PATENT SPECIFICATION

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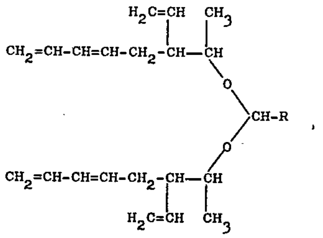
(54) IMPROVEMENTS IN OR RELATING TO AQUEOUS FILM-FORMING COMPOSITIONS

(71) We, KANSAI PAINT CO., LTD., a Company of Japan, of 365, Kanzaki, Amagasaki-shi, Hyogo-ken, Japan, and KUREHA CHEMICAL INDUSTRY CO., LTD., a Company of Japan, of 1—8, Nihonbashihoridome-cho, Chuo-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 an aqueous film-forming composition. More particularly, the invention relates to the improvement in vinyl polymer emulsions prepared by radically polymerizing unsaturated vinyl or vinylidene monomer with emulsion stabilizers of oxidation curing polymeric water-soluble resins.

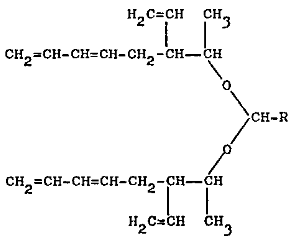
The inventors of the present invention have made deep and extensive studies on the emulsions with oxidation curing polymeric water-soluble resins as emulsion stabilizers. When these emulsions are cured by oxidation, several characteristic features different from those of other common emulsions can be obtained; however, the former emulsions have the defect that the lowest temperature for film formation cannot be compatible with the desirable hardness of obtained coating films when they are, in practice, used as low-pollution coating materials. The present invention has been made as the result of earnest studies in order to eliminate or at least mitigate the above drawback.

According to the first aspect of the present invention there is provided an aqueous film-forming composition, which comprises an emulsion prepared by radically polymerizing unsaturated vinyl or vinylidene monomer in the presence of an emulsion stabilizer of oxidation curing polymeric water-soluble resin, the emulsion having impregnated therein from 0.1 to 150% by weight (based on the solids content of the emulsion) of a compound (A) having the general formula:



in which R represents a hydrogen atom or an alkyl radical having 1 to 18 carbon atoms, a phenyl radical, an alkyl (C_{1-18}) phenyl radical, a cyclohexyl radical or an alkyl (C_{1-18}) cyclohexyl radical.

According to the second aspect of the present invention there is provided a process of preparing an aqueous film-forming composition, which process comprises preparing an emulsion by radically polymerizing unsaturated vinyl or vinylidene monomer in the presence of an emulsion stabilizer of oxidation curing polymeric water-soluble resin, and impregnating the emulsion with from 0.1 to 150% by weight (based on the solids content of the emulsion) of a compound (A) having the general formula:



in which R represents a hydrogen atom or an alkyl radical having 1 to 18 carbon atoms, a phenyl radical, an alkyl (C_{1-18}) phenyl radical, a cyclohexyl radical or an alkyl (C_{1-18}) cyclohexyl radical.

The present invention enables the provision of an improved aqueous film-forming composition which can be cured at a lower temperature forming a coating film of sufficient hardness, as well as an aqueous film-forming composition which can be applied to the surfaces of several articles without difficulty so as to form coating films of other excellent properties, and an aqueous film-forming composition which can be produced easily at relatively low cost in industrial practices.

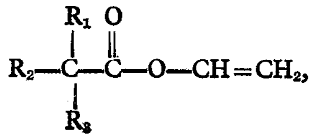
The polymer emulsion used in the present invention has to be produced or have been produced with an emulsifying agent of a polymeric water-soluble resin which can be cured by oxidation. Such emulsion, containing the emulsifying agent as a dispersion stabilizer, is able to stand the shock caused by the mixing of the compound (A) because the emulsifying agent is a high polymer, apparently because it is firmly joined to the surfaces of emulsion particles, and the molecular weight is further increased by the grafting reaction which occurs during the emulsion polymerization. Furthermore, in the curing of the coating material, since the oxidation curing polymeric resin is contained, the curing of compound (A) is promoted by the gel effect and the network of gel is easily spread throughout so that tough coating film can be formed.

The portion of the oxidation curing polymeric water-soluble resin used as an emulsion stabilizer in the present invention which is in contact with water is preferably largely hydrophobic, because the emulsion itself is easily and stably formed; in addition, it facilitates the impregnation of the compound (A) being large hydrophobic. Exemplified as such resins are the conventionally known maleinized polydiene, maleinized alkyd resin, maleinized fatty acid-modified epoxy resin, maleinized oil,. maleinized stand oil, maleinized boiled-oil, maleinized fatty acid-modified acrylic resin, and fatty acid-modified acrylic resin. Further, as applicable water-soluble resins, there are water-soluble alkyd resin and oil-modified water-soluble epoxy resin.

The number average molecular weights of these water-soluble resins are normally within the range of from 500 to 50,000, preferably from 800 to 15,000, and the acid values are normally in the range of from 20 to 350, preferably from 30 to 200.

These water-soluble resins are preferably neutralized with volatile amines or ammonia, and if necessary, they are made water-soluble with the addition of water-soluble organic solvents.

The emulsion of vinyl polymer can be obtained by radically polymerizing unsaturated vinyl or vinylidene monomer in the above-described aqueous solution. The preferable unsaturated vinyl or vinylidene monomer to be used is not so strongly hydrophilic and produces radicals of relatively small activity having a Q-value of not less than 0.1 in the Q—e scheme. When the hydrophilic property is too strong, the impregnation of the compound (A) becomes hard as well as the synthesis of the emulsion becoming difficult. Further, when the radical activity is too strong, reaction with the oxidizing reactive groups of the water-soluble resin is caused to occur, so that the activity of the surface cured by oxidation is lost; at the same time, the polymerization is inhibited. Exemplified as preferable monomers are styrene, α-methyl styrene, vinyltoluene, esterified products of acrylic acid or methacrylic acid with alcohols having 1 to 26 carbon atoms, condensates of glycidyl acrylate or glycidyl methacrylate with carboxylic acids having 2—26 carbon atoms, methoxybutyl acrylate, methoxybutyl methacrylate, methoxyethyl acrylate, methoxyethyl methacrylate, ethoxybutyl acrylate, ethoxybutyl methacrylate, allyl acrylate, allyl methacrylate, butadiene, isoprene and chloroprene. These monomers can be used singly or in a mixture of two or more. The above monomers can be used together with other monomers (however, the above monomers should preferably be contained therein in an amount of more than 50%, more preferably more than 70% relative to the total quantity of the monomers), exemplified by 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, acrylonitrile, methacrylonitrile, acrylic acid, methacrylic acid, glycidyl acrylate, glycidyl methacrylate, vinyl acetate, Veova monomer (made by Shell Chemical Co.: the general formula is



$$R_2-\overset{R_1}{\underset{R_3}{\overset{|}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-O-CH=CH_2,$$

wherein R_1, R_2 and R_3 each represent a saturated alkyl radical), N-n-butoxymethyl acrylamide, acrylamide, vinylpyridine, N-methylol acrylamide, and other common radically polymerizable monomers. The above monomers can be, of course, used as a mixture of two or more. In order to facilitate the impregnation of the compound (A), it is preferable that the Tg-point of the whole monomer mixture is lower than 70°C. The word "Veova" is a Trade Mark.

The quantity of water soluble resin for stabilising the emulsion is so determined as to make the acid value of the whole solid content including unsaturated monomer generally in the range of from 1.5 to 150, preferably from 10 to 50. (The acid value is the amount of potassium hydroxide (in mg) required to neutralise 1g of the whole solid content).

The compound (A) impregnated in the above emulsion has a rapid curing property that is characteristic of dienes and quite large plasticizing effect as compared with common plasticizers. Accordingly, an ideal emulsion can be prepared which is sufficiently soft when it is used for coating but becomes very hard in a short time.

The compound (A) used in the present invention can be produced by the condensation of a precursor of 1 - methyl - 2 - vinyl-4,6 - heptadiene - 1 - ol and aldehydes represented by the general formula: RCHO. The aldehydes to be used are, for example, aliphatic aldehydes, alicyclic aldehydes and aromatic aldehydes having from 1 to 18 carbon atoms. Above all, preferable ones are aliphatic aldehydes having 8 or less carbon atoms such as formaldehyde, acetaldehyde, butyraldehyde and octyl aldehyde.

The impregnation quantity of the compound (A) relative to (or based on) the solids content of the emulsion is in the range of from 0.1 to 150% by weight, preferably from 3 to 50% by weight.

When the compound (A) is impregnated, although it can be used by mixing as it stands, it is preferable that the compound (A) is previously emulsified or solubilized by adding water-soluble resin or common emulsifying agent so as to prevent the occurrence of troubles such as lump formation. As the above water-soluble resin, from 1 to 600%, preferably from 5 to 200%, of the oxidation curing water-soluble resin that is used as the stabilizer for the emulsion of the present invention, is mixed well with the compound (A).

The aqueous film-forming composition of the present invention is of quite good quality in that it forms coating films at normal temperature; however, the composition can be made a thermosetting type one by adding melamine or the like. Further, the composition of the present invention can be used for preparing resin processing agents and adhesives as well as coating materials.

In order that those skilled in the art may better understand the present invention and the manner in which it is practised, the following specific Examples and reference Examples are given. In these Examples, unless otherwise indicated, all parts and percentages are by weight.

Reference Example 1.

Maleinized polybutadiene having an acid value of 100 was prepared by the maleinization of 1,2-vinyl type polybutadiene having a number average molecular weight of 3,000. This was neutralized with 0.95 equivalents of ammonia per carboxylic group and, after adding 35% by weight of butyl Cellosolve, it was dissolved in water. Then, 259% by weight of *n*-butylmethacrylate was added to the solution and it was emulsified by stirring well. To this emulsion was added 0.25% by weight (vs. *n*-butyl methacrylate) of ammonium peroxide and the emulsion was then heated to 80°C and maintained at this temperature for 2 hours. An emulsion of fine particles containing 40% of solids content was thus obtained. The word "Cellosolve" is a Trade Mark.

Reference Example 2.

A polymer having a peak molecular weight of about 7,000 and an acid value of 80 was prepared by dropping and polymerizing the following monomers in a solution of butyl Cellosolve:

	Parts
Adduct of safflower oil fatty acid glycidyl methacrylate	60
Styrene	27
Acrylic acid	13

Then, 0.16 parts (as metal) of cobalt naphthenate, 0.16 parts (as metal) of manganese naphthenate and 0.45 parts (as metal) of lead naphthenate were added to the above reaction product and it was neutralized with ammonia to obtain an auxiliary water-soluble resin containing 25% by weight of butyl Cellosolve.

Examples 1 to 3.

The quantities of compound (A) indicated in the following Table were respectively mixed with the auxiliary water-soluble resin obtained in Reference Example 2 and, after controlling the viscosities with water, they were added to respective portions of the emulsion obtained in Reference Example 1, with stirring to prepare aqueous film-forming compositions. The compounding ratio of the auxiliary water-soluble resin was 1 part of the water-soluble resin to 9 parts (as solid content) of the emulsion obtained in Reference Example 1. The properties of the prepared compositions are shown in the Table.

Comparative Example 1.

The mixture of 9 parts of the emulsion obtained in Reference Example 1 and 1 part of the water-soluble resin obtained in Reference Example 2, was prepared. The properties of the mixture are shown in the Table.

Examples 4 to 6.

To each of the aqueous film-forming compositions prepared in Examples 1 to 3, 80% by weight of titanium white was added and dispersed by a quick mill. The properties of the mixtures are shown in the Table.

Comparative Example 2.

A mixture was prepared by adding 80% by weight of titanium white to the composition obtained in Comparative Example 1, and it was dispersed well. The properties of this mixture are shown in the Table.

TABLE

Examples Items	Ex. 1$^{(*2)}$	Ex. 2	Ex. 3	C. Ex. 1$^{(*3)}$	Ex. 4	Ex. 5	Ex. 6	C. Ex. 2
Compounding ratio of compound (A) (% by weight) (*1)	5	10	20	0	5	10	20	0
Solid content of composition (%)	43	43	41	42	49	43	40	51
Viscosity of composition (PS), (6 rpm)	20	19	21	17	40	31	18	40
Lowest film-forming temperature (°C)	<–10	<–10	<–10	–5	<–10	<–10	<–10	1
Gloss (60°)	–	–	–	–	63	57	60	68
Gel fraction after drying at 20°C for 1 day (%)	20	31	67	10	–	–	–	–
Properties of coating film after drying at 20°C for 7 days Hardness	F	F	F	F	H	H	H	H
Erichsen test (mm)	8	8	8	6	7	>8	>8	2
Adhesiveness	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Impact resistance (cm)	50	45	45	35	35	40	40	30
Gasoline resistance (min.)	60	60	70	5	30	60	60	30
Salt spray test	(*4)			(*5)				
Water resistance (After 10 days)								

Notes for the Table:

(*1) The compound (A) used was the one which is represented by the foregoing general formula in which R represents a CH_3 radical.

(*2) Ex. means Example.

(*3) C. Ex. means Comparative Example.

(*4) The mark ○ means fair.

(*5) The mark ◎ means poor.

Example 7.

A mixture of RJ—101 (trademark of styrene-allyl alcohol copolymer made by Monsanto Chemical Co.)/linseed oil fatty acid in a ratio of 16 to 20, was esterified until it became less than 5 in acid value, then it was subjected to maleinization to obtain a resin of 100 in acid value. A 74% solution of this resin in butyl Cellosolve was prepared and it was neutralized with ammonia. Emulsion polymerization was carried out by adding 414 parts of monomer mixture (styrene/isobutyl methacrylate in a ratio of 3 to 7) to 160 parts (as solids content) of the above solution; a fine emulsion containing 40% of solids components was thus obtained. To this emulsion, 8.5% (as solids content) of the water-soluble resin containing 25% by weight of butyl Cellosolve obtained in Reference Example 2 was added. Further, 15.2% of the compound (A) in which "R" represents a methyl group was added to the above mixture. When the compound (A) was not added, film was not formed with the emulsion; however, the emulsion containing the compound (A) had the film-forming property and the lowest film-forming temperature was −1°C. After 20 hours from the film formation, the hardness was 4B and after 1 week, it became H. The gloss, hardness and water resistance were satisfactory for the use of clear coating material.

Notes for Tested Items:

Hardness: The coated surface was scratched by Mitsubishi UNI Pencils (trademark, made by Mitsubishi Pencil Co., Ltd., in Japan) of 6B to 9H in hardness. The value of hardness was represented by the hardest pencil with which any scratch was not made (the softer grade next to the pencil which made scratches on the coated surface).

Adhesiveness: 100 checkered square (1 × 1 mm) were made by cutting the coating film with a knife. Then, a piece of self-adhesive tape was applied to the cut squares and quickly peeled off. When the number of remained squares was *n*, the test result was represented by (*n*/100).

Erichsen test: An Erichsen film tester was used at 20°C.

Impact resistance: Measured at 20°C by using a weight of 500 g, 0.5 inch in diameter, and a Du Pont impact tester.

Gasoline resistance: Coating films were immersed in gasoline (made by Nippon Oil Co., Ltd.) and the times in which they were softened, were measured.

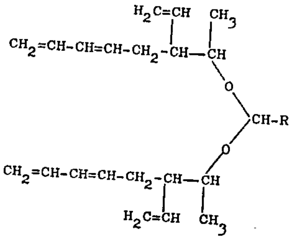
Salt spray test: Measured according to JIS (Japanese Industrial Standards) Z 2371.

Water resistance: Test pieces were immersed in water at 20°C for 10 days, then the occurrence of change in coating film was observed.

With the above-described test results, the advantages of the present invention will be understood.

WHAT WE CLAIM IS:—

1. An aqueous film-forming composition, which comprises an emulsion prepared by radically polymerizing unsaturated vinyl or vniylidene monomer in the presence of an emulsion stabilizer of oxidation curing polymeric water-soluble resin, the emulsion having impregnated therein from 0.1 to 150% by weight (based on the solids content of the emulsion) of a compound (A) having the general formula:



in which R represents a hydrogen atom or an alkyl radical having 1 to 18 carbon atoms, a phenyl radical, an alkyl (C_{1-18}) phenyl radical, a cyclohexyl radical or an alkyl (C_{1-18}) cyclohexyl radical.

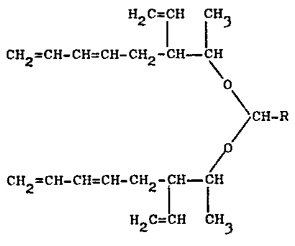
2. An aqueous film-forming composition according to Claim 1, wherein compound (A) is 1,1 - *bis*(1′ - methyl - 2′ - vinyl - 4′,6′-

heptadienoxy) - alkane in which R represents an alkyl radical having 1 to 18 carbon atoms or a hydrogen atom.

3. An aqueous film-forming composition according to Claim 1 or 2, wherein the quantity of compound (A) added is in the range of from 3 to 50% by weight (based on the solids content of the emulsion).

4. An aqueous film-forming composition according to Claim 1, 2 or 3, wherein the unsaturated vinyl or vinylidene monomer is at least one of styrene, α-methylene styrene, vinyltoluene, esters of acrylic acid and methacrylic acid with alcohols having 1 to 26 carbon atoms, condensates of glycidyl acrylate and glycidyl methacrylate with carboxylic acids having 2 to 26 carbon atoms, methoxybutyl acrylate, methoxybutyl methacrylate, methoxyethyl acrylate, methoxyethyl methacrylate, ethoxybutyl acrylate, ethoxybutyl methacrylate, allyl acrylate, allyl methacrylate, butadiene, isoprene and chloroprene.

5. A process of preparing an aqueous film-forming composition, which process comprises preparing an emulsion by radically polymerizing unsaturated vinyl or vinylidene monomer in the presence of an emulsion stabilizer of oxidation curing polymeric water-soluble resin, and impregnating the emulsion with from 0.1 to 150% by weight (based on the solids content of the emulsion) of a compound (A) having the general formula:



in which R represents a hydrogen atom or an alkyl radical having 1 to 18 carbon atoms, a phenyl radical, an alkyl (C_{1-18}) phenyl radical, a cyclohexyl radical or an alkyl (C_{1-18}) cyclohexyl radical.

6. A process according to Claim 5, wherein compound (A) is 1,1 - *bis*(1′ - methyl - 2′- vinyl - 4′,6′ - heptadienoxy) - alkane in which R represents an alkyl radical having 1 to 18 carbon atoms or a hydrogen atom.

7. A process according to Claim 5 or 6, wherein the quantity of compound (A) added is in the range of from 3 to 50% by weight (based on the solids content of the emulsion).

8. A process according to Claim 5, 6 or 7, wherein the unsaturated vinyl or vinylidene monomer is at least one of styrene, α-methyl styrene, vinyltoluene, esters of acrylic acid and methacrylic acid with alcohols having 1 to 26 carbon atoms, condensates of glycidyl acrylate and glycidyl methacrylate with carboxylic acids having 2 to 26 carbon atoms, methoxybutyl acrylate, methoxybutyl methacrylate, methoxyethylacrylate, methoxyethyl methacrylate, ethoxybutyl acrylate, ethoxybutyl methacrylate, allyl acrylate, allyl methacrylate, butadiene, isoprene and chloroprene.

9. An aqueous film-forming composition, substantially as described in foregoing Example 1.

10. An aqueous film-forming composition, substantially as described in foregoing Example 2.

11. An aqueous film-forming composition, substantially as described in foregoing Example 3.

12. An aqueous film-forming composition, substantially as described in foregoing Example 4.

13. An aqueous film-forming composition, substantially as described in foregoing Example 5.

14. An aqueous film-forming composition, substantially as described in foregoing Example 6.

15. An aqueous film-forming composition, substantially as described in foregoing Example 7.

16. A process for preparing an aqueous film-forming composition, substantially as described in foregoing Example 1.

17. A process of preparing an aqueous film-forming composition, substantially as described in foregoing Example 2.

18. A process of preparing an aqueous film-forming composition, substantially as described in foregoing Example 3.

19. A process of preparing an aqueous film-forming composition, substantially as described in foregoing Example 4.

20. A process of preparing an aqueous film-forming composition, substantially as described in foregoing Example 5.

21. A process of preparing an aqueous film-forming composition, substantially as described in foregoing Example 6.

22. A process of preparing an aqueous film-forming composition, substantially as described in foregoing Example 7.

23. An aqueous film-forming composition, whenever prepared by the process of any one of Claims 5 to 8 and 16 to 22.

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