers of bisphenols are liquid or solid and usually have a molecular weight of 350 to 3750 and an epoxy equivalent of 180 to 3500. Typical instances of these commercially available resins are as follows:

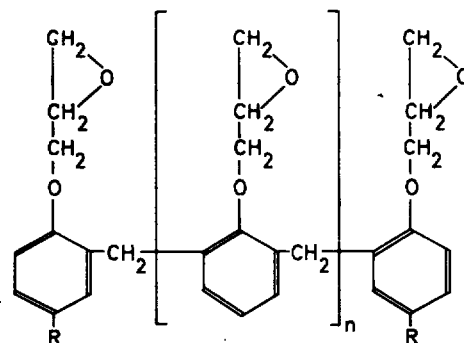
- (1) Epikote 815, Epikote 827, Epikote 834, Epikote 1001, Epikote 1004, Epikote 1007 and Epikote 1009 (trademarks for products manufactured by Shell Chemical Co.)
(2) DER 330, DER 331, DER 334, DER 337, DER 661, DER 664, DER 667 and DER 669 (trademarks for products manufactured by Dow Chemical Co.)
(3) Araldite GY250, Araldite GY252, Araldite GY260, Araldite GY280, Araldite GY6071, Araldite GY6084, Araldite GY6097 and Araldite GY6099 (trademarks for products manufactured by Ciba Limited)
(4) ERL 2774 and ERL 2795 (trademarks for products manufactured by Union Carbide Corporation)
(5) Epiclon 850 (trademark for product manufactured by Dainippon Ink and Chemicals Incorp.)

These commercially available resins can be used singly, or mixtures of two or more of them can also be employed.

The diglycidyl ether of a bisphenol is used as a vehicle. Use of a liquid vehicle epoxy resin is preferred because it is readily emulsified, but when the vehicle epoxy resin is solid, it can be emulsified or dispersed in water by mixing it with another liquid epoxy resin to dissolve it or by melting it under heating.

In this invention, in combination with the above vehicle epoxy resin (A) is preferably used an additive resin (B) selected from (1) novolak type epoxy resins, (2) glycidyl esters of dimer or trimer acids, and (3) condensates of β -methylepichlorohydrin and a bisphenol.

As the novolak type resin, there can be used those having the following structure:

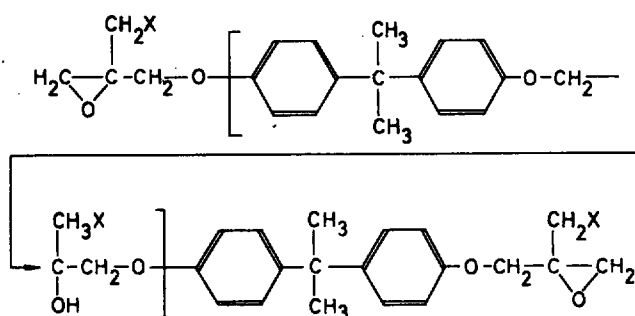


wherein n is a number of from 0 to 2 and R stands for a hydrogen atom or a methyl, ethyl or propyl group.

As commercially available additive resins (1); there can be mentioned Epikote 152 (product of Shell Chemical Co. having an epoxy equivalent of 172—179), Epikote 154 (product of Shell Chemical Co. having an epoxy equivalent of 176—181), DEN 431 (product of Dow Chemical Co. having an epoxy equivalent of 172—179), DEN 438 (product of Dow Chemical Co. having an epoxy equivalent of 175—182), EPN 1138 (product of Ciba Limited having an epoxy equivalent of 172—179), etc. These resins are generally prepared by reacting a novolak type phenolic acid-formaldehyde resin with epichlorohydrin.

The additive resin (2) is usually prepared by reacting a dimer or trimer acid with epichlorohydrin (the preparation process is disclosed in, for example, Japanese Patent Publication No. 7454/62 published on July 7, 1962 by Shell International Research Maatochappij N.V., Netherland), and as commercially available epoxy resins of this type, there can be mentioned, for example, Epikote 871 (product of Shell Chemical Co. having an epoxy equivalent of 390—470) and Epikote 872 (product of Shell Chemical Co. having an epoxy equivalent of 600—700).

The additive resin (3) used in this invention can be, for example, a resin having the following structure:



wherein n is 0 to 3 and X is hydrogen or chlorine. The epoxy resin (3) can be prepared by, for example, condensation of β -methyl epichlorohydrin or β -chloromethyl epichlorohydrin with bisphenol-A. The preparation process is disclosed in, for example, U.S. No. 3,553,165 (Patented on January 5, 1971 by Chiyoda Kako Kensetsu Kabushiki Kaisha).

As a commercially available resin of this type, there can be mentioned, for example, Epiclon 800 (product of Dainippon Ink and Chemicals Incorp. having an epoxy equivalent of 195—225).

In this invention, in order to prevent crystallization, there is preferably adopted combined use of the above mentioned vehicle resin with at least one member selected from the foregoing resins (1) to (3), each of which has a compatibility with the vehicle resin and a structure similar to that of the vehicle resin but is different therefrom in a part of the structure.

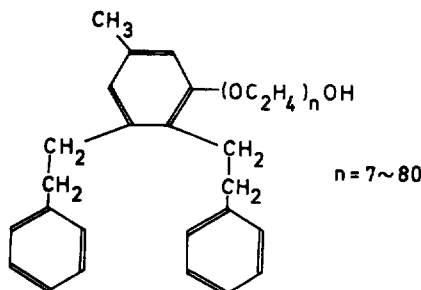
The additive epoxy resin (1), (2) or (3) is incorporated in the vehicle resin in such an amount that the additive resin in accounts for 2 to 50% by weight of the sum of the vehicle resin and the additive epoxy resin. When the amount of the additive epoxy resin (1), (2) or (3) is less than 2% by weight, no substantial effect of preventing crystallization can be obtained, and when the amount of the additive resin exceeds 50% by weight, the saline resistance, water resistance and moisture resistance of the resulting film are reduced.

As pointed out above, in this invention, by incorporating in the vehicle epoxy resin a suitable amount of at least one of the additive epoxy resins (1) to (3), each of which has a compatibility with the vehicle epoxy resin and a structure similar to that of the vehicle epoxy resin but is quite different therefrom in a part of the structure, it is possible to inhibit arrangement of the molecules of the vehicle epoxy resin, which results in crystallization, and thus prevent crystallization even at low temperatures.

The above-mentioned vehicle epoxy resin or its mixture with the above-mentioned additive epoxy resin (1), (2) or (3) is emulsified in water with a non-ionic surface active agent according to customary procedures.

As the non-ionic surface active agent, there can be mentioned, for example, surface active agents of the alkylaryl ether type having an HLB value of 10.9 to 19.5, such as polyoxyethylene nonyl phenyl ether and polyoxyethylene octyl phenyl ether, surface active agents of the alkyl ether type having an HLB value of 10.8 to 16.5, such as polyoxyethylene lauryl ether and polyoxyethylene oleyl ether, surface active agents of the alkyl ester type having an HLB value of 9.0 to 16.5, such as polyoxyethylene laurate, polyoxyethylene oleate and polyoxyethylene stearate, and surface active agents of the polyoxyethylene benzylated phenyl type having an HLB value of 9.2 to 18.

As another means for preventing crystallization, in this invention there can be adopted use of a polyoxyethylene benzylated phenyl ether having the structure



and an HLB value of at least 15 as a surface active agent for emulsifying the above bisphenol type epoxy resin or its mixture with the additive epoxy resin in water.

As the polyoxyethylene benzylated phenyl ether, there can be used, for example, such commercially available products as Newcol 714 (HLB=15) and Newcol 723 (HLB=16.6) (trademarks for products manufactured by Nippon Nyukazai Co., Ltd.), and Emulgen A-500 (HLB=18) (trademark for the product manufactured by Kao-Atlas Co., Ltd.).

For emulsification of the epoxy resin, the polyoxyethylene benzylated phenyl ether having an HLB value of at least 15 is preferably used in an amount of 0.1 to 20% by weight based on the epoxy resin.

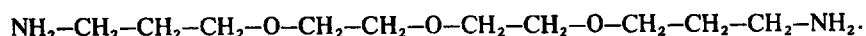
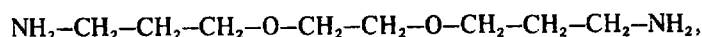
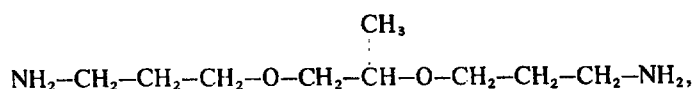
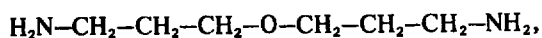
A polyoxyethylene benzylated phenyl ether having an HLB value not exceeding 15 does not have sufficient effect, and even if prevention of crystallization is attained by the use of such ether to some extent, the effect is retained only for about 30 days at longest.

As pointed above, undesired phenomenon of crystallization can be effectively prevented in this invention by adding to the vehicle epoxy resin at least one member selected from the above additive resins (1) to (3) having a compatibility with the vehicle epoxy resin and a structure similar to that of the vehicle epoxy resin but being quite different therefrom in a part of the structure, or by emulsifying the bisphenol type epoxy resin in water with a polyoxyethylene benzylated phenyl ether having an HLB value of at least 15. If the above two means are adopted in combination, the crystallization-preventing effect can be greatly enhanced.

In the composition of this invention, particular curing agents (as specified above) are added in order to cure the above-mentioned epoxy resin.

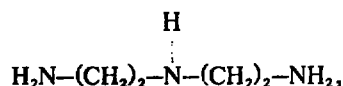
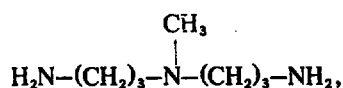
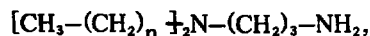
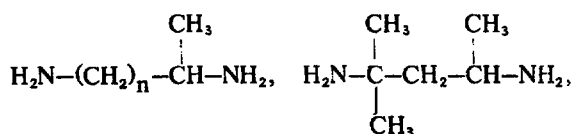
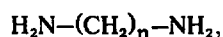
When it is intended to improve the film-forming property especially under high-humidity conditions, good results are obtained when a polyamide resin prepared from a dimer acid and an ether diamine, preferably such polyamide resin having an amine value of 250 to 500, is employed as the curing agent.

The dimer acid to be used for forming the above polyamide resin is a product prepared by employing an unsaturated fatty acid having 18 carbon atoms as the starting material, and the product is composed mainly of a dimer acid and includes small amounts of a trimer acid and a monomer acid. As the ether diamine to be used for forming the above polyamide resin, there can be mentioned, for example,

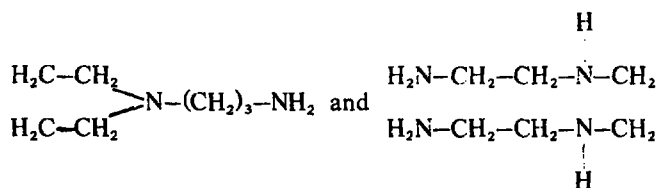


The intended polyamide resin can be obtained by reacting such ether diamine with the dimer acid at 150 to 250°C. for 1 to 4 hours according to customary procedures.

In this invention, the intended polyamide resin, preferably having an amine value of 250 to 500, can also be prepared by substituting a part of the ether diamine by one or more of aliphatic amines such as



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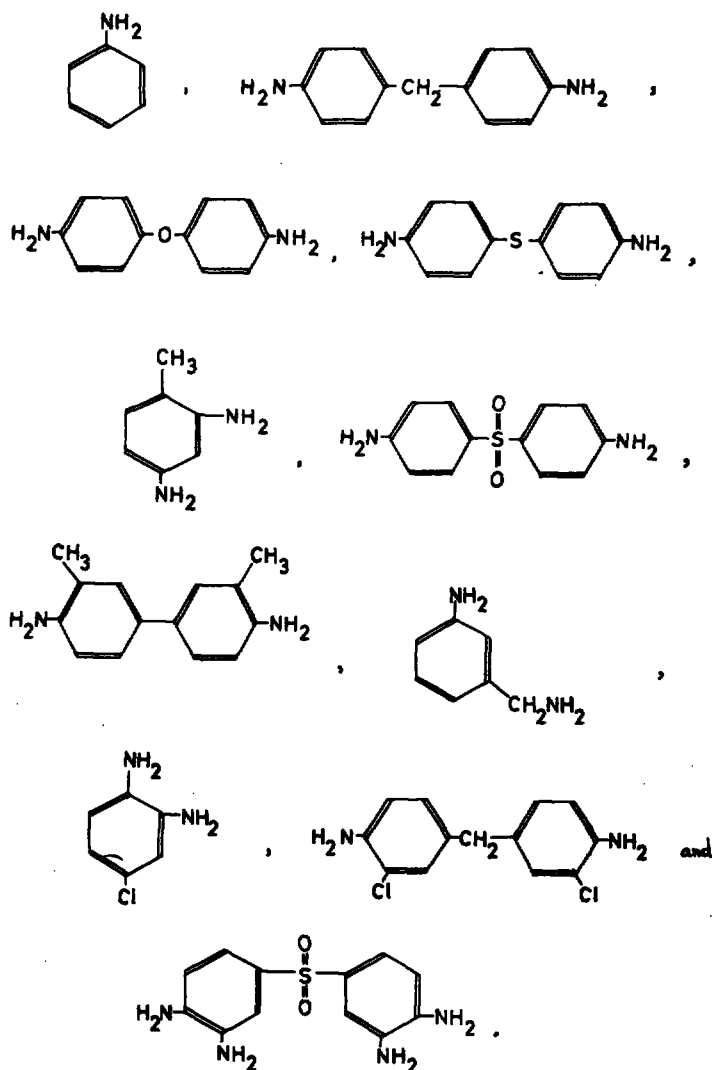


It is preferred that the aliphatic amine be used in an amount of 0.1 to 4 moles per mole of the ether diamine.

In order to increase the molecular weight of the polyamide resin curing agent, it is possible to add and react a chain extender at the reaction between the dimer acid and ether diamine or the reaction among the dimer acid, ether diamine and aliphatic amine. As the chain extender, there can be used, for example, acrylonitrile, methyl methacrylate, formaldehyde, a polyglycol type epoxy resin or a glycerin type epoxy resin. When the so obtained high-molecular-weight polyamide resin, preferably having an amine value of 250 to 500, is used as the curing agent, the resulting composition is excellent in film-forming property under high-humidity conditions and gives a film excellent in anti-cracking property.

Further, an aromatic amine compound can be used in combination with the above polyamide resin. As such aromatic amine compound, the following compounds can be mentioned:

(1) Aromatic amines having a structure such as shown below (when these amines are solid at room temperature, they are used in the state melt-mixed with the above polyamide resin or other curing agent mentioned below):



(2) Reaction products between an aromatic amine and an epoxy resin obtained according to customary procedures (aromatic amine adducts).

(3) Polyamide resins prepared by employing an aromatic amine.

When such aromatic amine compound is used in combination with the above-mentioned polyamide resin curing agent, the moisture resistance, saline dipping resistance and salt spraying resistance are highly improved in the resulting film.

It is preferred that the ratio of the above aromatic amine to the polyamide resin derived from a dimer acid and an ether diamine be within a range of from 5/95 to 50/50 as expressed in the non-volatile component weight ratio.

The so obtained curing agent or curing agent composition is mixed with an epoxy resin emulsion according to customary procedures to form an aqueous epoxy resin paint composition of this invention.

In this invention, it is preferred that the mixing ratio of the epoxy resin and curing agent be such that the ratio of the epoxy groups to the active hydrogen group is within a range of from 0.5 to 1.5.

The aqueous epoxy resin paint composition of this invention may further comprises additives customarily used in this field, such as organic pigments, inorganic pigments, surface active agents and thickeners.

The use of a conventional anti-corrosive pigment of the chromate type is restricted because of the toxicity of chromium ions dissolved out of the film; it is preferred that at least one member selected from the group consisting of molybdic acid salts of strontium, calcium, potassium, iron (divalent), barium and ammonium be used instead of the chromate type anti-corrosive pigment.

The molybdate type anti-corrosive pigment is non-toxic and its corrosion resistance is superior to comparable to that of the conventional chromate type anti-corrosive pigment, and it is further characterized in that it promotes the film-forming property of the resulting composition under high-humidity conditions and even when the composition is applied in a large thickness, the curing is accomplished uniformly throughout the film so that the degree of curing does not differ between the surface portion and the interior of the film (this property will hereinafter be referred to as "curing uniformity").

It is preferred that this molybdate type anti-corrosive pigment be incorporated in the paint composition in an amount of 0.1 to 20% by weight. If the amount incorporated of the pigment is smaller than 0.1% by weight, no substantial anti-corrosive effect is obtained and the film-forming property under high-humidity conditions is not promoted. In contrast, if the amount incorporated of the pigment is larger than 20% by weight, the pigment concentration increases and tendency of reduction of physical properties of the film is observed.

In view of the rust-preventive effect and from the economical viewpoint, it is especially preferred that the molybdate type anti-corrosive pigment be incorporated in an amount of 5 to 10% by weight.

It has been found that especially good results are obtained when among the foregoing molybdate type anti-corrosive pigments, strontium molybdate or calcium molybdate obtained by calcining a mixture of molybdenum oxide and calcium carbonate or strontium carbonate at 600 to 800°C. is chosen and used.

In the aqueous epoxy resin paint composition of this invention, at the time of application the main components (the epoxy resin emulsion, the pigment, etc.) are mixed with the curing agent, the mixture is diluted appropriately with water and the resulting composition can be applied to a substrate to be coated according to customary coating methods, for example, brush-coating, spray-coating and air spray-coating methods. Since the paint composition of this invention has a very high thixotropic property, a thick coating having a thickness of more than 100 μ can be obtained by one coating.

This invention will now be illustrated by the following Examples, in which all "parts" and "%" are by weight.

Example 1.

In a main component comprising 10 parts of red iron oxide, 35 parts of talc, 34 parts of water, 20 parts of a diglycidyl ether of a bisphenol (Epikote 828 having an epoxy equivalent of 190) and 2 parts of polyoxyethylene laurate (Newcol 150 having an HLB value of 10.5; trade mark for a product manufactured by Nippon Nyukazai Co., Ltd.), a portion of the Epikote 828 was replaced by an epoxy resin having a similar structure, which is indicated in Table 1, and the state of formation and growth of crystals was examined.

When a polyamide resin derived from a dimer acid and an ether diamine, for

example, a polyamide resin of an amine value of 350 formed by condensing 1 mole of a dimer acid and 12 moles of $\text{H}_2\text{N}-(\text{CH}_2)_3-\text{O}-(\text{CH}_2)_3-\text{NH}_2$, or a mixture formed by mixing the above polyamide resin at a mixing weight ratio of 1:1 with an amine adduct obtained by reacting a diglycidyl ether of a bisphenol (Epikote 828) and metaphenylene diamine at a mole ratio of 2:1, was used as the curing agent and this curing agent was mixed with the main component so that the epoxy groups in the emulsion and the active hydrogen groups in the curing agent were equivalent to each other, a very excellent film-forming property under high-humidity conditions was attained and a film having excellent chemical and physical properties was obtained.

In compositions shown in Table 1, in order to evaluate the crystallization-preventing effect, the formulation of components was made almost equal in each composition, but it was confirmed that similar results were obtained when other epoxy resins were used or ordinary organic or inorganic pigments or the like were incorporated into the compositions.

Example 2.

20 parts of a diglycidyl ether of a bisphenol (DER 331) were emulsified in water with a polyoxyethylene benzylated phenyl ether having an HLB value of 15 (Newcol 714), and 10 parts of red iron oxide and 35 parts of talc were added to the emulsion according to a customary method. There was no formation and growth of crystals in the main component (sample No. 6) thus obtained.

The curing agent prepared in Example 1 was mixed with the main component to form an aqueous epoxy resin paint composition. A film obtained from the paint composition has excellent chemical and physical properties.

Example 3.

The state of formation and growth of crystals was examined with respect to main components prepared in the same manner as in Example 2 except that a polyoxyethylene benzylated phenyl ether having an HLB indicated in Table 2 was used for emulsifying the diglycidyl ether of a bisphenol. Results are shown in Table 2.

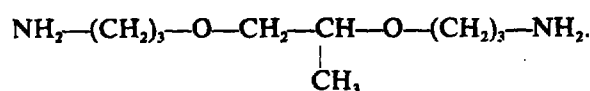
The curing agent prepared in Example 1 was mixed with each main component to form an aqueous epoxy resin paint composition. A film obtained from the each paint composition has excellent chemical and physical properties.

Example 4.

A main component was prepared by incorporating 10 parts of red iron oxide, 20 parts of talc, 12 parts of calcium carbonate and 30 parts of water into an epoxy resin emulsion comprising 27 parts of a diglycidyl ether of bisphenol (having an epoxy equivalent of 190), 6 parts of a polyoxyethylene benzylated phenyl ether having an HLB value of 12 and 6 parts of water. Then, 12 parts of the polyamide resin curing agent prepared in Example 1 of Application No. 41973/74 (Serial No. 1,472,198) was mixed with 88 parts of the so obtained main component (sample No. 10). The curing property (the degree of hardening observed when the sample was charged into a certain vessel, the vessel was sealed and the sample was allowed to stand still in this state for one week) and film-forming property under high-humidity conditions (degree of curing observed when the sample was applied to the inner surface of a certain vessel, the vessel was sealed and the coated sample was allowed to stand still for one week) were examined to obtain results shown in Table 3.

Example 5.

In the same manner as described in Example 4, polyamide resins having an amine value of 320 or 290 were prepared by reacting 1 mole of a dimer acid with 10 or 8 moles of an ether diamine having the structure



These polyamide resins were mixed with the main component obtained in Example 4 at mixing ratios of 10:90 (sample No. 11) and 15:85 (sample No. 12), respectively. Then, the curing property and film-forming property under high-humidity conditions were examined to obtain results shown in Table 3.

Example 6.

1 mole of a dimer acid was mixed with 3 moles of a polyester diamine $[H_2N(CH_2)_3-O-(CH_2)_3-NH_2]$ and 7 moles of an aliphatic amine (triethylene tetraamine), and 5 moles of methyl methacrylate and 0.3 mole of a polyglycol type epoxy resin (product manufactured and sold under tradename "Eponitt 014" by Nitto Kasei Co., Ltd.) were added as chain extenders to the mixture. In the same manner as described in Example 1 of the Application No. 41973/74, (Serial No. 1,472,198) the mixture was reacted under heating to obtain a polyamide resin having an amine value of 442.

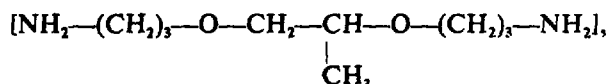
The so obtained resin was mixed with the main component prepared in Example 4 at a prescribed mixing ratio (sample No. 13), and the resulting composition was subjected to the above-mentioned comparative tests to obtain results shown in Table 3.

Example 7.

In the same manner as described in Example 6, polyamide resins were prepared by using components shown below, and each polyamide resin was mixed with the main component prepared in Example 4 and the composition was subjected to the above-mentioned comparative tests to obtain results shown in Table 3.

Sample No. 14:

1 mole of a dimer acid, 5 moles of triethylene tetraamine, 3 moles of an ether diamine

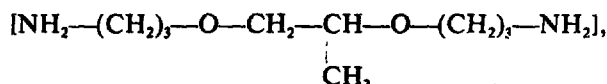


4 moles of methyl methacrylate and 0.25 mole of Eponitt 014.

The obtained polyamide resin had an amine value of 405.

Sample No. 15:

1 mole of a dimer acid, 12 moles of a polyether diamine



5 moles of methyl methacrylate and 1 mole of a glycerin type epoxy resin (Epikote 812 having an epoxy equivalent of 150 to 170).

The obtained polyamide resin had an amine value of 293.

Sample No. 16:

1 mole of a dimer acid, 10 moles of an ether diamine



4 moles of methyl methacrylate and 3 moles of formaldehyde.

The obtained polyamide resin had an amine value of 289.

Sample No. 17:

1 mole of a dimer acid, 6 moles of an ether diamine



4 moles of triethylene tetraamine, 4 moles of methyl methacrylate and 0.5 mole of Epikote 812.

The obtained polyamide resin had an amine value of 378.

Example 8.

A diglycidyl ether of a bisphenol (Epikote 828 having an epoxy equivalent of 184 to 194) was reacted with metaphenylene diamine at a mole ratio of 2:1 to obtain an amine adduct.

The amine adduct was used in combination with the polyamide resin obtained in Example 6 at a prescribed mixing ratio (samples No. 18 and No. 19), and the results of comparative tests are shown in Table 4. For comparison, results obtained when the above amine adduct alone was used as the curing agent are also shown in Table 4 (comparative sample No. 1).

Example 9.

Results obtained when a part of the polyamide resin obtained in Example 6 was replaced by metaphenylene diamine are shown in Table 4 (sample No. 20).

Example 10.

A dimer acid was reacted with metaphenylene diamine according to a customary method to obtain a polyamide resin. Results obtained when the so obtained resin was used in combination with the polyamide resin obtained in Example 6 at a prescribed mixing ratio (samples No. 21 and No. 22) and results obtained when the above resin prepared from a dimer acid and methaphenylene diamine alone was used as the curing agent (comparative sample No. 2) are shown in Table 4.

For comparison, in the same manner as in Example 6, polyamide resins were prepared from components shown below, and each of the so obtained polyamide resins was mixed with the above-mentioned main component and the resulting composition was subjected to comparative tests to obtain results shown in Table 3.

Comparative Sample No. 3:

1 mole of a dimer acid, 10 moles of metaxylene diamine, 4 moles of methyl methacrylate and 0.5 mole of Epikote 812.

The obtained polyamide resin had an amine value of 302.

Comparative Sample No. 4:

1 mole of a dimer acid, 15 moles of metaxylene diamine and 4 moles of methyl methacrylate.

The obtained polyamide resin had an amine value of 383.

Comparative Sample No. 5:

15 moles of metaxylene diamine, 7 moles of methyl methacrylate and 1 mole of Epikote 812.

The obtained resin had an amine value of 454.

Comparative Sample No. 6:

1 mole of a dimer acid and 3 moles of triethylene tetraamine.

The obtained polyamide resin had an amine value of 420.

From the foregoing results of the comparative tests, it will readily be understood that the paint composition of this invention has an excellent film-forming property under high-humidity conditions and it can readily be cured under such conditions where water is present. Accordingly, the paint composition of this invention can provide a film of sufficient properties even when applied in a sealed chamber or on the inner face of a sealed tank.

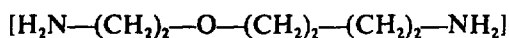
When the paint composition is applied in an ordinary state (under low-humidity conditions or under a current of air), it can provide a film having properties superior or comparable to those of films prepared from conventional paints.

With respect to the above samples No. 12, No. 16, No. 17, No. 18, No. 19, No. 20, No. 21 and No. 22, a polyoxyethylene benzylated phenyl ether having an HLB value of 16.6 was used for emulsifying the epoxy resin in water and the above comparative tests were conducted. It was found that in each case a paint of a good storage stability in which no crystals were formed at low temperatures was obtained.

Example 11.

9 parts of red iron oxide, 10 parts of talc, 9 parts of strontium molybdate and 30 parts of water were kneaded. Then, the kneaded mixture was mixed with an epoxy resin emulsion formed by emulsifying 20 parts of a diglycidyl ether of a bisphenol in 7 parts of water with 2 parts of a polyoxyethylene benzylated phenol ether having an HLB value of 16.6 to form a main component.

A polyamide curing agent having an amine value of 320 was prepared by condensing 1 mole of a dimer acid with 10 moles of an ether diamine

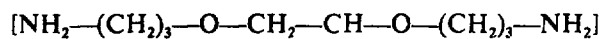


at 160°C according to a customary method and reacting the condensate at 200 to 250°C.

The above main component was mixed with the so obtained curing agent at a mixing weight ratio of 90/10 to form a paint composition of this invention. The paint composition was applied to a substrate in a thickness of 150μ and naturally dried for one week. The resulting film was subjected to various comparative tests to obtain results shown in Table 5.

Example 12.

An anti-corrosive paint composition was prepared in the same manner as in Example 11 except that a polyamide derived from 1 mole of a dimer acid, 7 moles of triethylene tetraamine and 3 moles of an ether diamine

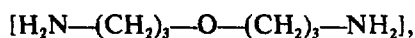


was used as the curing agent, and 7 parts of calcium molybdate and 13 parts of talc were employed.

Example 13.

In the main component of Example 11, the amount of talc was changed to 13 parts and 5 parts of potassium molybdate was used as the anti-corrosive pigment.

1 mole of a dimer acid, 7 moles of triethylene tetraamine, 3 moles of an ether diamine



5 moles of methylmethacrylate and 0.3 mole of a polyglycol type epoxy resin (Eponitt 014) were reacted in the same manner as in Example 11 to obtain a polyamide resin having an amine value of 442, which was used as a curing agent.

The above main component was mixed with the so obtained curing agent at a mixing weight ratio of 90/10 to obtain an anti-corrosive paint composition.

Example 14.

An anti-corrosive paint composition was prepared in the same manner as in Example 13 except that 5 parts of barium molybdate was used as the anti-corrosive pigment. The resulting composition was subjected to comparative tests to obtain results shown in Table 5.

Example 15.

An aqueous epoxy resin paint composition was prepared in the same manner as in Example 11 except that a mixture of 3 parts of strontium molybdate and 5 parts of calcium molybdate was used as an anti-corrosive pigment.

Example 16.

An aqueous epoxy resin paint composition was prepared in the same manner as in Example 11 except that 9 parts of iron (divalent) molybdate was used as an anti-corrosive pigment.

Comparisons.

Comparative Sample No. 7:

The aqueous epoxy resin emulsion of Example 11 was mixed with 16 parts of talc and 9 parts of red iron oxide to form a main component, which was then mixed with an ordinary aliphatic amine adduct as a curing agent, to obtain a paint composition.

Comparative Sample No. 8:

The aqueous epoxy resin emulsion of Example 11 was mixed with 9 parts of red iron oxide, 10 parts of talc, 10 parts of strontium chromate and 30 parts of water to form a main component, which was then mixed with the same curing agent as used in comparative sample No. 7, to obtain an anti-corrosive paint composition.

Comparative Sample No. 9:

The aqueous epoxy resin emulsion of Example 11 was kneaded with 9 parts of red iron oxide, 10 parts of talc, 10 parts of zinc borate and 30 parts of water to form a main component, which was then mixed with the same curing agent as used in comparative sample No. 7, to obtain a paint composition.

From the foregoing results of the comparative tests, it will readily be understood that the paint composition of this invention is superior or comparable to paint compositions comprising a conventional strontium chromate type pigment in respect to the anti-corrosive property, and that the paint composition of this invention is much superior to such conventional paint compositions in the film-forming property under high-humidity conditions and the curing uniformity.

TABLE 1

Additive Resin

Sample	Kind	Amount	Epikote 828	State of Formation and Growth of Crystals ¹⁾
Sample No. 1	Epilcon 800 (having epoxy equivalent of 195-225)	2%	98%	not observed
Sample No. 2	ditto	5%	95%	not observed
Sample No. 3	ditto	10%	90%	not observed
Sample No. 4	Epikote 152 (having epoxy equivalent of 172-179)	10%	90%	not observed
Sample No. 5	Epikote 871 (having epoxy equivalent of 390-470)	10%	90%	not observed

Note:

- 1) The above main component was placed in a can and the can was sealed and allowed to stand still in a thermostat chamber maintained at 0 to 5°C for 6 months. Then, the can was opened. The case where glittering crystals were floating on the paint surface is indicated as "observed" and the case where no crystals were formed is indicated as "not observed". The upper portion of the paint in which crystals were formed was ladled out and washed with water, and the residue was examined with a microscope to confirm formation of crystals. (In the subsequent Examples, the state of formation and growth of crystals was examined by the above method).

TABLE 2

Sample	HLB and Trade Name of Surface Active Agent	State of Formation and Growth of Crystals
Sample No. 7	15 (Newcol 714*)	not observed
Sample No. 8	16.6 (Newcol 723*)	not observed
Sample No. 9	18 (Emulgen A-500**)	not observed

* Manufactured by Nippon Nyukazai Co., Ltd.

** Manufactured by Kao-Atlas Co., Ltd.

TABLE 3
Results of Comparative Tests

Sample	Main Component/Curing Agent Mixing Ratio	Curing Property of Resulting Paint Composition 1)	Film-Forming Property under High-Humidity Conditions 2)	Remarks
Sample No. 10	88/12	good	good	this invention
Sample No. 11	90/10	good	good	this invention
Sample No. 12	85/15	good	good	this invention
Sample No. 13	90/10	good	good	this invention
Sample No. 14	90.6/9.4	good	good	this invention
Sample No. 15	87.4/12.6	good	good	this invention
Sample No. 16	86/14	good	good	this invention
Sample No. 17	90/10	good	good	this invention
Comparative Sample No. 3	88/12	bad	bad	comparison
Comparative Sample No. 4	91.4/8.6	bad	bad	comparison
Comparative Sample No. 5	92.4/7.6	bad	bad	comparison
Comparative Sample No. 6	88.8/11.2	somewhat good	bad	comparison

- 1) After the main component was mixed with the curing agent, a prescribed amount of the resulting composition was immediately charged in a polyethylene cup, and the composition was allowed to stand still in the sealed state for one week. Then, the polyethylene cup was stripped off to separate the inside solid from the vessel. The solid was cut into halves with a knife to examine whether or not the outer portion and the interior of the solid was completely cured. The case where both the outer portion and the interior were completely cured is indicated as "good". The case where the resulting solid was soft and rubber-like is indicated as "bad", and the case where the degree of curing was different between the outer portion and the interior is indicated as "somewhat good".
- 2) After the main component was mixed with the curing agent, the composition was applied to the inner face of a metal can and the can was immediately sealed. The coated composition was allowed to stand still in this state for one week. Then, the can was opened and the condition of the film was examined with fingers. The case where no abnormality was felt is indicated as "good", and the case where the film was viscous or it adhered to fingers is indicated as "bad".

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TABLE 4

Results of Comparative Tests

Sample	Mixing Weight Ratio ¹⁾	Film-Forming Property under High-Humidity Conditions	Properties of film (150 μ thick film)			Remarks
			Saline Dipping Test ²⁾	Salt Spraying Test ³⁾	Moisture Resistance ⁴⁾	
Sample No. 13	—	good	30 days	300 hours	300 hours	this invention
Sample No. 18	80/20	good	60 days	500 hours	500 hours	this invention
Sample No. 19	50/50	good	60 days	500 hours	500 hours	this invention
Sample No. 20	80/20	good	60 days	500 hours	500 hours	this invention
Sample No. 21	80/20	good	60 days	500 hours	500 hours	this invention
Sample No. 22	50/50	good	60 days	500 hours	500 hours	this invention
Comparative Sample No. 1	0/100	bad	not tested because no film was formed			comparison
Comparative Sample No. 2	0/100	bad	not tested because no film was formed			comparison

Notes:

- 1) ratio of (polyamide resin derived from dimer acid and polyether diamine)/(aromatic amine adduct, aromatic amine or polyamide resin formed by employing aromatic amine).
- 2) dipped in 3% aqueous solution of NaCl.
- 3) 5% aqueous solution of NaCl was sprayed at 35°C.
- 4) measured at temperature of 50°C. and relative humidity of 100%.

TABLE 5

Results of Comparative Tests

Sample	Film-Forming Property under High-Humidity ¹⁾	Curing Uniformity of Film ²⁾	Salt Spray- ing Test ³⁾	Moisture Resistance ⁴⁾	Saline Dip- ping Test ⁵⁾	Water Resistance ⁶⁾
(This invention)						
Example 11	◎	◎	◎	◎	◎	◎
Example 12	◎	◎	◎	◎	◎	◎
Example 13	◎	◎	◎	○	◎	◎
Example 14	◎	◎	◎	◎	◎	◎
Example 15	◎	◎	◎	◎	◎	◎
Example 16	◎	◎	◎	◎	◎	◎
(Comparisons)						
Comparative Sample No. 7	×	×	×	×	△	○
Comparative Sample No. 8	×	×	◎	◎	◎	◎
Comparative Sample No. 9	×	×	○	○	◎	◎

◎: very good, ○: good, △: somewhat bad, ×: bad

Notes: 1) After the main component was mixed with the curing agent, the composition was applied on the inner face of a certain vessel and the film was allowed to stand still in the sealed state for 7 days. After passage of 7 days the vessel was opened and the state of the film was examined with the fingers. Namely, it was checked whether the film was sticky or the film adhered to the fingers.

2) The paint was coated in a thickness of about 1 cm on a substrate, and after passage of 7 days, the film was cut with a knife to examine the curing uniformity.

3) A 3% aqueous solution of NaCl was sprayed at 35°C. for 500 hours.

4) The film was allowed to stand still at a temperature of 50°C. and a relative humidity of 100% for 500 hours.

5) The film was immersed in a 5% aqueous solution of NaCl for 30 days.

6) The film was immersed in water for 30 days.

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Attention is drawn to our copending Application No. 41973/74 (Serial No. 1,472,198) which describes and claims an aqueous epoxy resin paint composition comprising an epoxy resin emulsion formed by emulsifying in water containing, as a non-ionic surface active agent, a polyoxyethylene benzylated phenyl ether having an HLB value of at least 15 (A) 98 to 50% by weight of a diglycidyl ether of a bisphenol and (B) 2 to 50% by weight of at least one additive resin selected from (1) novolak type epoxy resins, (2) glycidyl esters of dimer or trimer acids and (3) condensates of β -methylepichlorohydrin and a bisphenol.

WHAT WE CLAIM IS:—

1. An aqueous epoxy resin paint composition comprising an epoxy resin emulsion formed by emulsifying, in water containing a non-ionic surface active agent, a diglycidyl ether of a bisphenol, there being incorporated into the epoxy resin emulsion a curing agent comprising (i) a polyamide resin derived from a dimer acid and an ether diamine, (ii) a polyamide resin derived from a dimer acid, an ether diamine and an aliphatic amine, (iii) a polyamide resin derived from a dimer acid, an ether diamine and a chain extender, or (iv) a polyamide resin derived from a dimer acid, an ether diamine, an aliphatic amine and a chain extender.

2. A composition as claimed in claim 1, wherein the curing agent further comprises (i) an aromatic amine, (ii) an aromatic amine/epoxy resin adduct, or (iii) a polyamide derived from an aromatic amine.

3. A composition as claimed in claim 2, wherein the weight ratio of the further component of the curing agent to the polyamide resin of the curing agent is from 5:95 to 50:50.

4. A composition as claimed in any of claims 1 to 3, further comprising from 0.1 to 20% by weight, based on the total weight of the composition, of at least one member selected from molybdic acid salts of strontium, calcium, potassium, iron (divalent), barium and ammonium.

5. An aqueous epoxy resin paint composition in accordance with claim 1, substantially as described in any of the foregoing Examples.

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