

Coating composition

The present invention relates to a coating composition, in particular coating compositions which contain alkyd resins, as used for example in solvent-based paints.

- Alkyd resins are polyesters derived from polyhydric alcohols and acids, which are normally long alkyl-chain fatty acids, often derived from naturally occurring oils and alcohols such as glycerol. They are widely used in many coatings applications, e.g. as wood coatings or industrial paints. It is common to modify alkyd resins with other compounds, e.g. phenolic resins for increasing hardness and solvent resistance, epoxy resins for improved adhesion and silicones for improved heat resistance and resistance to thermal shock. A more detailed description on modifiers for alkyds can be found in 'Encyclopaedia of Polymer Science and Technology' 1st Edition, Volume 1, Page 663 (Wiley 1964). Acrylic compounds are also used as alkyd modifiers, for example to improve durability, enhance colour and colour retention, improve gloss and gloss retention and to reduce drying time of the resultant coatings. In order to achieve modification the modifying resin must be miscible in alkyd resins and soluble in the carrier system, e.g. white spirit or xylene. Amongst thermoplastic acrylic resins, low molecular weight linear polyisobutyl methacrylate polymer resin is known to have good solubility in white spirit and miscibility with alkyds and is preferred for commercial use compared to other thermoplastic acrylic resins for alkyd modifier applications.
- It is an object of the present invention to provide alternative resins which are suitable for use in alkyd resin systems.

- According to the invention we provide a coating composition comprising a solvent, an alkyd resin, and a vinylic star polymer comprising the residue of a polyfunctional thiol compound having at least three functional thiol groups and at least three vinylic chains each comprising the residue of at least one monofunctional vinylically unsaturated monomer such as an alkyl acrylate or alkyl (alk)acrylate.

In a second aspect of the invention, we provide the use of a vinylic star polymer comprising the residue of a polyfunctional thiol compound having at least three functional thiol groups and at least three vinylic chains each comprising the residue of at least one

monofunctional vinylically unsaturated monomer such as an alkyl acrylate or alkyl (alk)acrylate, as a component of a coating composition based on an alkyd resin system.

In a third aspect of the invention, we provide a method of manufacturing a coating composition comprising the steps of forming a solution or dispersion of an alkyd resin in a solvent and then adding a vinylic star polymer comprising the residue of a polyfunctional thiol compound having at least three functional thiol groups and at least three vinylic chains comprising the residue of at least one monofunctional vinylically unsaturated monomer such as an alkyl acrylate or alkyl (alk)acrylate and mixing the resulting mixture to effect solution of the acrylic polymer.

10 Polymers having the composition described are known as "star" polymers because their star-shaped morphology given by the at least three acrylic chains arranged around a thiol-derived hub portion. Star polymers are described in WO-A-96/37520. However, their compatibility with alkyd resins and therefore their utility as modifiers for alkyd resin systems has not previously been described and is unexpected. The star polymers
15 described have improved solubility in the solvents used for processing alkyds, such as white spirit, and also provide improved miscibility with alkyd resins compared with some of the known acrylic-type alkyd resin modifying compounds. Such features can provide performance benefits, e.g. coatings formulations which have lower application viscosity or which have higher loadings of acrylic modifier in the alkyd resin.

20 The vinylic polymer comprises a hub portion derived from a polyfunctional thiol compound. The hub portion comprises a core group X and at least three linking groups Y-S. X is preferably at least part of the residue of a tri- to hexa-functional alcohol such as glycerol, sorbitol, pentaerythritol, dipentaerythritol, tripentaerythritol, trimethyloethane, trimethylolpropane, pentahydroxypentane, triquinoyl and inositol. Preferably the linking
25 group, Y, is alkylate, particularly C₂₋₁₀ alkylate and especially C₂₋₆ alkylate.

The hub portion is preferably the residue of a tri- to octa-functional and particularly tri- to hexa-functional mercaptan. Such a mercaptan may be an ester formed from an alcohol and a thio-C₂₋₁₀ alkanolic acid, particularly thio-C₂₋₆ alkanolic acid. Examples of suitable
30 acids are 2-mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 4-mercaptobutyric acid, 5-mercaptopentanoic acid, 6-mercaptohexanoic acid and

10-mercaptodecanoic acid. Preferably the acid is 2-mercaptoacetic acid or 3-mercaptopropionic acid.

Examples of suitable polyfunctional mercaptans include trimethylolethane tris
5 (3-mercaptopropionate), pentaerythritol tetra(3-mercaptopropionate), pentaerythritol
tetrathioglycolate, trimethylolethane trithioglycolate, trimethylolpropane
tris(3-mercaptopropionate), trimethylolpropane trithioglycolate, pentaerythritol
tetrathiolactate, pentaerythritol tetrathiobutyrate, dipentaerythritol
hexa(3-mercaptopropionate), dipentaerythritol hexathioglycolate, tripentaerythritol
10 octa(3-mercaptopropionate), tripentaerythritol octathioglycolate.

Mixed polymer systems may be manufactured by selecting more than one type of hub
compound, e.g. by polymerising the acrylic monomers to form the chains in the presence
of more than one polyfunctional thiol compound or of one or more polyfunctional thiol
compounds and one or more monofunctional or bifunctional thiol compounds. Suitable
15 monofunctional thiol compounds include propyl mercaptan, butyl mercaptan, hexyl
mercaptan, octyl mercaptan, dodecyl mercaptan, thioglycolic acid, mercaptopropionic
acid, 2-ethyl hexyl thioglycollate, mercaptoethanol, mercaptoundecanoic acid, thiolactic
acid and thiobutyric acid. Suitable bifunctional compounds include glycol
dimercaptoacetate, polyethyleneglycol di(3-mercaptopropionates), ethylene
20 bis(3-mercaptopropionate), polyethyleneglycol dimercaptoacetates.

Mixtures of star polymers may be formed from such mixed polymerisations or formed
simply by mixing together more than one type of pre-formed star polymer resin or one or
more preformed star polymer resins with one or more linear vinylic polymers. Such
mixtures may be used very effectively in the coatings of the present invention. The vinylic
25 chains of each vinylic star polymer or linear polymer may be formed from a vinylic
monomer composition which is either the same as or different from each other vinylic star
or linear polymer in the mixture.

The vinylic polymer chain is formed from at least one mono-olefinically unsaturated
monomer which may be selected from any of the mono-olefinically unsaturated monomers
30 known in the art.

Suitable monofunctional vinylically unsaturated monomers may be selected from the

- acrylic type monomers such as acrylic, methacrylic and chloroacrylic acids (i.e. $\text{CH}_2=\text{CHCO.OH}$), acrylamide and methacrylamide, acrylonitrile and methacrylonitrile, alkoxyalkyl acrylamides and methacrylamides, e.g. butoxymethyl acrylamide and methoxymethyl methacrylamide, hydroxyalkyl acrylamides and methacrylamides, e.g.
- 5 N-methylol acrylamide and methacrylamide, the metal acrylates and methacrylates, and the esters of acrylic, methacrylic and chloroacrylic acids with alcohols and phenols; the vinyl aromatic compounds, e.g. styrene and substituted derivatives thereof such as the halogenated derivatives thereof and vinyl toluene; the vinyl esters, e.g. vinyl acetate, and vinyl pyrrolidone.
- 10 Preferred monofunctional vinylically unsaturated monomers include acrylic or methacrylic acid and esters thereof having the formula $\text{CH}_2=\text{C(R)CO.OR}^2$ where R is H, methyl or butyl, especially methyl, iso-butyl and n-butyl, and R^2 is optionally substituted hydrocarbyl (e.g. optionally halo or hydroxy substituted hydrocarbyl) and in particular is a C_{1-8} alkyl, a
- 15 C_{6-10} cycloalkyl or a C_{6-10} aryl group. Specific examples of such monomers include the non-substituted esters of acrylic and methacrylic acids such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate, benzyl methacrylate, phenyl methacrylate and isobornyl acrylate and the substituted esters of
- 20 acrylic and methacrylic acids such as hydroxyethyl methacrylate and hydroxypropyl methacrylate. More particularly, the monofunctional vinylically unsaturated monomer is a C_{1-8} alkyl ester of methacrylic acid. Methyl methacrylate, iso-butyl methacrylate and n-butyl methacrylate are especially preferred monomers.
- 25 The at least three vinylic polymer chains may be formed from a mixture of monofunctional vinylically unsaturated monomers, for example a mixture of the monomers described above.
- Each vinylic polymer chain may typically be formed from 10 to 1500, for example 25 to
- 30 1500, monomer units and preferably from 20 to 800 and particularly from 30 to 800 such units. When a mixture of monomer units is used, the copolymer may be a block or random copolymer of such units. Preferably the copolymer is a random copolymer as produced through conventional free radical polymerisation.
- 35 Each vinylic polymer chain may be formed using the polythiol as a chain transfer agent

through the polymerisation processes conventionally employed in the preparation of poly(methacrylates). Such processes include bulk, solution, emulsion and suspension polymerisation of the acrylic polymer chains. Preferred processes are suspension polymerisation and bulk polymerisation processes.

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When used, the suspension polymerisation process is typically conducted, at least initially, in the range 10 to 120°C, preferably in the range 50 to 110 °C, particularly in the range 70 to 110°C and especially about 75 - 100°C. Suitable bulk polymerisation processes are conducted at temperatures in the range 70 - 130 °C.

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Preferred processes are bulk, solution, emulsion and suspension polymerisation processes which employ a free radical initiator.

Suitable free radical initiators include organic peroxides, hydroperoxides, persulphates and azo compounds. Examples of such initiators are methyl ethyl ketone peroxide, benzoyl peroxide, cumene hydroperoxide, potassium persulphate, azobisisobutyronitrile (AIBN), lauroyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy) hexane, diethyl peroxide, dipropyl peroxide, dilauryl peroxide, dioleoyl peroxide, distearyl peroxide, di(tertiary butyl) peroxide, di(tertiary amyl) peroxide, tertiary butyl hydroperoxide, tertiary amyl hydroperoxide, acetyl peroxide, propionyl peroxide, lauroyl peroxide, stearoyl peroxide, malonyl peroxide, succinyl peroxide, phthaloyl peroxide, acetyl benzoyl peroxide, propionyl benzoyl peroxide, ascaridole, ammonium persulphate, sodium persulphate, sodium percarbonate, potassium percarbonate, sodium perborate, potassium perborate, sodium perphosphate, potassium perphosphate, tetralin hydroperoxide, tertiary butyl diperphthalate, tertiary butyl perbenzoate, 2,4-dichlorobenzoyl peroxide, urea peroxide, caprylyl peroxide, p-chlorobenzoyl peroxide, 2,2-bis(tertiary butyl peroxy) butane, hydroxyheptyl peroxide.

It is preferred that the ratio of initiator to polythiol is less than 6:1 on a molar basis, for example in the range 6:1 to 1:6, and particularly preferred that the ratio of initiator to polythiol is less than 3:1 on a molar basis, for example in the range 3:1 to 1:3. It is preferred that the molar ratio of polythiol to monomer is in the range 1:10 to 1:3000 and particularly preferred that the molar ratio of polythiol to monomer is in the range 1:25 to 1:1500.

When the polymerisation process is an emulsion polymerisation process the emulsifier may be chosen from those commonly used in the art. Such emulsifiers include fatty acid soaps, rosin soaps, sodium lauryl sulphate, polyethoxy alkylated phenols, dioctyl sodium sulphosuccinate and dihexyl sodium sulphosuccinate.

When the polymerisation process requires a solvent, such a solvent may be chosen from those commonly used in the art, for example benzene, toluene, xylene, aliphatic esters, aliphatic ethers, aliphatic ketones and aliphatic alcohols.

10 The molecular weight of the polymer is controlled by the mercaptan used to form the hub of the star polymer. The molecular weight (Mw) is normally in the range 4,000 - 80,000 Daltons, preferably 8,000 - 60,000 D.

The acrylic polymer may be present in the coating composition at a concentration in the range 1 - 80 wt%, preferably 1 - 60 wt %. The ratio of acrylic polymer to alkyd resin typically falls within the range 1:8 - 1:2, by weight.

15 The coating composition typically contains other ingredients in addition to the alkyd resin, acrylic resin and solvent. These other components are well known in the art of solvent-based coatings formulation. Typically these components include a drying component, for example salts of cobalt, lead, zinc, zirconium or calcium normally present at a concentration of between 0.1 and 1.0 % by weight of the alkyd resin component of the coating. The coating may also contain pigments and opacifiers such as titanium dioxide for example. When present, the pigment may be used typically at a concentration to give a ratio of pigment to binder of between 1:20 and 1.2 :1 by weight.

25 Typically the solvents used in such coatings are mineral spirits. The total solids level (i.e. all non-volatile components) in mineral spirits is typically 40 - 50 wt %.

The coating composition may also contain other components which are not mentioned above which may be known in the art of formulating solvent-based coatings.

The invention will be further described in the following examples.

Example 1 Preparation of mixed star polymer

4.5g of suspending agent (Natrosol HEC 250LR obtainable from Aqualon Inc, a division of Hercules Inc) were dissolved in 2.0l of deionised water contained in a 5 litre flask by heating in the range of 40 to 50 °C for 30 minutes whilst sparging with nitrogen and gentle stirring. A monomer phase premix was formed from 500g of isobutyl methacrylate and 1.75 phm (parts per hundred parts of monomer) each of dodecyl mercaptan (DDM), trimethylolpropane tris(3-mercaptopropionate) (TRIMP) and pentaerithritol tetra(3-mercaptopropionate) (PETMP). 5.0 g of AIBN initiator was washed into the deionised water using the premix whilst maintaining a nitrogen blanket and a water cooled reflux. The temperature was raised to 76 °C and the mixture was stirred at a speed of 1500 rpm. The polymerisation proceeded through to almost complete conversion of monomer to polymer whereupon the cooling water to the condenser was stopped. The polymer was then heat treated by raising the temperature to within the range from 90 to 95 °C for 30 min to complete the polymerisation and to drive off unreacted monomer. After heat treating the polymer, the nitrogen blanket was removed and the polymer was air cooled. The cooled polymer was then filtered, washed in deionised water and dried.

The polymer molecular weight was measured using gel permeation chromatography (GPC) using chloroform as solvent and polymethyl methacrylate standards. The results are shown in Table 1. The dissolution of the polymer in white spirit and viscosity of the resulting solution was assessed and the results are given in Table 2. The dissolution of a commercial thermoplastic solid polyisobutyl methacrylate alkyd modifier resin (designated CR in the following tables) having a measured molecular weight of $M_w = 9550$ and $M_n = 4750$ was also measured and was used to show the performance of a known acrylic alkyd modifier in comparison with the polymers of Examples 1 and 2.

Example 2 Preparation of medium molecular weight star polymer

The method of Example 1 was followed except that the DDM was omitted.

Example 3 (Comparative) Preparation of linear polymer

The method of Example 1 was followed except that the only mercaptan used was DDM at 1.75 phm.

The results show that the polymers described in Examples 1 & 2 are soluble in white spirit and produce relatively low viscosity solutions at up to 30% w/w concentration. In contrast, the linear control (Example 3) can not be fully dissolved in white spirit.

- It can be also be seen that, for a given solution viscosity, the resins of Examples 1 and 2 have the additional benefit of being capable of being dissolved to a higher solids level (e.g. in order to achieve lower solvent use) than the polyisobutyl methacrylate resin.

Table 1

Example	Mercaptan(s)	Mw	Mn	d
1	1.75 phm each of DDM, TRIMP, and PETMP	9450	5250	1.79
2	1.75 phm each of TRIMP and PETMP	14100	8700	1.63
3 (comp)	1.75 phm DDM	15500	7650	2.03
CR		9550	4750	2.00

Table 2

	Brookfield Viscosity (cP) at room temp		
Polymer	10% w/w	20%w/w	30%w/w
Example 1	2.5	5	14.5
Example 2	4.5	8	23.5
Example 3	Not completely soluble		
CR	9	23	152.5

Example 4 - miscibility with alkyd resins

- 10 1.0 g of each of the polymers made in Examples 1 - 3 and the polyisobutyl methacrylate resin was added to 9.0 g of each of a variety of commercial alkyd resin solutions. Each sample was then placed in a water bath at 90 °C and rotated occasionally for 6 hours. After cooling to room temperature, the degree of solubility was assessed visually and classified as follows:
- 15 A: Clear solutions - no insoluble particles observed.
 B: Clear solutions - few insolubles.
 C: Cloudy solution - small amount of undissolved resin settling out.
 D: Cloudy solution - large amount of undissolved resin settling out.
- The results are shown in Table 3.

Table 3

Alkyd Type	Alkyd commercial grade	Solvent Type	Acid Value	Polymer			
				CR	1	2	3
Long Soya Oil	Wresinol AS621	65% in white spirit	10 max	D	B	A	C
Long Linseed Oil	Wresinol AL668	65% in white spirit	10 max	A	A	A	B
Medium Soya Oil	Wresinol AS483	50% in white spirit	14 max	B	A	C	C
Short Soya Oil	Blagden Chemicals K674-50x	50% in xylene	30 max	D	B	D	D
Long Soya Oil	Blagden Chemicals 1426	65% in white spirit	10 max	A	A	B	C
Medium Linseed Oil	Blagden Chemicals 830-40	40% in white spirit	10 max	B	A	B	C

These results show that the star and part-star polymers in Examples 1 and 2 have miscibilities with the alkyd resins used which are at least as good as the known polyisobutyl methacrylate alkyd modifier. The linear polymer of Example 3 is generally

5 less miscible with these alkyds.

**Claims**

1. A coating composition comprising a solvent, an alkyd resin, and a vinylic star polymer comprising the residue of a polyfunctional thiol compound having at least three functional thiol groups and at least three vinylic chains each comprising the residue of at least one
5 monofunctional vinylically unsaturated monomer.
2. A coating composition as claimed in claim 1, wherein said polyfunctional thiol compound comprises a hub portion having a core group X and at least three linking groups Y-S, wherein X is at least part of the residue of a tri- to hexa-functional alcohol and the linking group Y is an alkylate.
- 10 3. A coating composition as claimed in claim 2, wherein said multifunctional alcohol is selected from glycerol, sorbitol, pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylolethane, trimethylolpropane, pentahydroxypentane, triquinoyl and inositol.
4. A coating composition as claimed in claim 2, wherein the linking group Y is C₂₋₁₀
alkylate.
- 15 5. A coating composition as claimed in any preceding claim, wherein said vinylic star polymer is a mixture of more than one vinylic star polymer each comprising the residue of a different polyfunctional thiol compound having at least three functional thiol groups and at least three vinylic chains, wherein the vinylic chains of each vinylic star polymer are formed from a vinylic monomer composition which is either the same as or different from
20 each other vinylic star polymer.
6. A coating composition as claimed in any preceding claim, wherein said coating composition additionally contains a linear vinylic polymer comprising residues of a vinylic monomer composition which is either the same as or different from the vinylic monomer composition from which the vinylic chains of the or each vinylic star polymer are formed.
- 25 7. A coating composition as claimed in claim 6, wherein said linear vinylic polymer comprises the residue of at least one thiol compound having one or two functional thiol groups.



8. A coating composition as claimed in any preceding claim, wherein said at least one monofunctional vinylically unsaturated monomer is selected from the group of compounds comprising acrylic type monomers, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, alkoxyalkyl acrylamides and methacrylamides, hydroxyalkyl
5 acrylamides and methacrylamides, metal acrylates and methacrylates, esters of acrylic, methacrylic and chloroacrylic acids with alcohols and phenols; vinyl aromatic compounds and substituted derivatives thereof and vinyl esters or mixtures of the afore-mentioned compounds.
9. A coating composition as claimed in claim 8, wherein said at least one monofunctional
10 vinylically unsaturated monomer is selected from acrylic or methacrylic acid and esters thereof having the formula $\text{CH}_2=\text{C}(\text{R})\text{CO.OR}^2$ where R is H, methyl or butyl, and R^2 is optionally substituted C_{1-8} alkyl, a C_{6-10} cycloalkyl or a C_{6-10} aryl group.
10. A coating composition as claimed in claim 9, wherein said at least one
15 monofunctional vinylically unsaturated monomer is a mixture of at least two acrylic or methacrylic acid esters.
11. The use of a vinylic star polymer comprising the residue of a polyfunctional thiol compound having at least three functional thiol groups and at least three vinylic chains each comprising the residue of at least one monofunctional vinylically unsaturated monomer, as a component of a coating composition based on an alkyd resin system.
- 20 12. A method of manufacturing a coating composition comprising the steps of forming a solution or dispersion of an alkyd resin in a solvent and then adding a vinylic star polymer comprising the residue of a polyfunctional thiol compound having at least three functional thiol groups and at least three vinylic chains comprising the residue of at least one monofunctional vinylically unsaturated monomer and mixing the resulting mixture,
25 optionally with further components selected from drying compounds, pigments, opacifiers, to effect solution of the acrylic polymer.