
(12) **UK Patent Application** (19) **GB** (11) **2 144 753 A**

(43) Application published **13 Mar 1985**

(21) Application No **8414916**

(22) Date of filing **12 Jun 1984**

(30) Priority data

(31) **8316601** (32) **17 Jun 1983** (33) **GB**

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(51) INT CL⁴

C08L 33/00 63/00 67/00 // C09D 3/48

(52) Domestic classification

**C3M 110 114 120 123C 124 125 201 F
U1S 1391 3009 3017 3030 3035 3037 3042 C3M**

(56) Documents cited

EP A1 0010888

(58) Field of search

**C3B
C3M**

(54) **Ambient temperature curing coating compositions**

(57) A two-component coating composition (paint) for use in motor-car refinishing which can be cured at ambient temperature and having low sensitivity to water and humidity comprises a first component including a polymer containing epoxide groupings, a second component including one or more acrylic resins containing amino or amide or amide groupings and, optionally, carboxylic acid groupings, and one or more polymers containing thiol groupings: and, optionally, carboxylic acid groupings.

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SPECIFICATION

Coating composition

- 5 The present invention relates to a coating composition. In particular the present invention relates to an organic solvent based coating composition, though comparatively minor modification of the resins' chemical structure would facilitate the formulation of water reducible coatings. The composition is capable of being cured at ambient temperatures and above to form a coating for a substrate of metal, wood or plastic and having good adhesion and a balanced combination of desired properties. In particular, properties such as gloss, hardness, adhesion, impact resistance, gloss retention and general durability, as well as resistance to such agents as atmospheric acids, petrol and grease.

INTRODUCTION – DEFINITION OF TERMS

1. *Acrylic resin*

- 15 This term is used to describe a polymer which is usually made by co-reacting α , β ethylenically unsaturated compounds of which a significant proportion are the esters of α , β ethylenically unsaturated carboxylic acids.

Examples of suitable monomers are alkyl acrylates such as ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate; and alkyl methacrylates, such as methyl methacrylate, ethyl methacrylate and butyl methacrylate.

- 20 Other suitable monomers can include other reactive groups such as epoxide, amino etc., for example glycidyl esters such as glycidyl methacrylate. Other suitable monomers include vinyl aromatic compounds such as styrene (or vinyl toluene) and vinyl derivatives, such as vinyl acetate or vinyl propionate. It is in addition possible to modify properties of the resin by the use of monomers such as acrylonitrile and/or methacrylonitrile.

- 25

2. *Acrylic adduct*

This term is used to describe a resin which is made by reacting an acrylic resin with a further component which may or may not of itself constitute a polymer.

- 30 3. *Alkyd resin, polyester resin, oil modified polyester resin*

These terms are used to described polymers made by the esterification of one or more polyhydric alcohols with one or more polyfunctional carboxylic acids. A proportion of one or more monobasic acids and/or (in rare cases) monohydric alcohols may also be included. Examples of suitable polyhydric alcohols are ethylene glycol, trimethylol propane, neopentyl glycol, propylene glycol.

- 35 Examples of polyfunctional carboxylic acids are phthalic anhydride, isophthalic acid, terephthalic acid, succinic acid, adipic acid, trimellitic anhydride.

Examples of suitable monofunctional carboxylic acids are benzoic acid, *p* tert butyl benzoic acid, lauric acid and one of the tertiary carboxylic acids. (An example of the latter material is marketed by the Shell Company under the name Versatic Acid. Versatic is a registered trade mark).

- 40 An alternative to using the acid itself is to use a derivative such as the glycidyl ester. This is also marketed by the Shell Company under the name Cardura E. Cardura is a registered trade mark).

- 45 It has been widely recognised that there is a need for coating compositions which are either non-polluting or, failing this, pollute the atmosphere to a minimal degree, but at the same time offer effective economy in the use of energy. In order to do this, such coatings need to dry at ambient temperatures and/or cure quickly at comparatively low stoving schedules. Such compositions would be particularly desirable in the refinish market (motorcar repair paint), although they would have application in other fields, for example:- motorcar finishes, wood finishes and general purpose industrial and marine finishes.

- 50 Considerable effort has been directed towards two component finishes where the two components react chemically after application to give durable paint films. A particularly suitable combination is one in which one of the components is a hydroxyl-bearing resin and the second component is a polymer containing isocyanate groupings. Paints made from these chemicals offer excellent performance but suffer from the toxicological disadvantage that the isocyanate component contains a proportion of the isocyanate monomer. Further, the proportion of free monomer can increase during storage of the prepolymer because of its partial decomposition.

- 55 More recently work has been directed towards two component finishes in which one component is a resin containing amine (or amide) groupings which is reacted with a second component containing epoxide groupings. These latter compositions have been the subject of Patents, for example US Patent 4,294,939 issued first October 13, 1981 to Eiji Taniguchi et al and assigned to Toray Industries, Tokyo, Japan.

- 60 Whilst products of this type meet many of the basic requirements enumerated above, there are practical difficulties in achieving fully satisfactory results. For example, it is widely known and accepted that for the highly durable finishes required for motorcars, the preferred major constituent is an acrylic resin. There are practical and commercial difficulties in obtaining acrylic resins containing primary or secondary amino groups. As a result, the resins used in epoxy/amine compositions tend to be based on tertiary amino groups which react more slowly, the chemical reaction proceeding, it is believed, *via* quaternary ammonium groupings. Coatings of this type are water sensitive, at least during the early stages of the curing reaction,
- 65

and can often remain so.

To produce commercially practical finishes, therefore, it is necessary to minimise the number of tertiary amine groups which results in the coating being relatively low in degree of chemical cross-linking.

5 Finishes based on these resin combinations, therefore, tend at least when dried at ambient temperatures, to be very sensitive to humid or wet conditions for a period of up to several days and have relatively poor hardness/flexibility properties even when fully dried. 5

10 More recently work has been carried out in the paint resin industry to modify the amino bearing acrylic resin so as to include a proportion of carboxyl groups. This latter group is also known to react with the epoxy compound at ambient temperatures but without generating water sensitivity. The disadvantage of this reaction lies in its slowness at ambient temperatures. The result is that finishes do not achieve their optimum properties for several days at least. 10

15 Thus there is a real need to accelerate the chemical reaction which takes place between the epoxide component and the amino/carboxylic acid component after the finish has been applied. This can be achieved by the addition of a mercapto compound, such as ethyl mercaptan. This technique is used in analytical methods to convert primary amines, which are difficult to separate by chromatographic methods, into amide derivatives which can be efficiently separated by chromatography. 15

20 It is also well established that mercapto compounds themselves can react with epoxide bearing materials. It is normally necessary that small proportions of amino compounds are present for this reaction to take place. The speed of reaction between the mercaptan with the epoxide is very much faster at comparatively low temperatures than that involving amino groups. Some well-known chemical adhesives make use this chemistry. 20

25 We have now found that the incorporation into coating compositions of certain thiol-containing resins can provide fast air drying chemically reacted finishes which utilise the chemical reaction between an epoxide adduct as one component and a mixture of resins as the second component. This mixture of resins is tailored so that some portions contain amino or amide groups, with or without, carboxylic acid groups and some contain the thiol groups, again with or without carboxylic acid groups. According to the present invention we provide a three-component coating composition comprising a first component including a polymer containing epoxide grouping, a second component including one or more acrylic resins containing amino or amide groupings and, optionally, carboxylic acid groupings, and a third component including one or more polymers containing thiol groupings; and, optionally, carboxylic acid groupings. 30

35 All three components must be mixed together prior to application of the composition to a substrate. The three components can be stored separately, or, preferably, components 2 and 3 may be combined as one component. The basic composition, therefore, generally consists of:- 35

Component 1

40 A polymer containing epoxide groupings. The composition of such that it offered good compatibility with component 2. Its structure is preferably either a mainly aliphatic di-epoxide or an acrylic polymer containing epoxide groupings. The remaining constituents are largely of a solvent nature, effectively to balance the application properties of the total finish. 40

Component 2

45 One or more substances containing amine and/or amide groupings. These substances may be polymeric in nature, e.g. an acrylic resin or a polyamide; or may be specific compounds containing these groupings. An acrylic resin must be formulated to have the correct balance of properties in terms of hardness, durability, gloss etc and contain amine and/or amide groupings. Amine groupings can be primary, secondary or tertiary, though for practical considerations the latter are normally used. This item, whether a polymer or a conventional compound may additionally contain carboxylic acid groupings. 50

Component 3

55 One or more substances containing thiol (mercaptan) groupings. Although in principle, low molecular weight compounds could be used, their particularly unattractive odour and adverse toxicology normally precludes their use. In practice, therefore, this item is normally a polymer containing mercaptan groupings formulated to have a proper balance of properties in terms of hardness, durability and gloss. From a wide range of possible polymers three are preferred:- 55

- i) An acrylic resin having the correct balance of properties and containing thiol groups.
- ii) An alkyd, oil free alkyd, or polyester resin containing thiol groups.
- 60 iii) An acrylic adduct containing thiol groups. 60

65 In addition to resins, paint contains pigments to provide colour and obliteration and a wide range of additives to promote flow, resistance to settling etc, together with a mixture of solvents to balance the application properties of the coating. In this product it is usually convenient to add solvents to both component 1 and components 2 and 3. The pigments and other additives, however, normally form part of either component 1 or components 2 and 3, though, exceptionally, it might also be advantageous to have 65

such additions to component 1 as well as to components 2 and 3.

For good results, the proportions of Components 1 and 2 must be balanced to ensure that:-

- i) the ratio of the total number of epoxide equivalents to the total number of amine, amide, carboxylic acid and thiol equivalents when added together is not greater than 10:1 and not less than 0.1:1, i.e. a range of (0.1 to 10):1; 5
- ii) the proportion of resin(s) containing thiol groups as a weight/weight percentage of all the resins containing groups which react with epoxide groups (i.e. amine, amide, carboxylic acid and thiol groups) is not less than 2% or more than 99.5%. 5
- 10 The invention thus consists essentially of a paint composition in which the applied film undergoes a chemical reaction between three components which most commonly would be of a polymeric nature. 10

1. Epoxy component

The epoxy component can in principle consist of virtually any poly-epoxy functional chemical or polymer. In practice, however, the normal requirements of the ultimate paint finish preclude the use of the use of the commonly available bisphenol A/epichlorhydrin resins widely marketed by a number of chemical companies. If, however, the composition is to be the basis of an undercoating product these considerations do not apply and the bisphenol A/epichlorhydrin resins are eminently suitable. 15

The normal requirements are:

- 20 i) Compatibility with the other resin components to ensure maximum initial gloss of the paint films. 20
- ii) Good chemical reactivity with the remaining resin components.
- iii) A composition which promotes gloss retention where needed. (Bisphenol A/epichlorhydrin resins frequently show loss of gloss due to the film deterioration known as chalking when exposed to outdoor weathering). 25
- iv) A composition which promotes maximum colour stability. Aromatic components are frequently more prone to yellowing on exposure than either aliphatic or acrylic types. 25

As a result, therefore, the preferred type of composition for a finishing coat will be either:-

- 30 a) An essentially aliphatic compound containing at least two epoxide groupings per molecule. Polymeric materials of this type should be formulated to contain at least an average of two epoxide groupings per molecule, or 30
- b) An acrylic resin containing an average of not substantially less than two epoxide groupings per molecule.
- 35 The acrylic resin must be formulated to have a reasonable balance of properties, such as hardness, flexibility, gloss retention etc. at least when combined with the other components such as plasticisers which may be either polymeric or solvent in type and may contain reactive groupings. A suitable method of introducing epoxide groupings into the acrylic resin would utilise glycidyl methacrylate as one of the monomers. 35
- 40 An example of the type of resin is shown as Example 1, though preferred materials have been provided commercially. 40

2. Aminelamide component

As in the case of the epoxy component, a very wide range of chemicals would in principle satisfy the requirements for this component. Thus, where the composition consists predominantly of epoxy and mercapto components, low molecular weight amines or polyamides offer the greatest advantage. If, however, the amine component is present as a high proportion of the total it is essential that it is of a polymeric nature capable of providing the basic film properties previously described. 45

In the first case, therefore, the paint film is largely created by chemical reaction between the epoxide and mercapto components. The amine or amide component is present primarily as a catalyst to facilitate this reaction. For this purpose the preferred amines are comparatively low molecular weight chemicals or resins containing amine functionality. Equally suitable are polyamide products, though these work most effectively in the presence additionally of amine. 50

The converse extreme case is represented by the composition in which the paint film is produced essentially by reaction between the amine and epoxy components. For this purpose, amine-containing resin of comparatively low functionality is most suitable. For maximum durability an acrylic resin is preferred as defined in the introduction, except that at least one of the monomers must contain an amino or amide group and optionally one or more monomers may contain a carboxylic acid group. 55

Examples of suitable amine containing monomers are dimethylaminoethyl methacrylate, and t-butylaminoethyl methacrylate. 60

Examples of suitable amide containing monomers are acrylamide or methacrylamide.

Examples of suitable carboxylic acid containing monomers are methacrylic acid, acrylic acid and itaconic acid.

When the amino component is carried in an acrylic resin which constitutes a major proportion of the total composition, that resin must be formulated to have a satisfactory balance of properties at least when it has 65

been blended and reacted with the other parts of the composition in terms of gloss, hardness, adhesion, impact resistance, gloss retention and general durability, as well as resistance to such agents as atmospheric acids, petrol and grease.

- The two compositions described above represent the extreme compositions covered by the application.
- 5 An intermediate position is, however, generally preferred in which both the mercaptan and amino bearing components contribute to the overall properties. Where the amine bearing component is an acrylic resin the level of amine bearing monomer is limited only by the properties of the final composition. Too high an amine value results in films which are water sensitive and/or exhibit blistering and/or loss of gloss, and/or colour change in humid conditions. Thus the preferred amine values depend on the proportion of the component in the overall composition. 10

Example 2 illustrates a resin suitable to be used primarily as a catalyst, whilst example 3 illustrates a resin suitable to be used as a major component. In the latter case preferred examples have been obtained commercially. For this type of amine component, preferred amine values lie between 5 and 30 measured as milligrams KOH per gramme of resin and preferred acid values between 10 and 50. 15

3. Thiol-containing reactant

- This component consists essentially of a resin containing a reactive mercapto grouping. It is the use of this component in the finish which is the essence of these compositions. In principle, virtually any film-forming resin would be suitable which is fully compatible in the system. On the grounds of compatibility, film integrity and durability, one of the two types described below is preferred. 20

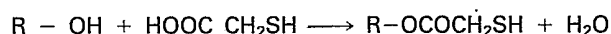
3.1 Alkyd, oil free alkyd or polyester resin containing thiol groupings

There are a wide range of compositions falling under the general heading above which would be suitable as a start material for this component. They are all essentially polymers as defined in the introduction.

- 25 It is possible to introduce the thiol groups *via* a number of chemical reactions. Commercially, the most attractive means, however, is by formulating the above resin to have a suitable excess of hydroxyl groupings over carboxylic acid groupings and then either concurrently, or preferably consecutively, reacting a proportion of the excess hydroxyls with mercaptoacetic acid. Using this preferred method approximately 70% of the theoretical level of thiol is achieved.
- 30 The formulation of alkyd/oil free alkyd/polyester resins is widely known and this invention does not depend on specific compositions of this base resin. In principle, any resin within this general type which permits the introduction of thiol groups is potentially suitable.

In practice, the requirements of the total paint film are most conveniently met if:-

- 35 i) the proportion of polyunsaturated monobasic acids is relatively low, thus facilitating compatibility within the system and minimising discoloration on exposure to outdoor conditions. 35
- ii) the balance of monofunctional, difunctional and polyfunctional constituents is such as to obtain a convenient viscosity/solids relationship without the need
- (a) for a large excess of hydroxyl equivalent over carboxyl equivalents (or *vice versa*). 40
- (b) to terminate the manufacture at a point where the acid value (measured in milligrams KOH per gram of resin (non-volatile) is in excess of 50. Preferably the acid value should be below 20.
- 45 iii) there must be suitable groups to facilitate the introduction of thiol groups. If the preferred route *via* mercaptoacetic acid is to be used the unreacted hydroxyl groups must be sufficient to stoichiometrically satisfy the reaction:- 45



where R is used as an abbreviation for the resin.

- 50 The thiol functionality of the resin (measured in gram molecules per kilo of resin) can be varied over a wide range and is determined by:- 50
- a) the properties of the final paint film.
- b) the stability of the resin and/or paint.
- c) the acceptability of the aroma of the composition.
- 55 Preferred functionality lies between 0.15 moles/Kg and 1.5 moles SH/Kg. 55
- Examples of suitable resins are described in Examples 4 and 5.

3.2 Acrylic resin

- An alternative of the type of resin described under 3.1 is an acrylic resin formulated inherently to have the properties required of the resin described in component 2, but in which at least one of the monomers is capable of subsequent reaction to facilitate the introduction of thiol groupings. 60

- (The alternative process of utilizing an α , β ethylenically unsaturated compound containing a mercapto grouping as a monomer during the production of resin is in practice difficult to achieve. This is because the mercapto group acts as a chain terminator and prevents the reaction producing a resin having the preferred characteristics.) 65

Examples of suitable reactive monomers are glycidyl methacrylate or hydroxyl-bearing monomers such as 2-hydroxyl ethyl methacrylate, 2-hydroxyethyl acrylate, and 2-hydroxy propylmethacrylate, 2 hydroxy-propyl acrylate and commercially available mixtures of the above. Derivatives of these monomers may also be used such as the ethylene oxide adduct of propylene glycol monomethacrylate sold by BP Chemicals

- 5 under the name Bisomer PPM6 5
- The manufacturing process is in two stages. The first is a conventional free radical polymerisation to produce an acrylic resin. The second stage consists of introducing the thiol groupings:-
- a) If the acrylic resin contains epoxide groupings, these can be reacted with polyfunctional mercaptan or mixture of polyfunctional mercaptans (for example ethylene di mercaptan).
- 10 This reaction can frequently be accelerated by the addition of a suitable catalyst. Inorganic and organic metallic compounds and amino compounds are among the wide range of materials which can have a catalytic effect on this reaction. 10
- b) If the acrylic resin contains hydroxyl groupings these can be esterified by mercapto acetic acid very similarly to the route described for alkyd resins under section 3.1.
- 15 Suitable acrylic resins are described under examples 6 and 7. 15

3.3 Acrylic adduct

- If a preparation similar to that described under 3.2 (a) is carried out using a high proportion of a polyfunctional mercaptan it can be sufficient to change the physical properties of the acrylic resin. Within
- 20 this specification such resins have been defined as acrylic adducts. Examples of suitable higher molecular weight polyfunctional mercaptans are the triester of trimethylol propane and mercaptoacetic acid, the tetra ester of pentaerythritol adducts. Examples of suitable higher molecular weight polyfunctional mercaptans are the triester of trimethylol propane and mercaptoacetic acid, the tetra ester of pentaerythritol and mercapto acetic acid as well as a range of commercially available materials. 20
- 25 The preferred functionalith has between 0.15 and 5.0 moles SH/kg. 25
- The preparation of a suitable acrylic adduct is described under example 8.
- The manufacture of the coating composition from the above resins preferably follows a conventional pattern viz:-
- “Activator Thinner” or Clear Lacquer.
- 30 Manufacture is achieved by simple blending under a stirrer. (See examples 9 and 10). 30
- Pigmented paints.
- Manufacture follows the conventional techniques and is in two or three stages depending on the dispersion equipment chosen.
- 35 Stage 1 – Premix (omitted if dispersion is by means of ball mill). 35
- All constituents are mixed for the dispersion stage under a high speed stirrer.
- Stage 2 – Dispersion phase.
- 40 The product from Stage 1 is passed through a sand grinder or horizontal bead mill. Alternatively, the dispersion phase is charged to a ball mill and run until required fineness is achieved. The dispersion means are dependent on pigment type, availability etc. and not on the nature of the resin composition. 40
- Stage 3 – The remaining constituents are added whilst stirring.
- 45 Examples of paint manufacture are described under Examples 11, 12 and 13. 45

*Example 1**Epoxy resin component*

5		g		5
	Methyl ethyl ketone	400	A	
	Toluene	400		
10	Methyl methacrylate	533		10
	Butyl methacrylate	106		
	Ethyl acrylate	62	B	
	Glycidyl methacrylate	399		
	Benzoyl peroxide	48		
15				15
	Butyl acetate	50		
	Benzoyl peroxide	12	C	
20				20
	Butyl acetate	50		
	Benzoyl peroxide	18	D	
	Butyl acetate	151	E	
25	<i>Method</i>			25
	Charge 'A' to a 5 litre flask fitted with a stirrer, thermometer, Liebig condenser, dropping funnel and with contents protected by a nitrogen purge. Premix 'B' and charge to dropping funnel.			
	Switch on heating and raise temperature until there is a steady reflux (ca 95°C). Commence addition of 'B'. Adjust dropping funnel to affect addition at an even rate over 4 hours. Check viscosity (6 - 7 poise) and			
30	continue reflux until there is no further viscosity increase (10 - 12 poise). Premix 'C' and charge to dropping funnel. Add over 1/2 hour and check viscosity when addition complete. Run (approx 2 hours) until there is no further increase in viscosity (15 - 20 poise). Repeat this process for components 'D'.			30
	Cool, check non-volatile content and adjust with 'E' to ca.50%.			
	Pass through filter.			
35	Final constants:-			35
	viscosity at 25°C ca.	10 poise		
	non volatiles	50.3%		
40	Epoxyde Equivalent			40
	(calc on non-volatiles (NV).	370g		
45	<i>Example 2</i>			45
	Toluene	435	A	
	Methyl ethyl ketone	435		
50	Methyl methacrylate	738		50
	Butyl acrylate	345		
	2-ethylhexyl acrylate	72	B	
	Dimethylaminoethyl acrylate	157		
	Benzoyl peroxide	66		
55				55
	Toluene	50	C	
	Benzoyl peroxide	22		
60				60
	Toluene	50	D	
	Benzoyl peroxide	30		
	Toluene (To NV)	240	E	
65	<i>Method</i>			65
	The method is identical to that of Example 1.			

Final Constants

	Viscosity (at 25°C)	8.5 poise	
5	NV	49.3%	5
	Amine Value (mg KOH on NV)	40.4	
10	Equivalent Wt (Calculated on NV)	1390	10

Example 3 Amine-containing resin component

15		g		15
	Xylene	370	A	
	Butyl acetate	400		
20				20
	Butyl methacrylate	197.5		
	Ethyl acrylate	181	A	
	Methyl methacrylate	650		
	<i>t</i> -Butylaminoethyl methacrylate	76		
25				25
	Methacrylic acid	49.5	B	
	Benzoyl peroxide	35		
	Butyl acetate	50		
30	Benzoyl peroxide	7	C	30
	Butyl acetate	50		
	Benzoyl peroxide	10	D	
35				35
	Butyl acetate	95		
	Xylene	165	E	

Method

Except that the reflux temperature is ca. 125°C, the method is identical to Example 1.

40				40
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Final Constants:

45	Viscosity at 25°C	18.5 poise		45
	Non-volatiles	49.8%		
	Amine value	29 mg KOH/g of resin.		
50	(calc. on non-volatiles)			50
	Acid value	26.4 mg KOH/g of resin.		
55	Equivalent (in reaction with epoxide groups) 1170g (calc.).			55

Example 4 Thiol-containing alkyd resin component

		g		
5	Glycerine	62		5
	Cardira E	460		
	Pentaerythritol	22	Stage I	
	Phthalic Anhydride	278		
	Adipic Acid	100		
10	Mercaptoacetic acid	35	Stage II	10
	Xylene	400		

Method

15	Charge all stage I reactants in a 2 litre flask fitted with Dean & Starke water removal equipment, thermometer and stirrer. The reactants are protected by a nitrogen purge throughout the process.			15
20	Add approximately 2% xylene as an entraining solvent and heat to $232 \pm 2^\circ$ over 5 hours removing the water continuously. The temperature is held and reflux maintained by adding xylene as required. Acid value is measured at intervals and when it reaches 14 ± 1 the heat is removed and the contents cooled to 60°C . The mercaptoacetic acid is added slowly and the mixture reheated to 200°C and reflux established. When the acid value reaches 12 ± 1 (6-7 hrs) the product is cooled to 160°C and thinned with xylene to 70% NV.			20

Stage I water of esterification 20 ml

Stage II water of esterification 8.2 ml

25	Final constants:-			25
	Viscosity	23.5 poises @ 25°C		
30	Non Volatiles	70.3% in xylene		30
	Acid Value	13.5 (100% NV)		
35	Colour	1.75 (PRS)		35

Example 5 Thiol-containing alkyd resin component

		g		
40	Xylene	90		40
	Neopentyl Glycol	813	Stage I	
	Trimethylol propane	543		
	Phthalic anhydride	1647		
45	Mercaptoacetic acid	224		45
	Para toluene sulphonic acid	5	Stage II	
50	Xylene	1180		
	Calcium carbonate	8	Stage III	50

Method

55	Charge stage I ingredients in a 5 litre flask equipped as in Example 5. Switch on the nitrogen purge and heat to 180°C over a 4 hour period. Hold at 180°C to reflux for one hour removing water (85 ml) and adding xylene as required to maintain reflux. Heat to 200°C and hold at this temperature until the acid value falls to 19. Water to esterification 195 g is removed over a period of 5 1/2 hours. Cool 60°C and add stage II ingredients. Reheat to 200°C and hold until the acid value falls to 24 ± 1 ; of water of esterification ca. 49 g is removed. Cool to 150°C . Thin to $70 \pm 1\%$ non-volatiles with xylene. Add Stage III magnesium oxide, stir thoroughly and hold for 30 minutes at 100°C before cooling and filtering.			55
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Final constants:-

	Viscosity	22 poise @ 25°C	
5	Non volatiles	70.3%	5
	Acid value	23.5 (@ 100% NV)	
10	Colour	3/8 (PRS).	10

Example 6 Thiol-containing acrylic resin component

		g	
15	Toluene	542	
	Methyl ethyl ketone	300	A
20	Methyl methacrylate	684	
	Bisomer PPM 6	176	
	Methacrylic acid	18	B
	2-Hydroxyethyl methacrylate	161	
	Benzoyl peroxide	31	
25	Butyl acetate	50	
	Benzoyl peroxide	7	C
30	Mercaptoacetic acid	95	
	<i>p</i> -Toluene sulphonic acid	2.1	D
	Calcium carbonate	2.5	E.

Method

35 The process follows Example 1 precisely until items A, B & C have been charged and reacted. (Viscosity ca.22 poise). 35

The reactants are cooled to 60°C and reactants 'D' added. The apparatus is modified to include Dean & Starke water removal equipment. The reactants are reheated to reflux (ca.94°C) and water removal commenced. The reaction is continued until all water is removed. 18.6 g should theoretically be obtained.

40 Practical quantities vary from 19 to 20.5 g. 40

The mixture is cooled to just below reflux and ingredient 'E' added. The temperature is maintained for 30 minutes after which it is cooled and filtered.

Final constants:-

45	Viscosity at 25°C	80 poise	45
	non-volatiles	55.2%	
50	Mercaptan value	0.658 moles/kg of resin (71% theor. value)	50
	Mercaptan equivalent	1520	

Example 7 Thiol-containing acrylic resin component

	Xylene	542		
	Pentoxone (Shell Chemicals)	300	A	
5	Methyl methacrylate	684		5
	Bisomer PPM6 (BP Chemicals)	176		
	Methacrylic acid	18	B	
	Hydroxyethyl methacrylate	161		
10	Octyl Mercaptan	4.2		10
	Benzoyl peroxide	22		
	Benzoyl peroxide	6		
	Butyl acetate	50	C	
15	Mercaptoacetic Acid	95	D	15

Method

20 The method is in principle the same as that for Example 3, except that the reflux temperature is approximately 130°C. The octyl mercaptan is added to 'B' to control the route of the reaction.

After the addition of the mercaptoacetic acid, water removal proceeds, though at a much slower rate, without the need for the *p*-toluene sulphonic acid catalyst because of the higher temperature of reaction. Magnesium oxide is not, therefore, required to remove any excess catalyst.

25 Final Constant:- 25

	Viscosity @ 25°C	58 poise		
30	Non volatiles	55.1%		30
	Mercaptan Value	0.621 Moles/kg resin (67% theor value)		
35	Mercaptan equivalent	1610		35

Example 8 Acrylic Adduct

40	Mercaptan Ester*	170		40
	Xylene	180		
	Toluene	60	A	
	DMP 30**	5		
45	Acrylic Resin (Example 1)	400	B	45
	Xylene	100		
	* Triester of Trimethylol propane and mercaptoacetic acid			
50	** DMP 30, supplied by Rohm & Haas.			50

Method

Charge reactants A to flask fitted with a Liebig condenser, dropping funnel, thermometer and stirrer using a nitrogen purge throughout. Switch on heating and raise to reflux temperature (ca 100°C).

55 Commence addition of reactants B adjusting the ratio so that all of it is added evenly over a period of 3 hours.

Maintain reflux throughout the addition, allowing the temperature to rise as necessary (ca 130°C).

Maintain temperature and reflux for 2 hours after the addition is complete.

Final constants:

	Viscosity at 25°C	2.1 poise	
5	NV	38.4%	5
	Epoxide content	effectively nil	
10	Mercaptan content (on NV)	2.3 mols/kg	10
	Mercaptan equivalent (calc on NV)	435	

15 *Example 9 Thinner / Activator* 15

	*Epoxide Crosslinker	512	
20	Butyl acetate	1162	20
	Cyclohexanone	184	
	Xylene	828	
25	Methyl isobutyl ketone	552	25
	Acetone	364	
30	Toluene	398	30
	* Epoxide bearing crosslinking agent supplied commercially and reduced to 50% NV with butyl acetate.		

Method

35	Add items in order stirring continuously and until fully homogeneous. The product of Example 9 should be blended with the products of the following Examples as follows:-		35
	90g Example 9 with 100 g Example 11		
	110g Example 9 with 100g Example 12		
40	135g Example 9 with 100g Example 10		40
	60g Example 9 with 100g Example 13		

before application. Additional solvents can be added if desired to improve flow characteristics.

45 *Example 10 Clear Lacquer (Pigment free paint)* 45

		g.	
50	*Acrylic resin 1	871	50
	*Acrylic resin 2	618	
	Thiol containing polyester (Example 5)	139	
55	Flow agent	1.5	55
	Re-odourants	4	
60	UV adsorbers	24	60
	Toluene	54	

*Amine containing resins supplied commercially and reduced to 45% NV with toluene.

Method

Add in order shown under continuous stirring.

Run until homogeneous.

5				5
	<i>Example 11 White Finishing Paint</i>			
	Titanium dioxide	1196		
	Antisettling agent	2		
10	*Acrylic resin 1	209	A	10
	Dispersant	12		
	Xylene	377		
	* Acrylic resin 1	1438		
15	**Acrylic resin 2	1168		15
	Thiol containing polyester (70% NV, Example 6)	263		
	Re-odourant	5	B	
	Flow agent	4.5		
20	Toluol	267		20
	* Amine-containing resin provided by Kunstharfabriek Synthese BV, Holland, adjusted to 45% NV with xylene.			
25	** Resin provided by Cray Valley Products Ltd. UK.			25

Process

Premix ingredients 'A' under high speed stirrer and pass through laboratory horizontal sand grinder. Transfer to container with stirring facilities and add items in 'B' in order shown.

30				30
	Final constants:			
	non volatiles	55.2%	Pigment:Binder = 0.8:1	
	Viscosity	62 secs	BSB4 @ 25°C	

35	<i>Example 12</i>				35
	Carbon Black	91			
	*Acrylic Resin 1	740	A		
40	Acrylic resin (Example 2)	180		40	
	Dispersant	1			
	Xylene	246			
	Acrylic resin 1	418	B		
45	Acrylic resin 1	667		45	
	Acrylic resin (Example 3)	142	C		
	Xylene	100			
	Acrylic resin 1	1000			
50	Acrylic resin containing thiol group (Example 6)	234		50	
	Thiol containing polyester (Example 5)	180	D		
	Flow agent	4			
55	Re-odourant	4		55	
	Toluene	400			

Method

Charge ingredients 'A' to ball mill and grind 48 hours. Check fineness and if satisfactory add item 'B'. Run 4 hours. Premix items 'C' and add to mill. Run 2 hours. Drop into container fitted with stirrer and items 'D' in order shown.

Example 13 Primer Surfacer

		g	
5	Carbon black pigment	12	5
	Titanium dioxide pigment	360	
	Air floated silica	160	
	Micronised Barytes	480	
	China clay	400	A
10	Micronised Talc	400	10
	Wetting Agent	20	
	Acrylic resin 1	1400	
	Flow agent	1	
	Methyl ethyl ketone	290	
15	Toluene	100	15
	Toluene	150	B
	*Acrylic resin 1	747	
20	Thiol-bearing Polyester (Example 4)	128	C
	Antisetting agent	48	20

Method

Charge all ingredients 'A' to ball mill. Run 48 hours and check fineness. Transfer to container with stirring facilities. Use item 'B' to ensure complete transfer. Add items 'C' in order shown with continuous stirring.

	Viscosity @ 25°C	91 secs BSB4	
30	Pigment/Binder	1.76/1	30
	Non-volatiles	52.1%	

CLAIMS

- 35 1. A three-component coating composition comprising a first component including a polymer containing epoxide groupings, a second component including one or more acrylic resins containing amino or amide or amide groupings and, optionally, carboxylic acid groupings, and a third component including one or more polymers containing thiol groupings; and, optionally, carboxylic acid groupings.
- 40 2. A composition according to claim 1, in which a resin in the third component is an acrylic resin or acrylic adduct containing thiol groupings.
3. A composition according to claim 1, in which a resin in the third component is an alkyd, oil-free alkyd or polyester resin containing thiol groupings.
4. A composition according to any of claims 1 to 3, in which the ratio of the total number of epoxide equivalents to the total number of amine, amide, carboxylic acid and thiol equivalents when added together is no greater than 10 and not less than 0.1 to 1, (i.e. 0.1 to 10):1.
5. A composition according to any of claims 1 to 4, in which the proportion of resin(s) containing thiol groups as a weight/weight percentage of all the resins containing groups which react with epoxide groups (ie amine, amide, carboxylic acid and thiol groups) is not less than 2% or more than 99.5%.
- 50 6. A composition according to any of claims 1 to 5, in which the polymer containing epoxide groupings is an essentially aliphatic compound containing not substantially less than two epoxide groupings per molecule, or an acrylic resin containing an average of not substantially less than two epoxide groupings per molecule.
7. A composition according to any of claims 1 to 6, in which the amine-containing resin has an amine content equivalent to 5 to 30 mg KOH/g.
- 55 8. A composition according to claim 7, in which said resin also has an acid value of from 10 to 50mg KOH/g.
9. A composition according to any of claims 1 to 8, in which the thiol-containing resin contains mercaptoacetate groups.
- 60 10. A composition according to any of claims 1 to 9, in which the thiol-containing resin is a polyester containing from 0.15 to 1.5 moles SH/kg; an acrylic resin containing from 0.15 to 4.0 moles SH/kg or an acrylic adduct containing from 0.15 to 5.0 moles SH/kg.

11. A two-pack coating composition according to any of claims 1 to 10, containing the epoxide-containing resin in one pack and the amine-containing resin and the thiol-containing resin plus pigments in the other pack.

Printed in the UK for HMSO, D8818935, 1/85, 7102.

Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.