

PATENT SPECIFICATION (11) 1 590 414

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- (21) Application No. 30816/77 (22) Filed 22 Jul. 1977
(31) Convention Application No. 708252 (32) Filed 23 Jul. 1976 in
(33) United States of America (US)
(44) Complete Specification Published 3 Jun. 1981
(51) INT. CL.³ C08F 220/02
(52) Index at Acceptance
C3P 210 220 268 302 322 FE
C3V BC
C3W 209 227
C3Y B230 B240 B241 G100 G140 H660



(54) RADIATION CURABLE COATINGS COMPOSITIONS

(71) We, LORD CORPORATION, a corporation of the State of Pennsylvania, United States of America, located at 1635 West 12th Street, Erie, State of Pennsylvania, United States of America, 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 radiation curable coating and ink compositions. More particularly, the invention relates to radiation curable compositions containing unsaturated addition-polymerizable urethane resin.

5 Increasing concern with energy, environmental protection, and health factors have operated to enhance the potential of radiation curable coatings. In principle, such coatings comprise a polymerizable mixture that can be applied as a thin film to a substrate and polymerized at a rapid rate by exposure to a radiation source such as an electron beam, plasma arc, ultra violet light, and the like. Advantages of radiation curable coatings include a practical method of at least reducing air pollution from volatile vapor loss, rapid cure rates at ambient temperatures, reduced operating costs, the use of heat-sensitive substrates, and improved product performance. 10

15 Among the more notable achievements in the field of radiation curing has been the development of the so-called 100 percent reactive solids systems based on unsaturated addition-polymerizable urethane resin. A characteristic feature of such systems is the substantial absence of conventional inert volatile solvents. Instead, the systems contain reactive diluents which react during curing to become an integral part of the cured coating. Such systems have been widely accepted commercially. While such systems provide high-performance coatings which can be cured at high line speeds, they have also provided a new set of problems for the coatings formulators. 15

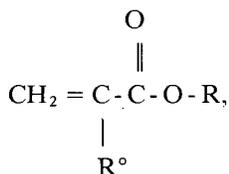
20 While unsaturated addition-polymerizable urethane resins can be prepared by several known reaction routes, the preferred method of preparation for obtaining premium-quality coatings is by capping an isocyanate-functional prepolymer with an appropriate addition-polymerizable monomer having a single isocyanate-reactive active hydrogen group, with the reaction being effected in the presence of a diluent system which is inert with respect to the capping reaction but which is reactive at cure conditions with the unsaturated addition-polymerizable urethane resins. One particularly vexing problem of compositions containing such polymerizable urethane resins, regardless of how the resin is prepared, is the high viscosity of the resin compositions which makes application by conventional industrial techniques difficult, if not impossible. Because the use of conventional inert solvents such as are employed with moisture-cure polyurethanes is undesirable, there has been developed the so-called reactive diluent systems, which generally comprise a mixture of monofunctional and polyfunctional unsaturated addition-polymerizable monomeric compounds which are copolymerizable with the addition-polymerizable urethane resin and thus become part of the cured coating. Certain of the lower molecular weight monomeric diluents such as butyl acrylate are effective in affording clear coating compositions which can be applied by conventional industrial techniques; however, their use is often undesirable because of their relatively high volatility, toxicity, noxiousness and other hazards. While higher molecular weight diluents such as 2-ethyl hexyl acrylate, octyl acrylate, stearyl acrylate and the like are preferred because they do not present the volatility, toxicity and handling problems associated with their lower molecular weight counterparts, they are not without their problems. 30 35 40

Generally, greater amounts of the preferred higher molecular weight diluents are required for effective viscosity reduction. A particularly undesirable phenomenon which is characteristic of diluent systems containing the higher molecular weight reactive monomer diluents is physical instability of the compositions which results in thixotropy or cloudiness leading to eventual separation of the compositions into distinct resin-rich and monomer-rich phases. The adverse phenomena appear common to all diluent systems containing the higher molecular diluents and is most likely to occur with compositions containing higher molecular weight resinous components. Thus, there appears to be a maximum diluent level, which varies with the amount and composition of higher molecular weight diluent present in the diluent system, that the unsaturated addition-polymerizable urethane resins can tolerate before separation takes place. The ability to produce compositions which will remain homogeneous and which can be readily and uniformly applied to substrates and rapidly cured to a dried film is of important commercial importance. It is equally important that harmful emissions to the atmosphere be minimized and that toxic, noxious and other health hazards be at least reduced, if not entirely eliminated.

During the course of an extensive study of the viscosity and thixotropy of radiation curable compositions, particularly such compositions containing unsaturated addition-polymerizable urethane resins, it was discovered that the addition of minor amounts of acrylic acid to radiation curable compositions has the unexpected and inexplicable effects of inhibiting, if not entirely eliminating, physical instability as the reactive diluent level increases, causing an increase in flowability; and affording significant improvements in cured film properties; the effects being out of proportion to the amount of free acrylic acid employed. One measure of this inexplicable effect is that the use of methacrylic acid, among other organic and inorganic acids, does not afford the same benefits as are obtained with acrylic acid. The present invention permits the use of higher molecular weight reactive monomer diluents such as 2-ethyl hexyl acrylate at higher diluent levels than heretofore. As well, the present invention provides compositions having a more manageable viscosity at higher resin content than heretofore possible.

In accordance with the present invention, there is provided a radiation curable composition comprising

- a) at least one unsaturated addition polymerizable urethane resin;
- b) a reactive diluent system comprising at least one unsaturated addition-polymerizable monofunctional monomeric compound selected from the group consisting of esters having the general formula



wherein R is hydrogen or methyl and R^o is an aliphatic or cycloaliphatic group having from 6 to 18 carbon atoms; and

- c) acrylic acid,
- wherein the amount of said unsaturated resin is in the range from 30 to 90 weight percent and the amount of acrylic acid is in the range from 0.1 to 10 weight percent, said weight percents being based on the combined weight of said unsaturated urethane resin and said reactive diluent system.

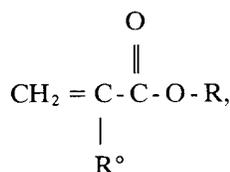
The composition also optionally includes at least one photoinitiator. The photoinitiator, which will generally be employed when curing is effected with a low energy radiation source such as ultraviolet light radiation, will generally be in the range from 0.01 to 30, preferably 0.1 to 15, parts by weight per 100 parts by combined weight of unsaturated addition-polymerizable resin and reactive diluent system.

Preferably, the amount of unsaturated addition-polymerizable urethane resin is in the range from 50 to 75 wt%, based on the combined weight of unsaturated urethane resin and reactive diluent system, whereas the amount of acrylic acid is preferably in the range from 1 to 5 wt%, based on the combined weight of unsaturated urethane resin and reactive diluent system.

The unsaturated addition-polymerizable urethane resins which are suitable for use in the practice of the invention are characterized by the presence of at least one, preferably at least two, polymerizable ethylenically unsaturated group(s) having the structure $\text{>C}=\text{C}<$. The polymerizable ethylenically unsaturated group is preferably a terminal vinyl group having the structure $\text{CH}_2=\text{C}<$. Especially preferred unsaturated addition-polymerizable urethane resins are the acrylyl urethane resins, i.e., urethane resins containing a polymerizable acrylyl, methacrylyl, acrylamide, methacrylamide, and the like moiety in the molecule, characterised

by the presence of at least one, preferably at least two, terminal ethylenically unsaturated group(s) having the structure $\text{CH}_2=\text{C}$. For brevity, the unsaturated addition-polymerizable urethane resins will be referred to hereinafter in this disclosure and the ensuing claims as unsaturated urethane resins. Such unsaturated urethane resins are well-known in the art and do not require further elaboration herein. A particularly preferred class of unsaturated urethane resins are those obtained by fully capping an isocyanate-functional prepolymer with an appropriate unsaturated addition-polymerizable monomer, e.g., 2-hydroxyethyl acrylate, especially such unsaturated urethane resins derived from isocyanate-functional prepolymers obtained by reacting at least one polyisocyanate and at least one polyol at an NCO:OH ratio greater than 2:1.

A further essential ingredient of the coating compositions of this invention comprises a reactive diluent system. Broadly, the reactive diluent comprises at least one unsaturated addition-polymerizable monomer which is copolymerizable with the unsaturated resin upon exposure to radiation. In the general case, such unsaturated addition-polymerizable monomeric diluents can be monofunctional or polyfunctional with combinations of one or more monofunctional reactive diluents and one or more polyfunctional reactive diluents being presently preferred. In the case of the present invention, the reactive diluent systems contain at least one unsaturated addition-polymerizable monofunctional monomeric compound selected from the group consisting of esters having the general formula



wherein R° is hydrogen or methyl and R is an aliphatic or cycloaliphatic, preferably alkyl or cycloalkyl, group having from 6 to 18 preferably 6 to 9 carbon atoms. Representative of such esters are hexyl acrylate, cyclohexyl acrylate, 2-ethyl hexyl acrylate, octyl acrylate, nonyl acrylate, stearyl acrylate, and the corresponding methacrylates. Optionally, the diluent systems can contain one or more of the known reactive monofunctional monomeric diluents in addition to the required acrylic and methacrylic esters having at least 6 carbon atoms in the non-acid moiety of the molecule. In many instances, the reactive diluent systems advantageously will include one or more reactive polyfunctional monomeric diluents. Such optional reactive monofunctional and polyfunctional monomeric diluents include, without limitation thereto, styrene, methyl methacrylate, butyl acrylate, isobutyl acrylate, dicyclopentenyl acrylate, 2-phenoxyethyl acrylate, 2-methoxyethyl acrylate, 2-(N,N-diethylamino)-ethyl acrylate, the corresponding methacrylates, acrylonitrile, methacrylonitrile, methacrylamide, neopentyl glycol diacrylate, ethylene glycol diacrylate, hexylene glycol diacrylate, diethylene glycol diacrylate, trimethylol propane triacrylate, pentaerythritol di-, tri-, or tetra-acrylate, the corresponding methacrylates, vinyl acrylate, vinyl methacrylate and the like. Generally, the reactive diluent system will comprise from 10 to 70, preferably 25 to 50, weight percent, based on total weight of unsaturated urethane resin and reactive diluent system, of the radiation curable compositions of the invention. It is presently preferred that the diluent system contain at least 50 weight percent of acrylic and methacrylic esters having at least 6 carbon atoms in the non-acid moiety of the molecule. Reactive diluent systems are well-known to those skilled in the art of radiation curing and the selection of an appropriate diluent system in any given instance is sufficiently encompassed by such knowledge as to require no further discussion here.

As previously indicated, a photoinitiator system will generally be employed when curing is effected by exposure to low energy radiation sources such as ultra violet light. Any of the known photoinitiators can be used within the concentration ranges previously set forth. Illustrative photoinitiators, without limitation thereto, include benzophenone, benzoin, acetophenone, benzoin methyl ether, Michler's ketone, benzoin butyl ether, xanthone, thioxanthone, propiophenone, fluorenone, carbazole, diethoxyacetophenone, the 2-, 3- and 4-methylacetophenones and methoxyacetophenones, the 2- and 3- chloroxanthenes and chlorothioxanthenes, 2-acetyl-4-methylphenyl acetate, 2,2'-dimethoxy-2-phenylacetophenone, benzaldehyde, fluorene, anthroquinone, triphenylamine, 3- and 4-allylacetophenone, p-diacetylbenzene, 3-chloro-2-nonylxanthone, and the like, and mixtures thereof.

The invention compositions can also include pigments, fillers, wetting agents, flattening agents, and other additives typically present in coating compositions, with the exception of inert volatile solvents or diluents. These are well-known to those skilled in the art and do not require further elaboration herein. Also well-known are the concentrations at which such additives are used.

The radiation curable compositions of the present invention have an increased flowability and fluidity, and exhibit a markedly improved viscosity stability, i.e., a substantially reduced tendency to phasing, at any diluent level in comparisons to compositions which do not contain any free acrylic acid. Thus, the invention compositions can be applied to wood, metal fabric and plastic substrates in a more economical and efficient manner to afford a smoother and more uniform film. In addition, the modulus and ultimate film properties of cured films derived from the compositions of this invention are noticeably better than the corresponding properties of cured films derived from radiation curable compositions which do not contain any free acrylic acid.

The improved coating compositions of this invention can be applied and cured by any of the conventional known methods. Application can be by roll coating, curtain coating, airless spray, dipping or by any other procedure. The cure can be effected by exposure to any high energy source, such as ionizing radiation, or low energy source, such as ultraviolet light radiation. The equipment utilized for curing, as well as the appropriate time for curing, and the conditions under which the curing is effected are well-known to those skilled in the art of radiation curing and do not require further elaboration herein.

The invention is illustrated in greater detail by the following Examples, but these examples are not to be construed as limiting the present invention. All parts, percentages and the like are in parts by weight, unless otherwise indicated.

EXAMPLE I

An unsaturated acrylyl urethane resin composition is prepared by reacting methylenebis(cyclohexyl isocyanate) and polycaprolactone triol having an average molecular weight of about 900 in the presence of 2-ethyl hexyl acrylate and stannous octoate at an NCO:OH mol ratio of 2.5:1. The reaction is terminated at an end point corresponding to 100 percent depletion of hydroxyl value, as determined by isocyanate titration. When the end point is reached there is immediately added to the isocyanate-functional prepolymer-containing reaction mixture sufficient 2-hydroxyethyl acrylate to react with the free isocyanate functions of the prepolymer. Radiation curable compositions are prepared at several diluent (2-ethyl hexyl acrylate) levels with the following results:

Composition	A	B	C
Unsaturated urethane resin	70	65	60
2-ethyl hexyl acrylate	30	35	40
Time to separation ^a	2 mos	30 days	24 hrs
Viscosity, cps	27,500	12,000	8,400

a = separation of composition into distinct resin-rich and monomerrich phases

The data are demonstrative of the physical instability of radiation curable compositions comprising unsaturated urethane resin and reactive diluent system containing acylic and methacrylic acid esters having at least 6 carbon atoms in the non-acid moiety of the ester molecule.

EXAMPLE II

Composition C of Example I is heated at 58° for 30 minutes with constant stirring. The resin phase is redispersed into the diluent phase to form a homogeneous system. The composition is now separated into four separate portions. After standing for 24 hours, phasing has occurred in each portion. To three portions, there is added acrylic acid at 1, 3 and 5 percent levels. In each instance, the addition of acrylic acid results in resolubilization of the separated unsaturated urethane. Also in each instance, the addition of acrylic acid significantly reduces the viscosity and thixotropy of the composition to marked increase the flowability of the compositions. The results are tabulated below:

<i>Composition</i>	<i>C</i>	<i>C-1</i>	<i>C-2</i>	<i>C-3</i>
Unsaturated urethane	60	60	60	60
2-ethyl hexyl acrylate	40	40	40	40
Acrylic acid, weight percent	0	1	3	5
Viscosity, cps	8,400	5,600	3,800	3,000
Time to separation	24 hrs	2 mos	>2 mos	>2 mos

To each of compositions C, C-1, C-2 and C-3 is added an effective amount of a benzoin-type photoinitiator. The compositions are then coated onto aluminum panels and cured by exposure to ultraviolet radiation (200 watts/in.) at a line speed of 50 feet per minute for three passes. Compositions C-1, C-2 and C-3 are significantly less viscous and are more easily and uniformly applied to the substrate than is composition C, which contains no acrylic acid. In the case of composition C, phasing again occurs within 24 hours; no discernible phasing is observed with any of compositions C-1, C-2 and C-3 after two months storage. The properties of the cured films are tabulated below:

<i>Composition</i>	<i>C</i>	<i>C-1</i>	<i>C-2</i>	<i>C-3</i>
Tensile strength, psi	3816	3065	3570	4480
Youngs modulus, psi	77000	75000	92000	118000

The data demonstrate the unexpected effects afforded by the present invention in reducing viscosity and thixotropy of radiation curable compositions, improving viscosity stability, and significantly improving cured film properties.

EXAMPLE III

Employing the unsaturated acrylyl urethane resin composition of Example I, the following formulation is prepared:

Unsaturated urethane	60
2-ethyl hexyl acrylate	40

The formulation is divided into several portions. After 24 hours at room temperature, phase separation has occurred with each portion. There is added to individual portions acrylic acid, methacrylic acid, acetic acid, p-toluene sulfonic acid and hydrochloric acid, respectively, at a level of 3 weight percent, based on total weight of urethane resin and diluent system. Acetic acid, p-toluene sulfonic acid and hydrochloric acid do not resolubilize the resin phase. The resin phase is resolubilized by the addition of methacrylic acid but phasing again occurs within 24 hours. The resin phase is resolubilized by the addition of acrylic acid and substantially no phasing has occurred after 2 months storage. The data demonstrates the completely unexpected results which are obtained by the addition of minor amounts of acrylic acid to radiation curable compositions.

Attention is also directed to our co-pending British Patent Application No. 30815/77 (Serial No. 1590413).

WHAT WE CLAIM IS:-

1. A coating composition comprising
 - a) at least one unsaturated addition polymerizable urethane resin;
 - b) a reactive diluent system containing at least one unsaturated addition-polymerizable monofunctional monomeric compound selected from the group consisting of esters having the general formula



wherein R^o is hydrogen or methyl and R is an aliphatic or cycloaliphatic group having from 6 to 18 carbon atoms; and

c) acrylic acid

wherein the amount of said unsaturated resin is in the range from 30 to 90 weight percent and the amount of acrylic acid is in the range from 0.1 to 10 weight percent, said weight percents being based on the combined weight of said unsaturated urethane resin and said reactive diluent system.

- 5 2. A composition according to Claim 1, wherein said unsaturated urethane resin is characterised by the presence of at least two terminal ethylenically unsaturated groups having the structure $\text{CH}_2 = \text{C} \begin{array}{l} \diagup \\ \diagdown \end{array}$.
- 10 3. A composition according to Claim 1 or Claim 2, containing from 0.01 to 30 parts by weight, per 100 parts by combined weight of said unsaturated urethane resin and said reactive diluent system, of at least one photoinitiator compound.
- 15 4. A composition according to any one of Claims 1 to 3, wherein R is an alkyl or cycloalkyl group having from 6 to 18 carbon atoms.
5. A composition according to any one of Claims 1 to 3, wherein R is an alkyl or cycloalkyl group having from 6 to 9 carbon atoms.
- 15 6. A composition according to any one of Claims 1 to 5, wherein the amount of said unsaturated urethane resin is in the range of 50 to 75 weight percent.
- 20 7. A composition according to any preceding Claim, wherein said unsaturated urethane resin is derived from an isocyanate-functional prepolymer obtained by reacting a polyol having at least two hydroxyl groups and a polyisocyanate having at least two isocyanate groups at an NCO:OH ratio greater than 2:1.
- 20 8. A composition according to any one of Claims 2, 3, 6 and 7 wherein R° is hydrogen and R is 2-ethyl hexyl.
- 25 9. A composition according to any preceding Claim, wherein the amount of acrylic acid is in the range from 1 to 5 percent.
- 25 10. A coating composition as claimed in Claim 1, substantially as hereinbefore described with reference to the Examples.
- 30 11. A method of coating a substrate comprising applying to the substrate a coating composition as claimed in Claim 3, and exposing said coated substrate to ultraviolet radiation for a time sufficient to cure said coating.
- 30 12. A substrate coated by a method as claimed in Claim 11.

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