



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <b>(51) International Patent Classification <sup>5</sup> :</b><br><br><b>C09D 167/02</b>   | <b>A1</b>  | <b>(11) International Publication Number:</b> <b>WO 90/08811</b><br><br><b>(43) International Publication Date:</b> 9 August 1990 (09.08.90) |
| <b>(21) International Application Number:</b> PCT/GB90/00175<br><b>(22) International Filing Date:</b> 5 February 1990 (05.02.90)<br><br><b>(30) Priority data:</b><br>8902584.5                      6 February 1989 (06.02.89)      GB<br><br><b>(71) Applicant (for all designated States except US):</b> COUR-<br>TAULDS COATINGS (HOLDINGS) LIMITED [GB/<br>GB]; 18 Hanover Square, London W1A 2BB (GB).<br><br><b>(72) Inventors; and</b><br><b>(75) Inventors/Applicants (for US only):</b> GREEN, Kevin, Hilton<br>[AU/AU]; 44 Brooks Street, Lane Cove, NSW 2066<br>(AU). McKAY, Garry, Michael [AU/AU]; 29 Melissa<br>Street, Strathmore, VIC 3041 (AU).<br><br><b>(74) Agent:</b> HALE, Stephen, Geoffrey; J.Y. & G.W. Johnson,<br>Furnival House, 14-18 High Holborn, London WC1V<br>6DE (GB). | <b>(81) Designated States:</b> AT (European patent), AU, BE (Euro-<br>pean patent), BR, CA, CH (European patent), DE (Euro-<br>pean patent), DK (European patent), ES (European<br>patent), FI, FR (European patent), GB (European pa-<br>tent), IT (European patent), JP, KR, LU (European pa-<br>tent), NL (European patent), NO, SE (European patent),<br>US.<br><br><b>Published</b><br><i>With international search report.</i> |  |
| <b>(54) Title:</b> COATING PROCESS AND COMPOSITION   |  |  |
| <b>(57) Abstract</b><br><br>A surface is coated with a coating composition comprising (A) a hydroxy component having at least two free hydroxy groups and (B) an anhydride component having at least two cyclic carboxylic anhydride groups, at least one of (A) and (B) being a film-forming polymer. An atomised liquid mixture of the hydroxy component (A) and the anhydride component (B) is sprayed on the surface and a separately packaged volatile amine is incorporated in the spray. The invention includes a liquid coating composition comprising the hydroxy component (A) and the anhydride component (B) and a separately packaged volatile amine having a boiling point in the range 50 to 300° C, preferably 50 to 170° C.   |  |  |

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COATING PROCESS AND COMPOSITIONTechnical field

This invention relates to curable coating compositions and to their application to surfaces and curing. The invention is particularly applicable to the curing of coatings at ambient temperature.

Background art

US Patent 4452948 describes a two-pack coating composition comprising a hydroxy component and an anhydride component, in which the hydroxy component is a polymer having at least two free hydroxy groups per molecule and also has in its molecule amine groups and the anhydride component is a polymer having at least two cyclic carboxylic acid anhydride groups per molecule. In a less preferred modification the amine groups are present in a separate amine compound rather than on the molecule of the hydroxy component. The coatings of U.S. patent 4452948 have the advantage that they are ambient temperature curing without the use of toxic isocyanates and have been used successfully as finish coats for automobiles, particularly in re-finishing, and as paints for yachts.

European Patent Application 259172 describes a coating composition comprising an anhydride polymer and a polymer containing hydroxyalkylamino, hydroxyalkoxyalkylamino, hydroxy-substituted acyloxyalkylamino, hydroxy-substituted polyacyloxyalkylamino, mercaptoalkylamino or oxazolidino groups. One of the polymers comprises a flexible polymer chain and has its functional groups present as terminal groups at the ends of the flexible polymer chain.

UK Patent 2136441 describes a method for applying a liquid coating composition comprising an aromatic hydroxy-functional compound and a multi-isocyanate cross-linking agent by forming an atomising gas flow which comprises an intimate mixture of a carrier gas bearing a catalytic amount of vaporous tertiary amine and atomising the liquid coating composition with the carrier gas flow. Interna-

tional Patent Application W084/02665 describes a method and apparatus for applying a curable coating to a substrate in which a curing agent such as an amine is simultaneously deposited with the coating. Curable coatings described  
5 comprise isocyanate-functional polymers cured with active hydrogen reagents such as polyols, and epoxy resins cured with polyamides. UK Patent Applications 2175912 and 2176197 describe similar processes in which a nitro-alcohol or a mercaptan is cured with a polyisocyanate, and UK  
10 Patent Application 2200126 describes a process in which a mercaptan is cured with a thiourethane. European Patent Application 142838 describes a method for producing a polyurethane resin which comprises contacting a compound having a 1-oxa-3,5-diazine-2,4,6-trione ring and isocyanate  
15 groups and a compound having active hydrogen with a tertiary amine present in gaseous phase.

#### Disclosure of invention

A process according to the invention for coating a surface with a coating composition comprising (A) a hydroxy  
20 component having at least two free hydroxy groups and (B) an anhydride component having at least two cyclic carboxylic anhydride groups, at least one of (A) and (B) being a film-forming polymer, is characterised in that an atomised liquid mixture of the hydroxy component (A) and the  
25 anhydride component (B) is sprayed on the surface and a separately packaged volatile amine is incorporated in the spray.

A liquid coating composition according to the invention comprises (A) a hydroxy component having at least two  
30 free hydroxy groups and (B) an anhydride component having at least two cyclic carboxylic anhydride groups, at least one of (A) and (B) being a film-forming polymer, and amine groups for catalysing the reaction between the hydroxy groups of component (A) and the anhydride groups of component (B), and is characterised in that the amine groups  
35 are provided by a separately packaged volatile amine having a boiling point in the range 50-300°C.

The coating process and compositions of the invention have advantages over those described in US Patent 4452948 and European Patent Application 259172. The coatings of the invention can use a wide variety of hydroxy-functional  
5 polymers, including unmodified commercial polymers. The hydroxy component and the anhydride component can often be packaged together in a single pack.

In other cases, when separate packs for the hydroxy and anhydride components are acceptable, the process will  
10 allow longer potlife as well as faster cure. The volatile amine gives more rapid cure than an equal weight of less volatile amine packaged with one component of the coating and reduces the possibility of stickiness after drying of the coating by evaporation but before full curing occurs.

Another area in which the process as described can be advantageously used is for the curing of hydroxy/anhydride coatings at low temperatures. Use of the process allows fast cure at low temperatures, for example 0 to 15°C, while retaining reasonable potlife. If additional low volatility  
15 catalyst was added to a conventional coating to achieve this rate of cure at low temperatures, then too short a  
20 potlife would result.

The hydroxy component (A) and anhydride component (B) are preferably dissolved in one or more organic solvents.

The hydroxy component (A) is preferably a film-forming polymer and can be selected to give the desired properties in the cured coating. For example it can be an addition copolymer having pendent hydroxy groups such as an acrylic copolymer containing 10-80 per cent by weight, preferably  
25 15-50 per cent by weight, of a hydroxyalkyl acrylate or methacrylate such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate or hydroxypropyl acrylate. Examples of olefinically unsaturated monomers  
30

which can be copolymerised with the hydroxyalkyl ester are acrylic esters such as butyl acrylate, methyl methacrylate, butyl methacrylate, ethyl acrylate and hexyl acrylate and vinyl compounds such as styrene, vinyl acetate and vinyl chloride. The hydroxy component can be a copolymer containing a polyester segment, for example a graft polymer of acrylic monomers onto an unsaturated polyester. The acrylic monomers are preferably selected from those mentioned above and include a hydroxy-containing monomer, e.g. a hydroxyalkyl acrylate or methacrylate. The polyester segment is preferably a low molecular weight (below 1000) polyester derived from a polyol such as ethylene glycol, propylene glycol or trimethylolpropane and an acid or anhydride such as phthalic anhydride, isophthalic acid or adipic acid with a minor amount of an unsaturated acid or anhydride such as maleic anhydride. The polyester can for example form up to 50 per cent by weight, preferably 5-25 per cent by weight, of the graft copolymer. Coatings prepared using an acrylic hydroxy-functional component or an acrylic/polyester graft copolymer hydroxy-functional component have excellent gloss, flow and appearance after spraying.

An alternative method of preparing an addition copolymer having pendent hydroxy groups is to prepare a copolymer having amide groups, for example acrylamide or methacrylamide units, and to form N-methylol groups on the amide by reaction with formaldehyde. The hydroxy-functional component can alternatively be a copolymer of allyl alcohol, for example a styrene/allyl alcohol copolymer optionally containing allyl ether units.

The hydroxy-functional component can alternatively be a telechelic polymer having hydroxy groups at each end of a polymer chain, such as a polyether, a polyester, particularly an aliphatic polyester, or a diene polymer, hydrogenated diene polymer, silicone, polyurethane, polyisobutylene or polyacrylate. The use of such a telechelic polymer can

give cured coatings having high impact- and abrasion-resistance. Such a telechelic polymer preferably contains more than two hydroxy groups per molecule, for example it can be a polyester or polyether having three or four arms  
5 each terminated by a hydroxy group. One example of such a hydroxy-terminated polyester sold commercially is a polycaprolactone tetraol of molecular weight about 1000. Alternative hydroxy-functional polyesters can be prepared from polyols such as ethylene glycol, propylene glycol or  
10 neopentyl glycol with dicarboxylic components such as phthalic anhydride, isophthalic acid or adipic acid and a trifunctional compound such as trimethylolpropane or trimellitic anhydride, using an excess of the polyols to obtain a hydroxy-tipped polymer. Various hydroxy-tipped  
15 polyethers are sold commercially, for example under the Trade Marks "Teracol" and "Terathane", typically having molecular weights in the range 600-2400. These are generally formed by the reaction of a polyol with propylene oxide and/or ethylene oxide or with tetrahydrofuran.  
20 Hydroxy-tipped addition polymers, for example hydroxy-tipped polybutadienes or butadiene/styrene or butadiene/acrylonitrile polymers can also be used. Hydroxy-tipped polyurethanes can alternatively be used, formed for example from a polyisocyanate and an excess of a polyol component  
25 which may comprise a polyether or polyester polyol and a low molecular weight polyol.

The hydroxy-functional polymer can contain unsaturated residues such as olefinically unsaturated double bonds. It can for example be an unsaturated polyester containing  
30 maleic residues or can contain oligomers of pentaerythritol triacrylate containing residual unsaturation. Addition of amine to the unsaturated residue can take place, retaining some amine groups in the polymer to catalyse continued curing. Alternatively, the hydroxy-functional polymer can  
35 contain one or more epoxide groups; for example a hydroxy-acrylic polymer can contain glycidyl acrylate or methacrylate units which react with amine to retain amine groups in

the polymer. The hydroxy component need not, and usually will not, contain amine groups, but can contain amine groups of the type described in US Patent 4452948 if desired.

5 The polymer containing anhydride groups can for example be a copolymer of an olefinically unsaturated cyclic carboxylic acid anhydride such as maleic, itaconic, citraconic or vinylsuccinic anhydride or vinyl trimellitate anhydride with one or more olefinically unsaturated  
10 comonomers such as an alpha-olefin, for example styrene, ethylene or propylene, or an ester of acrylic or methacrylic acid, for example butyl acrylate, ethyl acrylate, methyl methacrylate or butyl methacrylate. Preferred copolymers contain 10-40 per cent, most preferably 15-30  
15 per cent, by weight, maleic or itaconic anhydride groups and have a molecular weight of 4000-20000. The polymer containing anhydride groups can alternatively be an anhydride adduct of a diene polymer such as maleinised polybutadiene or a maleinised copolymer of butadiene, for  
20 example a butadiene/ styrene copolymer. Terpene/maleic anhydride copolymer resins are a further alternative. An anhydride adduct of an unsaturated fatty acid ester, for example a styrene/allyl alcohol copolymer esterified with an unsaturated fatty acid and maleinised, can also be used.

25 Alternative anhydride-containing polymers can be formed from hydroxy-containing polymers, for example copolymers of hydroxyethyl acrylate or hydroxyethyl methacrylate or styrene/allyl alcohol copolymers, by reaction with a tricarboxylic compound capable of introducing  
30 anhydride groups, for example as described in European Patent Application 259172. A further alternative type of polymer containing anhydride groups is an adduct of trimellitic anhydride and a polyol, for example as described in European Patent Application 134691.

35 The polymer containing anhydride groups can alterna-



tively be formed by the reaction of a polymer containing thiol groups with an olefinically unsaturated cyclic carboxylic acid anhydride such as maleic anhydride or itaconic anhydride. The polymer containing thiol groups is preferably thiol-tipped; it can for example be a multi-  
5 limbed telechelic polymer formed by reaction of a corresponding hydroxy-tipped polymer with mercaptoacetic acid.

The coating composition can additionally contain a minor amount of a mono-functional hydroxy compound or a  
10 mono-functional anhydride compound, for example hexahydrophthalic anhydride. If used, such a mono-functional compound should preferably provide less than 10% of the hydroxy or anhydride groups in the composition.

The coating composition can contain a polyepoxide as  
15 well as a hydroxy component and an anhydride component. Examples of polyepoxides are diglycidyl ethers of bisphenols, for example bisphenol A, and condensed glycidyl ethers of bisphenols; epoxy novolac resins; and aliphatic or cycloaliphatic diepoxides. If a polyepoxide is used,  
20 the ratio of epoxide groups in the composition to hydroxy groups in the hydroxy component is preferably less than 1:1, most preferably less than 1:2.

The volatile amine preferably has a boiling point in the range 50-170°C. The amine can be a tertiary amine, for  
25 example triethylamine, and can contain a hydroxy group such as N,N-dimethyl ethanolamine or a further amino group such as N,N-dimethyl propane-1,3-diamine. The amine should preferably not contain more than one hydroxy group. Tertiary amines are described as preferred in US Patent  
30 4452948. Surprisingly we have found that volatile secondary amines, such as diethylamine, di-n-propylamine, di-n-butylamine, diisobutylamine, diisopropylamine or N-methyl ethanolamine, and even primary amines such as n-butylamine, are also very effective as curing agents when applied using  
35 the process of the present invention. These secondary and

primary amines might be expected to react with anhydrides to form inactive amides, but we have found that they form well-cured films with extensive cross-linking between the hydroxy groups of (A) and the anhydride groups of (B),  
5 although some bound amine can also be detected in the cured film. Mixtures of volatile amines can be used, for example a mixture of a tertiary amine and a secondary amine.

The volatile amine is preferably used at 0.5 to 5 per cent by weight based on the hydroxy component (A) and  
10 anhydride component (B). The amine is preferably delivered to the spray in vaporous form although some of it, even most of it, may be present as an atomised liquid, particularly for amines of boiling point above about 150°C. The amine can if desired be dissolved in a volatile carrier  
15 solvent which may help evaporation and/or atomisation of the amine. The amine is delivered to the spray in a carrier gas which may be inert, such as nitrogen or carbon dioxide, or may be air, or mixtures thereof. Minimum temperatures and pressures of the atomising gas stream may  
20 be maintained to ensure that the amine catalyst remains vaporous and does not condense in any lines. Amine vapour may condense onto the paint droplets after leaving the spray gun.

Various amine vapour generators are commercially  
25 manufactured, for example for use with the cold box process in the foundry industry. Types of amine generators in common use include the liquid injector type and the vaporised type. The injector type amine generator forces liquid amine into a stream of fast-moving carrier gas, either  
30 compressed air or inert gas such as dry CO<sub>2</sub> or N<sub>2</sub>. The turbulent carrier stream evaporates the volatile amine and transports it to the spray gun. The amine catalyst is forced into the carrier gas line by one of two mechanisms. The first mechanism is a calibrated piston operating  
35 against check or diverter valves. The second method is a pressurised amine holding tank which delivers amine for a

pre-set length of time. The vaporised type of amine generator accomplishes the evaporation or atomisation of the amine catalyst either by bubbling carrier gas through a deep bath of liquid amine (bubbler type), or by heating  
5 (boiling) the amine prior to blending with the carrier gas (proportioner type).

A representative amine vapour generator used in the foundry core industry is shown in US Patent 4051886. An amine generator which has been suggested for use in connection with curing coatings is shown in Figure 1 of International Patent Application W084/02665. Another is described  
10 in US Patent 4540531.

From the amine generator, the atomising gas flow bearing volatile amine catalyst is transported to the spray  
15 gun. The piping to the spray gun may be steam traced or heated to maintain the amine as a vapour. The atomising gas flow bearing amine atomises the liquid coating composition in conventional fashion through the spray gun. It is possible to preheat the liquid coating composition for  
20 ensuring appropriate viscosity for spraying and/or to achieve special effects. Because amine is being exhausted from the spray gun, it is preferred that spraying takes place in a conventional paint spray booth or paint spray hood. The coating is generally capable of curing on the  
25 substrate to a hard film which is tack-free and resistant to solvent so that it can be overcoated within 24 hours at ambient temperature, for example 10-40°C. Maximum hardness, solvent-resistance and impact-resistance generally develop over a number of days at ambient temperature, for  
30 example 2-10 days. Curing can be carried out at temperatures above ambient, for example in the range 40-100°C or even 150°C, for shorter times if this is more convenient.

The anhydride component (B) and the hydroxy component (A) are each preferably dissolved in an organic solvent,  
35 such as a hydrocarbon and/or a polar organic solvent, for

example xylene or toluene or trimethylbenzene or mixtures thereof with an ester such as butyl acetate or ethoxyethyl acetate or methoxypropyl acetate or with a ketone such as methylisobutylketone or methylisoamylketone. Reactive  
5 solvents such as alcohols should preferably not be used. The components (A) and (B) are preferably compatible both in solution and in the absence of solvent so that a clear coating can be obtained. The solutions of components (A) and (B) are mixed, together with any additives used such as  
10 pigments (the coating is usually pigmented), fillers and flow control additives, to form the liquid coating composition. The proportion of anhydride groups in the anhydride component (B) to hydroxy groups in the hydroxy component (A) is preferably 0.5:1-2:1.

15 The hydroxy component (A) and anhydride component (B) can generally be stored as a single package for at least 6 months at ambient temperatures of up to 35°C. Alternatively, the hydroxy component (A) and anhydride component (B) can be packaged separately and only mixed immediately prior  
20 to application. This is particularly useful if one of the components, preferably the hydroxy component (A), contains some low volatility catalyst (either bound to the polymer, or as free amine). In this case use of the process as described in this application imparts faster cure of the  
25 coating composition than would be achieved without it.

The invention is illustrated by the following Examples. The composition formulations are by weight.

#### Examples 1 to 3

A coating composition was prepared based on two  
30 hydroxy components (A1 and A2) and an anhydride component (B). The principal hydroxy component (A1) was an acrylic solution copolymer with the following composition.

|   |                              |            |
|---|------------------------------|------------|
|   | Styrene                      | 27         |
|   | 2-Hydroxy ethyl methacrylate | 13         |
|   | Butyl acrylate               | 6          |
|   | Methyl methacrylate          | 14         |
| 5 | Butyl acetate solvent        | 14         |
|   | Xylene solvent               | 26         |
|   |                              | <u>100</u> |

10 The second hydroxy component (A2) was a commercial polyester, Desmophen 670, with a hydroxy value of 142.

The anhydride component (B) was an acrylic solution copolymer containing reacted itaconic anhydride with the following composition.

|    |                       |            |
|----|-----------------------|------------|
| 15 | Itaconic anhydride    | 8          |
|    | Styrene               | 8          |
|    | Butyl acrylate        | 8          |
|    | Methyl methacrylate   | 8          |
|    | Butyl acetate solvent | 68         |
| 20 |                       | <u>100</u> |

The formulation of the coating composition was as follows:

|    |                         |            |
|----|-------------------------|------------|
| 25 | Hydroxy component (A1)  | 21         |
|    | Hydroxy component (A2)  | 2          |
|    | Aluminium silicate      | 3          |
|    | Titanium dioxide        | 13         |
|    | Additional solvent      | 15         |
| 30 | Anhydride component (B) | 46         |
|    |                         | <u>100</u> |

The ratio of hydroxy groups in components (A1 + A2) to

anhydride groups in component (B) was approximately 1:1.

Volatile amine as listed in Table 1 was supplied to the catalyst reservoir of a "Chemidry" vapour generator apparatus sold by: Chemidry Pty. Ltd., No. 1 Unit 2  
5 Hargraves Place, Wetherill Park, 2164, New South Wales, Australia.

This apparatus is of the vaporiser type. Compressed air was passed through the "Chemidry" unit at an approximate pressure of 40 psi (275 kPa). The compressed air  
10 containing entrapped amine vapour was then used as the carrier gas in a spray gun which applied the coating composition described above to a metal surface. The coating composition was allowed to cure at ambient temperature.

15 The above coating was applied with three different volatile amine catalysts as shown in Table 1 and also with no volatile amine in order to demonstrate the improvements induced by the volatile amine. In each case the resistance of the coating to rubbing with xylene was measured after  
20 1, 3 and 14 days at ambient temperature and the results are shown in Table 1. The figures quoted in the Table are the number of double rubs withstood by the coating.

The amine content of the cured coating was measured in Example 1 as 0.48 per cent by weight, and in Example 3 as  
25 1.4 per cent by weight.

TABLE 1

| Example No.           | Volatile Amine Catalyst    | Xylene Resistance (double rubs) |        |                  |
|-----------------------|----------------------------|---------------------------------|--------|------------------|
|                       |                            | 1 day                           | 3 days | 14 days          |
| 5 comparative example | -                          | 7                               | 9      | 25               |
| 1                     | N,N-dimethyl amino ethanol | 22                              | 27     | greater than 100 |
| 2                     | Tri-ethylamine             | 10                              | 22     | 90               |
| 10 3                  | Di-n-propylamine           | 10                              | 16     | greater than 100 |

Examples 4 to 6

A coating composition was prepared comprising the hydroxy acrylic polymer listed in Examples 1 - 3 as (A1) and a maleic anhydride polymer as component (B). The anhydride polymer had the following composition:

|    |                       |            |
|----|-----------------------|------------|
|    | Maleic anhydride      | 10         |
|    | Styrene               | 10         |
|    | Butyl acrylate        | 10         |
|    | Methyl methacrylate   | 10         |
| 20 | Butyl acetate solvent | 60         |
|    |                       | <u>100</u> |

The formulation of the coating composition was:

|    |                         |            |
|----|-------------------------|------------|
| 25 | Hydroxy component (A1)  | 21         |
|    | Black iron oxide        | 13         |
|    | Barytes                 | 26         |
|    | Butyl acetate           | 15         |
| 30 | Anhydride component (B) | 25         |
|    |                         | <u>100</u> |

The ratio of hydroxy groups in component (A1) to anhydride groups in component (B) was approximately 1:1.

The coating composition was sprayed onto a metal substrate using compressed air containing volatile amine catalysts generated using a "Chemidry" apparatus as described in Examples 1 - 3.

The volatile amine catalysts used are listed in Table 2 along with the xylene resistance measured. In all cases a hard, coherent, dry film was produced within six minutes of application.

TABLE 2

| Example No. | Volatile Amine            | Xylene Resistance (double rubs) |         |               |
|-------------|---------------------------|---------------------------------|---------|---------------|
|             |                           | 1 day                           | 2½ days | 4 days        |
| 4           | N,N-dimethyl-aminoethanol | 55                              | 147     | 140           |
| 5           | Di-isopropylamine         | 62                              | 180     | more than 200 |
| 6           | Di-n-propylamine          | 66                              | 193     | more than 200 |

20

Example 7

A coating composition was prepared comprising the hydroxy acrylic copolymer listed as (A1) in Examples 1 - 3 and the anhydride copolymer listed as component (B) in Examples 4 - 6. The composition had the following formulation.

|    |                         |            |
|----|-------------------------|------------|
|    | Hydroxy component (A1)  | 34         |
|    | Titanium dioxide        | 19         |
|    | Butyl acetate           | 6          |
| 30 | Anhydride component (B) | 41         |
|    |                         | <u>100</u> |



The coating composition was sprayed onto a metal substrate using compressed air containing volatile diethylamine catalyst generated using a "Chemidry" apparatus as described in Examples 1 - 3. Hardness and xylene solvent resistance was measured after 1, 7 and 14 days as shown in Table 3.

TABLE 3

|    |                                    | <u>1 day</u> | <u>7 days</u>    | <u>14 days</u>   |
|----|------------------------------------|--------------|------------------|------------------|
| 10 | Xylene resistance<br>(double rubs) | 120          | greater than 200 | greater than 200 |
|    | Pencil hardness                    | B            | HB               | F                |

Example 8

A coating composition was prepared comprising a commercial polyester as the hydroxy component (A) and the anhydride copolymer listed as component (B) in Examples 4-6. The hydroxy component (A) was Desmophen 670 of hydroxyl value 142, and the coating composition had the following formulation.

|    |                          |            |
|----|--------------------------|------------|
| 20 | Hydroxy component (A)    | 17         |
|    | Titanium dioxide pigment | 19         |
|    | Butyl acetate            | 14         |
|    | Anhydride component (B)  | 50         |
| 25 |                          | <u>100</u> |

The coating composition was sprayed onto a metal substrate using compressed air containing volatile diethylamine catalyst generated using a "Chemidry" apparatus as described in Examples 1 - 3. The hardness and xylene resistance of the film as measured after 1, 7 and 14 days is shown in Table 4.

TABLE 4

|                                      | <u>1 day</u> | <u>7 days</u> | <u>14 days</u> |
|--------------------------------------|--------------|---------------|----------------|
| 5 Xylene resistance<br>(double rubs) | 15           | 90            | 140            |
| Pencil hardness                      | 6B           | B             | F              |

CLAIMS

1. A process for coating a surface with a coating composition comprising (A) a hydroxy component having at least two free hydroxy groups and (B) an anhydride component having at least two cyclic carboxylic anhydride groups, at least one of (A) and (B) being a film-forming polymer, characterised in that an atomised liquid mixture of the hydroxy component (A) and the anhydride component (B) is sprayed on the surface and a separately packaged volatile amine is incorporated in the spray.

2. A process according to claim 1, characterised in that the volatile amine is injected into a stream of carrier gas which evaporates the amine and transports it to the spray gun.

3. A process according to claim 1, characterised in that the amine is evaporated or atomised by bubbling a stream of a carrier gas through a bath of the amine and the said stream of carrier gas transports the amine to the spray.

4. A process according to claim 1, characterised in that the amine is evaporated by heating prior to blending with a stream of a carrier gas which transports the amine to the spray.

5. A process according to any of claims 2 to 4, characterised in that the said stream of carrier gas is used to atomise the liquid coating composition comprising hydroxy component (A) and anhydride component (B).

6. A process according to any of claims 1 to 5, characterised in that the amine is dissolved in a volatile solvent.

7. A process according to any of claims 1 to 6, characterised in that the proportion of amine incorporated in the spray is 0.5 to 5% by weight based on the total of the hydroxy component (A) and the anhydride component (B).
- 5 8. A liquid coating composition comprising (A) a hydroxy component having at least two free hydroxy groups and (B) an anhydride component having at least two cyclic carboxylic anhydride groups, at least one of (A) and (B) being a film-forming polymer, and amine groups for catalysing the reaction between the hydroxy groups of component  
10 (A) and the anhydride groups of component (B), characterised in that the amine groups are provided by a separately packaged volatile amine having a boiling point in the range 50 to 300°C.
- 15 9. A coating composition according to claim 8, characterised in that the hydroxy component and the anhydride component are packaged together in a single pack.
- 20 10. A coating composition according to claim 8 or claim 9, characterised in that the volatile amine has a boiling point in the range 50 to 170°C.
11. A coating composition according to any of claims 8 to 10, characterised in that the volatile amine is a tertiary amine optionally containing a hydroxy group or a further amino group.
- 25 12. A coating composition according to any of claims 8 to 10, characterised in that the volatile amine is a secondary amine.
- 30 13. A coating composition according to claim 12 characterised in that the volatile amine is diethylamine, di-n-propylamine, di-n-butylamine, diisobutylamine or diisopropylamine.

14. A coating composition according to any of claims 8 to 10, characterised in that the volatile amine is a primary amine.

15 15. A coating composition according to any of claims 8 to 14, characterised in that the hydroxy component (A) is an acrylic copolymer having pendent hydroxy groups.

16. A coating composition according to any of claims 8 to 14, characterised in that the hydroxy component (A) is a telechelic polymer having hydroxy groups at each end of  
10 the polymer chain.

17. A coating composition according to any of claims 8 to 16, characterised in that the hydroxy component (A) is a hydroxy-functional polymer containing olefinically unsaturated double bonds.

15 18. A coating composition according to any of claims 8 to 16, characterised in that the hydroxy component (A) is a hydroxy-functional polymer containing at least one epoxide group.

19. A coating composition according to any of claims  
20 8 to 18, characterised in that the anhydride component (B) is a copolymer of an olefinically unsaturated cyclic carboxylic acid anhydride with one or more olefinically unsaturated comonomers.

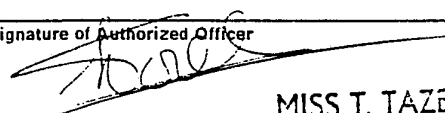
20. A coating composition according to any of claims  
25 8 to 19, characterised in that the composition contains a polyepoxide, the ratio of epoxide groups in the composition to hydroxy groups in the hydroxy component (A) being less than 1:1.

21. A process according to any of claims 1 to 7,  
30 characterised in that the volatile amine is as defined in any of claims 10 to 14.

22. A process according to any of claims 1 to 7 or 21, characterised in that the coating composition is as defined in any of claims 15 to 20.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/00175

|   |   |                                     |
|---|---|-------------------------------------|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>   |   |                                     |
| According to International Patent Classification (IPC) or to both National Classification and IPC<br><b>IPC5: C 09 D 167/02</b>   |   |                                     |
| <b>II. FIELDS SEARCHED</b>  |   |                                     |
| Minimum Documentation Searched <sup>7</sup>   |   |                                     |
| Classification System   | Classification Symbols  |                                     |
| IPC5  | C 09 D  |                                     |
| Documentation Searched other than Minimum Documentation<br>to the Extent that such Documents are Included in Fields Searched <sup>8</sup>                               |   |                                     |
| (Empty space for additional search results)   |   |                                     |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>   |   |                                     |
| Category *  | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>  | Relevant to Claim No. <sup>13</sup> |
| X   | US, A, 4798745 (J.T. MARTZ ET AL.)<br>17 January 1989, see column 4,<br>line 63 - line 64; claims 1,6,14,18,19<br><p style="text-align: center;">--</p>   | 1,8                                 |
| X   | US, A, 4452948 (A.R. MARRION ET AL.)<br>5 June 1984, see claim 1<br>cited in the application<br><p style="text-align: center;">--</p>   | 1,8                                 |
| X   | GB, A, 1444797 (CHEMISCHE WERKE HÜLS<br>AKTIENGESELLSCHAFT) 4 August 1976,<br>see page 2, line 68; page 2, line 84<br><p style="text-align: center;">--</p>   | 1,8                                 |
| * Special categories of cited documents: <sup>10</sup>  |   |                                     |
| "A" document defining the general state of the art which is not considered to be of particular relevance  | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention   |                                     |
| "E" earlier document but published on or after the international filing date  | "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step   |                                     |
| "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. |                                     |
| "O" document referring to an oral disclosure, use, exhibition or other means  | "&" document member of the same patent family   |                                     |
| "P" document published prior to the international filing date but later than the priority date claimed  |   |                                     |
| <b>IV. CERTIFICATION</b>  |   |                                     |
| Date of the Actual Completion of the International Search<br><b>26th April 1990</b>   | Date of Mailing of this International Search Report<br><b>10. 05. 90</b>  |                                     |
| International Searching Authority<br><b>EUROPEAN PATENT OFFICE</b>  | Signature of Authorized Officer<br><br><b>MISS T. TAZELAAR</b>  |                                     |

| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) |  |                      |
|--|--|----------------------|
| Category *   | Citation of Document, with indication, where appropriate, of the relevant passages   | Relevant to Claim No |
| X  | EP, A2, 0134691 (IMPERIAL CHEMICAL INDUSTRIES PLC)<br>20 March 1985, see page 13, line 25;<br>page 13, line 30 - page 14, line 1;<br>claim 1 | 1,8                  |
|  | --   |                      |
| A  | US, A, 4343839 (J.R. BLEGEN) 10 August 1982,<br>see column 2, line 35;<br>claim 1  | 1                    |
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| A  | US, A, 4365039 (J.R. BLEGEN) 21 December 1982,<br>see column 9, line 63 - line 65;<br>claim 1  | 8                    |
|  | --   |                      |
| A  | GB, A, 1583316 (HOECHST AKTIENGESELLSCHAFT)<br>21 January 1981, see page 7, line 31;<br>page 7, line 35; claims 1,10                         | 1,8                  |
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|  | -----  |                      |



ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.PCT/GB 90/00175

SA 34332

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|  |                  | JP-A- 1090267           | 06/04/89         |
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PCT/GB 90/00175  
SA 34332

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The members are as contained in the European Patent Office EDP file on 30/03/90  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent document cited in search report | Publication date | Patent family member(s)        | Publication date     |
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82