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(54) IMPROVEMENTS IN OR RELATING TO AQUEOUS
 COATING 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, Nihonbashi-horidome-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:—

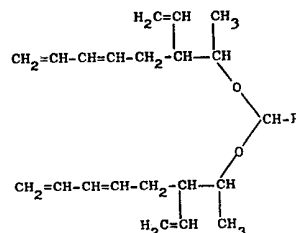
This invention relates to an aqueous coating composition. More particularly, the invention relates to an aqueous coating composition of improved vinyl or vinylidene polymer emulsion prepared by radically polymerizing unsaturated vinyl or vinylidene monomer with a surface active agent of ionic or nonionic compound.

The emulsion is very useful as the resin material for preparing pollution-free coating compositions, so that it has been employed for various purposes. The emulsion has, however, a disadvantage in that the lowest film-forming temperature thereof is not compatible with the hardness of the coating film formed by using the emulsion. In other words, when the lowest film-forming temperature is lowered to a sufficient degree, the film hardness becomes insufficient; on the contrary, when the film hardness is made high enough, the emulsion cannot be used practically at lower temperatures. If an organic solvent is added to the emulsion to eliminate this defect, the advantage of non-pollution will be lost.

In order to eliminate the above-described defects in the prior art, the inventors of the present application have carried out various extensive studies, and as the result, it has been found out that the following compound (A) facilitates the rapid curing of emulsion

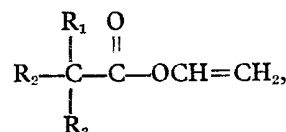
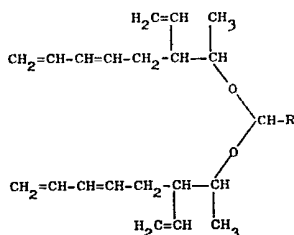
since the permeability and plasticizing effect of the compound (A) to the emulsion are quite excellent and the rate of oxidation curing is large. Further, the compound (A) is free from pollution as it does not evaporate.

According to the first aspect of the present invention there is provided an aqueous coating composition, which comprises an emulsion prepared by radically polymerizing unsaturated vinyl or vinylidene monomer in the presence of an ionic or nonionic surface active agent, 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 (C₁₋₁₈) phenyl radical, a cyclohexyl radical or an alkyl (C₁₋₁₈) cyclohexyl radical.

According to the second aspect of the present invention there is provided a process of preparing an aqueous coating composition, which process comprises preparing an emulsion by radically polymerizing unsaturated vinyl or vinylidene monomer in the presence of an ionic or nonionic surface active agent, and impregnating the emulsion with from 0.1 to 150% by volume 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 coating composition in which the lowest film-forming temperature is compatible with the hardness of the formed coating films, as well as an aqueous coating composition which can be applied to the surfaces of various articles without causing air pollution, an aqueous coating composition which can be cured rapidly but forms the coating films having excellent properties, and an aqueous coating composition which can be prepared without difficulty at relatively low cost in industrial practices.

The invention enables the provision of aqueous coating compositions having a lowest film-forming temperature of a sufficiently low value and which forms coating films having excellent properties including quite high hardness.

The surface active agents used for preparing the emulsion of the present invention are commonly used ones of anionic, cationic or nonionic and low molecular or polymeric compounds. Exemplified as the anionic surface active agents are fatty acid salts, salts of higher alcohol sulphuric esters, sulphates of aliphatic amines and aliphatic amides, salts of aliphatic alcohol phosphoric esters, aliphatic amide sulphonates and alkylaryl sulphonates. As the cationic surface active agents, there are exemplified salts of aliphatic amines, quaternary ammonium salts and alkylpyridinium salts. Further, the nonionic surface active agents are exemplified by polyoxyethylene alkyl ether, polyoxyethylene alkyl phenol ether, polyoxyethylene alkyl ester and sorbitan alkyl ester.

The unsaturated vinyl or vinylidene monomers used for the preparation of the emulsion in the present invention, are radically polymerizable ones. For example, there are ethylene, propylene, butylene, vinyl chloride, vinylidene chloride, vinyl acetate, Veova monomer (made by Shell Chemical Co; the general formula is

wherein R_1 , R_2 and R_3 each represent saturated alkyl radicals), styrene, α -methylstyrene, vinyltoluene, vinylpyridine, butadiene, pentadiene, chloroprene, isoprene, acrylic acid, methacrylic acid, acrylic esters, methacrylic esters, glycidyl acrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, acrylonitrile and methacrylonitrile. The word "Veova" is a Trade Mark.

The compound (A) used for the impregnation to the emulsion in the present invention can be prepared by the condensation of precursory material of 1-methyl-2-vinyl-4,6-heptadiene-1-ol with aldehydes that are represented by the general formula: RCHO . Such aldehyde to be used may be selected from the group consisting of aliphatic aldehydes, alicyclic aldehydes and aromatic aldehydes having 1 to 18 carbon atoms. Above all, preferable ones are aliphatic aldehydes, especially those having 8 or less carbon atoms such as formaldehyde, acetaldehyde, butyraldehyde and octylaldehyde.

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

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 oxidation curing water-soluble resin or common emulsifying agent so as to prevent the occurrence of troubles such as lump formation. The above oxidation curing water-soluble resin may be exemplified by maleinized polydiene, maleinized alkyd, 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. They are suitable for the emulsification of the compound (A) and they are advantageous in that they do not exert bad influence on the properties of coating film by self-curing since they have good storage stability. Further, water-soluble alkyd resin and oil-modified water-soluble epoxy resin can also be used. Furthermore, even when the above-mentioned anionic, cationic and nonionic surface active agents are used, the compound (A) does not receive any bad influence from the use of surface active agents be-

cause the compound (A) is easily dispersed as it has low molecular weight, large oiliness and high curing rate.

The quantities of the above-described self-curing water-soluble resins to be used are generally not restricted; however, the preferable quantities are less than 300% by weight, more preferably less than 50% by weight relative to the solids content of the emulsion. In the case of the latter common surface active agents, the quantities of use may be 10% by weight or less, or preferably less than 5% by weight.

The aqueous coating composition of the present invention can be advantageously used for forming coating films at ordinary temperatures; however, the composition can be thermally cured or it can be combined with other cross-linking agents.

The improved emulsion of the present invention can be used not only for coating but also for the preparation of several adhesives and resin processing agents.

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 are given. In these Examples, unless otherwise indicated, parts and percents are by weight.

Example 1.

A mixture of monomers in a compounding ratio of styrene/*n*-butyl acrylate/acrylic acid of 38.2/59.8/2 was prepared. A mixture of surface active agents in a compounding ratio of Triton X-200/Emulgen 911/Epan 410 of 1/1/0.5 was also prepared. 25% of the mixture of surface active agents was added to the former mixture of monomers, and an emulsion (I) containing 50% of solid component was synthesized by conventional method.

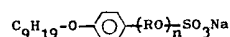
Meanwhile, to the compound (A) of the general formula in which R represents a CH₃ radical, were added 0.16% (as metal) of cobalt naphthenate, 0.16% (as metal) of manganese naphthenate and 0.45% (as metal) of lead naphthenate. Further, 10% of Noigen EA 143, 10% of Sorgen TW 60 and 2.5% of polyethylene glycol 4000 (m.w.: 4000) was added to the above mixture and then 50% of water was added and the mixture was emulsified with stirring to prepare an emulsion (II).

Five parts (as compound (A)) of the emulsion (II) was added to 100 parts (as solid) of the emulsion (I) with stirring to prepare a homogeneous emulsion. The properties of this emulsion are shown in the following Table.

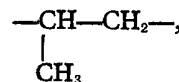
Notes:

The designations of the raw materials described above have the following meanings:

Triton X-200: Surface active agent represented by the general formula

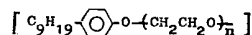


wherein R represents a mixture of $-\text{CH}_2-\text{CH}_2-$ and

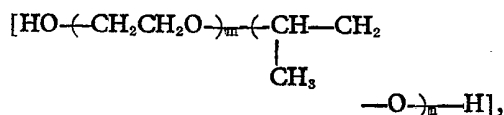


and *n* is about 30, made by Rohm & Haas Corp.

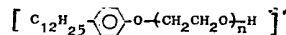
Emulgen 911: Surface active agent; polyoxyethylenenonylphenyl ether



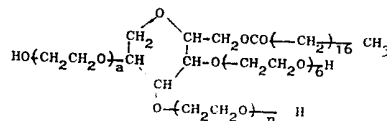
having a HLB (hydrophile lipophile balance) of 13.7, made by Kao Atlas Co. Ltd. Epan 410: Surface active agent; polypropyleneglycolpolyethyleneglycol ether



made by Daiichi Kogyo Seiyaku Co., Ltd. Noigen EA 143: Surface active agent; polyoxyethylenedodecyl phenyl ether



having a HLB of 14, made by Dai-ichi Kogyo Seiyaku Co., Ltd. Sorgen TW 60: Surface active agent; polyethyleneglycol sorbitan monostearate



having a HLB of 14.9, made by Dai-ichi Kogyo Seiyaku Co., Ltd.

The words "Triton", "Emulgen", "Epan", "Noigen" and "Sorgen" are Trade Marks.

Examples 2 to 4.

The compounding ratio of emulsions (I) and (II) in Example 1 was changed to 100/10, 100/20 and 100/40, respectively, so as to prepare three other kinds of homogeneous emulsion. The properties of these emulsions are shown in the following Table.

Example 5.

By using 1% of Emal O (trademark for a surface active agent consisting of sodium lauryl sulfate C₁₂H₂₅OSO₃Na, made by Kao Atlas Co., Ltd.), an emulsion (III) containing 50% of solid content was prepared by

the conventional method from a monomer mixture of Veova monomer/vinyl acetate in the ratio 40/60.

- 5 A homogeneous emulsion was prepared by mixing the materials in the ratio of emulsion (III)/emulsion (II) in Example 1 (as compound (A)) of 100/5 (as solid). The properties of the thus-obtained emulsion are shown in the following Table.

10 Example 6.

- An emulsion was prepared by using materials in the ratio of DM—60 (trademark of a styrene-butyl acrylate emulsion made by Hoechst Synthetics Co., Ltd.)/emulsion (II) (as compound (A)) of 100/5 (as solid). The properties of the thus-prepared emulsion are shown in the following Table.

Example 7.

- 20 An emulsion was prepared by using materials in the ratio of P—3 Emulsion (trademark of vinyl acetate-ethylene emulsion made by Showa Highpolymer Co., Ltd.)/emulsion (II) (as compound (A)) of 100/5 (as solid). The properties of the thus-prepared emulsion are shown in the following Table.

Comparative Example 1.

The emulsion (I) in Example 1 was solely used.

30 Comparative Example 2.

The composition used in this Example was prepared by adding 10% by weight of tricresyl phosphate to the emulsion I used in Example 1.

35 Comparative Examples 3 to 5.

In these Comparative Examples, the emulsion (III), DM—60 emulsion and P—3 emulsion that were used in Examples 5 to 7, were used solely.

Test Items:

Lowest film-forming temperature: A commercially available emulsion paint of vinyl chloride-vinyl acetate copolymer was applied to the surface of test plates to form thereon absorptive surfaces and the film-forming temperatures were measured by applying the emulsions to be tested to the absorptive surfaces.

Hardness: The coated surface was scratched by using Mitsubishi UNI Pencils (trademark, made by Mitsubishi Pencil Co., Ltd.) 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 squares (1×1 mm) were made by cutting the coating film with a knife. A piece of self-adhesive tape was then applied to the cut squares and quickly peeled off. When the number of remaining squares was *n*, the test result was indicated as (*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 film was immersed in gasoline (made by Nippon Oil Co., Ltd.), and the time in which the coating film was not softened was measured.

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

Water resistance: Test piece was immersed in water at 20°C for 1 day, then the occurrence of change in coating film was observed.

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TABLE

Items	Example	(*) Ex. 1	Ex. 2	Ex. 3	Ex. 4	(*) C. Ex. 1	C. Ex. 2
Compounding ratio of compound (A) (by weight)		5	10	20	40	—	—
Lowest film-forming temperature (°C)		5	<-10	<-10	<-10	20	16
Hardness, 20°C, after 7 days		HB	F	B (*)	B (*)	2B	B
Gel fraction, 20°C, after 1 day		0	5	14	25	0	0
After drying at 20°C for 7 days, Adhesiveness		100/100	100/100	100/100	100/100	100/100	100/100
Erichsen test (mm)		>8	>8	>8	>8	>8	>8
Impact resistance (cm)		5	5	5	5	5	5
Gasoline resistance (min.)		5	10	10	15	5	5
Salt spray test (1 day) (*)		Δ	Δ	Δ	Δ	Δ	Δ
Water resistance (*)		⊙	⊙	⊙	⊙	⊙	⊙

Notes: (*) : Ex. means Example. (*) : C. Ex. means Comparative Example.

(*) : After 2 weeks, hardness became F.

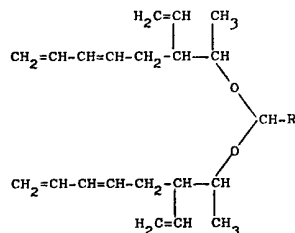
(*) : The mark Δ means fair and the mark ⊙ means poor.

TABLE (Cont.)

Items	Examples	Ex. 5	C. Ex. 3	Ex. 6	C. Ex. 4	Ex. 7	C. Ex. 5
Compounding ratio of compound (A) (by weight)		5	—	5	—	5	—
Lowest film-forming temperature (°C)		-4	>20	<-10	-4	<-10	0
Hardness, 20°C after 7 days		HB	HB	HB	HB	HB	HB
Gel fraction, 20°C, after 1 day		30	8	20	5	10	0
After drying at 20°C for 7 days, Adhesiveness		46/100	31/100	97/100	50/100	8/100	0/100
Erichsen test (mm)		>8	>8	>8	>8	>8	>8
Impact resistance (cm)		20	5	>50	>50	>50	45
Gasoline resistance (min.)		5	5	5	5	15	15
Salt spray test (1 day)		Δ	Δ	②	③	④	④
Water resistance		④	④	④	④	④	④

WHAT WE CLAIM IS:—

1. An aqueous coating composition, which comprises an emulsion prepared by radically polymerizing unsaturated vinyl or vinylidene monomer in the presence of an ionic or non-ionic surface active agent, 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:



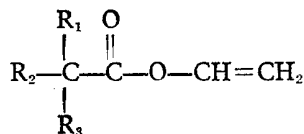
- in which R represents a hydrogen atom or an alkyl radical having 1 to 18 carbon atoms, a phenyl radical, an alkyl (C_{1-18}) phenyl radical, a cyclohexyl radical or an alkyl (C_{1-18}) cyclohexyl radical.

2. An aqueous coating 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 coating composition according to Claim 1 or 2, wherein before being impregnated into the emulsion, compound (A) is dispersed or solubilized in an oxidation curing water-soluble resin or surface active agent.

4. An aqueous coating composition according to Claim 1, 2 or 3, 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).

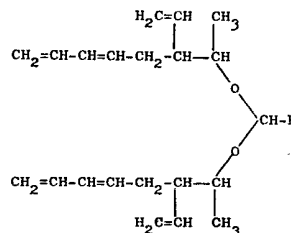
5. An aqueous coating composition according to any one of Claims 1 to 4, wherein the unsaturated vinyl or vinylidene monomer is at least one of ethylene, propylene, butylene, vinyl chloride, vinylidene chloride, vinyl acetate, a compound having the general formula



- wherein R_1 , R_2 and R_3 each represent a saturated alkyl radical, styrene, α -methylstyrene, vinyltoluene, vinyl pyridine, butadiene, pentadiene, chloroprene, isoprene, acrylic acid, methacrylic acid, acrylic ester, methacrylic ester, glycidyl acrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-

hydroxypropyl methacrylate, acrylonitrile and methacrylonitrile.

6. A process of preparing an aqueous coating composition, which process comprises preparing an emulsion by radically polymerizing unsaturated vinyl or vinylidene monomer in the presence of an ionic or nonionic surface active agent, 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:



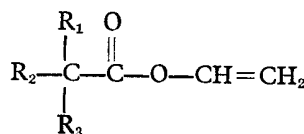
in which R represents a hydrogen atom or an alkyl radical having 1 to 18 carbon atoms, a phenyl radical, an alkyl (C_{1-18}) phenyl radical, a cyclohexyl radical or an alkyl (C_{1-18}) cyclohexyl radical.

7. A process according to Claim 6, 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.

8. A process according to Claim 6 or 7, wherein, before being impregnated into the emulsion, compound (A) is dispersed or solubilized in an oxidation curing water-soluble resin or surface active agent.

9. A process according to Claim 6, 7 or 8, 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).

10. A process according to any one of Claims 6 to 9, wherein the unsaturated vinyl or vinylidene monomer is at least one of ethylene, propylene, butylene, vinyl chloride, vinylidene chloride, vinyl acetate, a compound having the general formula



wherein R_1 , R_2 and R_3 each represent a saturated alkyl radical, styrene, α -methylstyrene, vinyltoluene, vinylpyridine, butadiene, pentadiene, chloroprene, isoprene, acrylic acid, methacrylic acid, acrylic ester, methacrylic ester, glycidyl acrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, acrylonitrile and methacrylonitrile.

11. An aqueous coating composition, substantially as described in foregoing Example 1.
12. An aqueous coating composition, substantially as described in foregoing Example 2.
13. An aqueous coating composition, substantially as described in foregoing Example 3.
14. An aqueous coating composition, substantially as described in foregoing Example 4.
15. An aqueous coating composition, substantially as described in foregoing Example 5.
16. An aqueous coating composition, substantially as described in foregoing Example 6.
17. An aqueous coating composition, substantially as described in foregoing Example 7.
18. A process of preparing an aqueous coating composition, substantially as described in foregoing Example 1.
19. A process of preparing an aqueous coating composition, substantially as described in foregoing Example 2.
20. A process of preparing an aqueous coating composition, substantially as described in foregoing Example 3.
21. A process of preparing an aqueous coating composition, substantially as described in foregoing Example 4.
22. A process of preparing an aqueous coating composition, substantially as described in foregoing Example 5.
23. A process of preparing an aqueous coating composition, substantially as described in foregoing Example 6.
24. A process of preparing an aqueous coating composition, substantially as described in foregoing Example 7.
25. An aqueous coating composition whenever prepared by the process of any one of Claims 6 to 10 and 18 to 24.

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