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(21) International Application Number: PCT/NL98/00382 (22) International Filing Date: 3 July 1998 (03.07.98) (30) Priority Data: 1006621 18 July 1997 (18.07.97) NL (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): DIAS, Aylvin, Jorge, Angelo, Athanasius [GB/NL]; Sphinxlunet 11f, NL-6221 JD Maastricht (NL). JANSSEN, Johan, Franz, Gradus, Antonius [NL/NL]; Marisstraat 11, NL-6165 AP Geleen (NL). (74) Agent: MOOIJ, Johannes, Jacobus; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HR, HU, ID, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: RADIATION-CURABLE COATING COMPOSITION (57) Abstract <p>The invention relates to a radiation-curable coating composition comprising a radiation-curable resin composition, an aliphatic maleimide and a tertiary amine. The tertiary amine may be aromatic or aliphatic. The invention also relates to an entirely or partly coated substrate characterised in that the radiation-curable coating composition according to the invention has been used as the coating.</p>		

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RADIATION-CURABLE COATING COMPOSITION

5 The invention relates to a radiation-
curable coating composition containing a radiation-
curable resin composition and an aliphatic maleimide.

 Such a radiation-curable coating
composition is described in "Initiator free
10 polymerisations of donor acceptor monomer systems" by
C.E. Hoyle, S. Jonsson, S.C. Clark, C. Miller and M.
Shimose (Radtech Europe, June 97, Lyons). This
describes a coating composition consisting of an
acrylate-functional resin and an aliphatic maleimide.
15 This composition cures under the influence of UV light.

 A drawback of such a coating composition is
that it cures at a low rate.

 The aim of the invention is to provide a
radiation-curable coating composition that has a higher
20 curing rate.

 This aim is achieved according to the
invention because the radiation-curable coating
composition also contains a tertiary amine. This
ensures that the radiation-curable coating composition
25 cures faster under the influence of radiation than the
known radiation-curable coating composition described
by Hoyle et al.

 An advantage of the presence of maleimides
as a photoactive compound is that it contains a
30 reactive bond that can co-react under the radiation
curing conditions. This ensures that in the radiation-
curing process the photoactive compound is incorporated

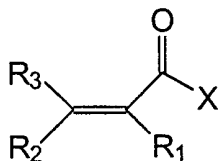
in resin and less residual photoactive compound can migrate. Consequently, the environment of the cured coating is contaminated less with residual photoactive compound.

5 EP-A-618,237 describes a coating composition based on an acrylate-functional resin and maleic anhydride. A drawback of the coating composition described in EP-A-618,237 is that it cures slowly, as a result of which the cured coating may also contain
10 residual monomer in addition to residual photoactive compound. An additional advantage of the radiation-curable coating composition according to the invention is that, when it has been cured, the cured resin contains less residual monomer.

15 Another advantage of the presence of tertiary amines in the radiation-curable coating composition according to the invention is that the curing of the surface in the presence of oxygen is better.

20 The radiation-curable resin composition consists of for example a reactive unsaturation connected to an electron-withdrawing group (a), optionally combined with a reactive unsaturation connected to an electron-donating group (b) or a an
25 allyl group-containing compound connected to an electron-donating group (c) or a mixture hereof (b+c).

 The reactive unsaturation connected to an electron-withdrawing group (a) is characterised by the following structural element.



X may be for example any one of the following groups:

OR₄ , NR₄R₅, SR₄.

- 5 R₁, R₂, R₃, may be for example independently of one another the following groups: H, C₁-C₂₀ alkyl, aryl, substituted aryl, COOR₆, CONR₆R₇, CH₂COOR₆, CH₂OR₆, OR₆, NR₆R₇, SR₆, Cl or CN, in which R₄, R₅, R₆ and R₇ are chosen from the following groups: H, C₁-C₂₀, alkyl
- 10 (including linear and cyclic structures), aryl, substituted aryl, O, S, N or P atoms-containing heterocyclic compounds, O, S, N or P atoms-containing aromatic heterocyclic compounds, COY, CH₂COY, CH₂OY, CH₂NYZ, CH₂SY, CH₂CH₂OY, CH₂CH₂NYZ, CH₂CH₂SY, CH₂CH(CH₃)OY, CH₂CH(CH₃)NYZ, CH₂CH(CH₃)SY, CH(CH₃)CH₂OY, CH(CH₃)CH₂NYZ,
- 15 CH(CH₃)CH₂SY, (CH₂O)_nY, (CH₂NZ)_nY, (CH₂S)_nY, (CH₂CH₂O)_nY, (CH₂CH₂NZ)_nY, (CH₂CH₂S)_nY, (CH₂CH(CH₃)O)_nY, (CH₂CH(CH₃)NZ)_nY, (CH₂CH(CH₃)S)_nY, (CH(CH₃)CH₂O)_nY, (CH(CH₃)CH₂NZ)_nY, (CH(CH₃)CH₂S)_nY, where n is a number ..
- 20 between 1 and 100. Y and Z can for example be chosen from any of the following groups H, C₁-C₂₀, alkyl (including linear and cyclic structures), aryl, substituted aryl, O, S, N or P atoms-containing heterocyclic compounds, O, S, N or P atoms-containing aromatic heterocyclic compounds. Derivatives of these
- 25 compounds can also be used, for example esters, urethanes, urea, thiourethanes and anhydrides.

Preferably use is made of the following

compounds or combinations hereof: acrylates ($X=OR_4$, $R_1=H$, $R_2=H$, $R_3=H$) methacrylates ($X=OR_4$, $R_1=CH_3$, $R_2=H$, $R_3=H$) acrylamides ($X=NR_4R_5$, $R_1=H$, $R_2=H$, $R_3=H$) fumarates ($X=OR_4$, $R_1=H$, $R_2=COOR_6$, $R_3=H$) maleates ($X=OR_4$, $R_1=H$, $R_2=H$, $R_3=COOR_6$) itaconates ($X=OR_4$, $R_1=CH_2COOR_6$, $R_2=H$, $R_3=H$) citraconates ($X=OR_4$, $R_1=CH_3$, $R_2=H$, $R_3=COOR_6$) and mesaconates ($X=OR_4$, $R_1=CH_3$, $R_2=COOR_6$, $R_3=H$) and derivatives hereof such as fumaric amide esters, maleamide esters, fumaric amides. Cyclic structures in which X is connected to R_1 , R_2 or R_3 can also be used. So can derivatives of these compounds, such as esters, urethanes, urea, thiourethanes and anhydrides.

As the reactive unsaturation connected to an electron-donating group (b) use is preferably made of a vinyl ether, a vinyl ester, a vinyl amide, a vinyl amine, a vinyl thioether or a vinyl thioester.

As the allyl group-containing compound connected to an electron-donating group (c) use is preferably made of an allyl ether, an allyl ester, an allyl amine or an allyl amide.

The amount of reactive unsaturation connected to an electron-withdrawing group (a) in the radiation-curable curing resin is between 25% and 100%. The amount of reactive unsaturation connected to an electron-donating group (b) or an allyl group-containing compound connected to an electron-donating group (c) or a mixture hereof (b+c) in the radiation-curable curing resin is between 0% and 75%, depending on the amount of reactive unsaturation connected to an electron-withdrawing group (a) in the radiation-curable curing resin.

According to a preferred embodiment, the amount of reactive unsaturation connected to an electron-withdrawing group (a) in the radiation-curable resin is 100%. According to another preferred
5 embodiment the amount of reactive unsaturation connected to an electron-withdrawing group (a) in the radiation-curable resin is 50% and the amount of reactive unsaturation connected to an electron-donating group (b) or an allyl group-containing compound
10 connected to an electron-donating group (c) or a mixture hereof (b+c) in the radiation-curable resin is 50%.

The reactive unsaturation connected to an electron-withdrawing group (a) may be connected to
15 polymers or oligomers via R_4 . Examples of such polymers or oligomers are polyurethanes, polyesters, polyacrylates, polyethers, polyolefins containing for example units from the group comprising ethylene, propene, butadiene and styrene, hydrocarbon polymers
20 such as (co)polymers of cyclopentadiene, polysilicates, polycarbonates, polyvinyl esters, rubbers such as polyisoprene, natural rubbers and polyepoxides. Copolymers such as polyether urethanes, polyester urethanes, polyether carbonates and polyepoxide esters.
25 Combinations of polymers or oligomers can also be used.

If the reactive unsaturation connected to the electron-withdrawing group (a) has another functionality besides R_4 , in the form of R_1 , R_2 or R_3 ,
30 for example COOR_6 , CONR_6R_7 , CH_2COOR_6 or CH_2OR_6 , the reactive unsaturation can be incorporated in the

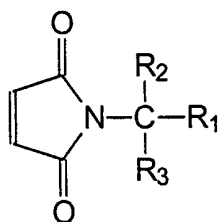
polymer or oligomer chain. Examples of such polymers or oligomers are unsaturated polyesters in which fumarate, maleate, itaconate, citraconate or mesaconate functionalities are incorporated in the structure of the polymer or oligomer. Preferably the number of reactive unsaturations connected to an electron-attracting group in a polymer or oligomer is greater than 1.

The reactive unsaturation connected to an electron-donating group (b) or the allyl group-containing compound connected to an electron-donating group (c) can be bound to the polymers or oligomers described above via ether, ester amine or amide bonds, or, in the case of a bifunctional reactive unsaturation connected to an electron-donating group or a bifunctional allyl compound, it can also be incorporated in a polymer or oligomer chain.

In addition to the reactive unsaturations connected to or in a polymer or oligomer described above, the radiation-curable resin composition may also contain low-molecular compounds containing a reactive unsaturation. These low-molecular compounds contain a reactive unsaturation in the molecule with side groups that may be aromatic, aliphatic or cycloaliphatic. These molecules may furthermore contain several functionalities, i.e. they may be mono- or multifunctional. Examples of this are ethyl acrylate, ethyl methacrylate, methyl methacrylate, hexane diol diacrylate, hexane diol dimethacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, acrylamides such as acrylamide, N-

methyl acrylamide, N-lauryl acrylamide, maleate esters such as ethyl maleate, diethyl maleate, methyl maleate, maleamides such as N,N'-bismaleamide, N,N'-dimethyl maleamide, fumarate esters such as ethyl fumarate, 5 diethyl fumarate, fumaric amides, itaconic esters such as methyl itaconate, dimethyl itaconate, ethyl itaconate, itaconic amides, itaconic imides, citraconic esters such as methyl citraconate, diethyl citraconate, mesaconic esters such as methyl mesaconate, diethyl 10 mesaconate, vinyl ethers such as butyl vinyl ether, ethercyclohexyl ether, triethylene glycol divinyl ether and hydroxybutyl vinyl etherallyl compounds such as allyl alcohol, allyl ether, diallyl ether, allylamine, diallylamine, triallylamine, allyl esters such as acetic 15 allyl ester, adipic diallyl ester and phthalic diallyl ester.

Aliphatic maleimides are characterised in that an aliphatic carbon is connected to the nitrogen atom of the maleimide, as represented in the following 20 structure.



For R₁, R₂, R₃, independently of one another, a choice 25 can be made from for example the group comprising H, C₁-C₂₀ alkyl, aryl, hydroxy, thiol, amines, ethers, thioethers, esters, thioesters, amides, thioamides,

urethanes, thiourethanes and combinations of these functionalities. R_1 , R_2 , R_3 may also form part of ring systems or they may be interconnected in this way, for example so that R_1 - R_2 is C_5H_{10} and R_3 is H, i.e.

5 cyclohexyl maleimide.

The aliphatic maleimide may also contain more than one maleimide group, i.e. a bis, tris, tetra, penta, hexa, etc. maleimide. If the aliphatic maleimide contains more than one maleimide group, these maleimide
10 groups may be connected via a chain comprising exclusively carbon. These maleimide groups may also be connected via other functionalities, such as amines, ethers, thioethers, esters, thioesters, amides, thioamides, urethanes and thiourethanes. The other
15 functionalities may form part of oligo(polymer) chains such as polyethers, polyesters, polyurethane, polyethylene. Combinations of functional groups are also possible here, such as a polyether urethane.

According to a preferred embodiment of the
20 invention use is made of maleimides with hydroxy, ether, ester or urethane functionalities.

According to another preferred embodiment of the invention the aliphatic maleimide contains more than one maleimide group.

25 According to a third preferred embodiment of the invention the aliphatic maleimide contains more than one maleimide group and a hydroxy, ether, ester or urethane functionality or combinations of these functionalities.

30 The amount of maleimide in the present radiation-curable coating composition is not critical.

Preferably the amount of maleimide used in this radiation-curable coating composition is between 0.1 and 15 wt.%, relative to the radiation-curable resin composition. With less than 0.1 wt.% maleimide the radiation-curable coating composition reacts too slowly. With more than 15 wt.% the properties of the cured radiation-curable coating composition are adversely affected.

The tertiary amine may be an aromatic or an aliphatic tertiary amine. An advantage of an aliphatic tertiary amine is that this compound increases the reactivity of the curing reaction to an extra extent while the advantage of an aromatic tertiary amine is that it is much less volatile and is consequently bound better by the cured radiation-curable coating composition.

In addition to the tertiary amine functionality, the tertiary amine may contain other functionalities, for example hydroxy, thiol, ether, ester, nitrile, acrylate, vinyl, urethane and amide functionalities. The tertiary amine may also be a monomer, oligomer or polymer with a tertiary amine functionality. An example of a tertiary amine without other functionalities is triethylamine. Examples of tertiary amines with a hydroxy functionality are N,N-dimethyl ethanol amine, N-methyl diethanol amine (Genocure MDEA, RAHN) and triethanol amine. An example of a tertiary amine with an ether functionality is N-methylmorpholine. Examples of aromatic tertiary amines are 2-ethylhexyl-4-dimethylaminobenzoate (Quantacure EHA, RAHN), ethyl-4-dimethylaminobenzoate (Quantacure

EPD, RAHN), 2-dimethylaminoethylbenzoate (Quantacure DMB, RAHN) and 2-butoxyethyl 4-(dimethylamino)benzoate. Examples of oligomer (polymer) tertiary amines are derivatives of the Jeff amines, Actilane 584 (AKCROS) and Actilane 587 (AKCROS). Examples of tertiary amines with a functionality that can co-react during the radiation curing, such as acrylates or vinyl ether functionalities, are Ebecryl P115 (UCB), Ebecryl 7100 (UCB), Genomer 5248 (RAHN), Genomer 8275 (RAHN), Genomer 5695 (RAHN), Actilane 705 (AKCROS), Actilane 715 (AKCROS), Actilane 735 (AKCROS), diethylaminoethyl vinyl ether (DEAVE, BASF). Derivatives of the tertiary amines mentioned above can also be used, as can mixtures of the tertiary amines mentioned above.

The amount of tertiary amine used in a radiation-curable coating composition is not critical. Preferably the amount of tertiary amine used in a radiation-curable coating composition is between 0.1 and 15 wt.%, relative to the radiation-curable resin composition. With an amount of tertiary amine of less than 0.1 wt. % the reaction rate of the curing reaction decreases substantially. With an amount of tertiary amine of more than 15 wt.% the tertiary amine can no longer be bound entirely in the cured radiation-curable coating composition.

The radiation-curable coating composition according to the invention may also contain additives such as pigments, fillers and matting agents.

In addition to the maleimide/tertiary amine combination described above, the radiation-curable coating composition may also contain other photoactive

compounds. Other photoactive compounds are ketonic and may be aromatic, such as xanthone, thioxanthone and benzophenone. Other examples of suitable aromatic ketones are Darocure 1173 (2-hydroxy-2-methyl-1-phenylpropane-1-one as the active component), Irgacure 184 (hydroxy-cyclohexyl phenyl ketone as the active component), Irgacure 369 (2-benzyl-2-dimethylamino-1-(morpholinophenyl)-butanone-1 as the active component), acylphosphines such as Lucerine TPO (2,4,6-trimethylbenzoyl diphenyl phosphine oxide). Chemical derivatives and combinations of these photoinitiators can also be used.

According to a preferred embodiment of the invention xanthone, thioxanthone and benzophenone and their derivatives are employed as photoactive compounds in combination with the maleimide/tertiary amine combination.

The radiation-curable coating composition can be cured by different kinds of radiation, such as UV and EB radiation.

The most preferred irradiation source is ultraviolet light. Ultraviolet light is preferably high intensity light to provide a dosage to achieve reasonable curing rates. In the event that lower energy light is applied, it may then be desired to subject the compositions also to elevated temperatures in order to reduce the time for adequate polymerisation to occur.

With respect to UV-curing equipment we refer to, for example, pages 161-234 of Chemistry and Technology of UV and EB-formulations, volume 1, Oldring 1991.

Suitable lamps employed to provide the desired high intensity and availability of wavelength and spectral distribution include for example that available from Fusion systems, Corp.

5 The radiation-curable coating composition according to the invention can be used on different substrates, for example glass, paper, wood, plastic, metals such as aluminium and iron.

 The invention will be further elucidated
10 with reference to the following examples without being limited thereto.

 The reactions were followed with the aid of real-time IR spectroscopy; the conversion of the double bonds during the photopolymerisation was followed using
15 an infrared machine (Bruker IFS55). The radiation time required to effect 97 mol.% conversion of the double bonds was taken as the reaction rate.

Experiment I

20 Preparation and curing of a coating composition containing an aliphatic maleimide and an aliphatic tertiary amine

 0.4 grams of N-cyclohexylmaleimide (2%) and 0.4 grams of N,N-dimethylethanolamine (2%) were
25 dissolved in a mixture of 9.2 grams of ethylene glycol methyletheracrylate and 9.2 grams of ethoxylated trimethylolpropane trisacrylate (Mw=450).

 A 10- μ m-thick film was applied to a gold-coated aluminium plate. This plate was subsequently cured in
30 the infrared machine using a dose of 500 mW/cm² and the conversion of the acrylate double bonds was followed. A

97 % degree of conversion was obtained after 5.2 seconds.

Experiment II

5 Preparation and curing of a coating composition
containing an aliphatic maleimide and an aliphatic
tertiary amine

0.4 grams of N-methylmaleimide (2%) and 0.4
grams of N,N-dimethylethanolamine (2%) were dissolved
10 in a mixture of 9.6 grams of ethylene glycol
methyletheracrylate and 9.6 grams of ethoxylated
trimethylolpropane trisacrylate (Mw=450).

A 10- μ m-thick film was applied to a gold-coated
aluminium plate. This plate was subsequently cured in
15 the infrared machine using a dose of 500 mW/cm² and the
conversion of the acrylate double bonds was followed. A
97% degree of conversion was obtained after 8.7
seconds.

20 Comparative example A

Preparation and curing of a coating composition
containing an aliphatic maleimide without a tertiary
amine

0.4 grams of N-cyclohexylmaleimide (2%) was
25 dissolved in a mixture of 9.2 grams of ethylene glycol
methyletheracrylate and 9.2 grams of ethoxylated
trimethylolpropane trisacrylate (Mw=450).

A 10- μ m-thick film was applied to a gold-coated
aluminium plate. This plate was subsequently cured in
30 the infrared machine using a dose of 500 mW/cm² and the
conversion of the acrylate double bonds was followed. A

97 % degree of conversion was obtained after 9.8 seconds.

Comparative example B

- 5 Preparation and curing of a coating composition containing an aliphatic maleimide without a tertiary amine

0.4 grams of N-methylmaleimide (2%) was dissolved in a mixture of 9.6 grams of ethylene glycol methyletheracrylate and 9.6 grams of ethoxylated trimethylolpropane trisacrylate (Mw=450).
A 10- μ m-thick film was applied to a gold-coated aluminium plate. This plate was subsequently cured in the infrared machine using a dose of 500 mW/cm² and the
15 conversion of the acrylate double bonds was followed. A 97% degree of conversion was obtained after 10.4 seconds.

Comparative example C

- 20 Preparation and curing of a coating composition containing an aromatic maleimide and a tertiary amine

0.4 grams of N-phenylmaleimide (2%) and 0.4 grams of N,N-dimethylethanolamine (2%) were dissolved in a mixture of 9.2 grams of ethylene glycol methyletheracrylate and 9.2 grams of ethoxylated trimethylolpropane trisacrylate (Mw=450).
A 10- μ m-thick film was applied to a gold-coated aluminium plate. This plate was subsequently cured in the infrared machine using a dose of 500 mW/cm² and the
25 conversion of the acrylate double bonds was followed. A 97 % degree of conversion was obtained after 171

seconds.

Experiments I and II and the comparative examples A, B and C clearly show that a high degree of conversion is obtained fastest by using the combination
5 of an aliphatic maleimide and a tertiary amine.

experiment III

Preparation and curing of a liquid formulation containing an aliphatic maleimide and an aliphatic

10 tertiary amine

0.1 grams of N-cyclohexylmaleimide(1%) and 0.1 grams of N-methyl diethanol amine was dissolved 9.8 grams of lauryl acrylate. An 100 µm thick film was prepared on a glass plate and irradiated under nitrogen
15 with a total dose of 1J/cm². The irradiated liquid formulation was dissolved in CDCl₃ and the acrylate double bond conversion was analysed by means of 200MHz ¹H-NMR. The acrylate double bond conversions using different lamps are: Fusion F600 H-bulb: 30%; Fusion
20 F600 D-bulb: 22%; Fusion VIP 308: 30%

Comparative example D

Preparation and curing of a liquid formulation containing an aliphatic maleimide without a tertiary

25 amine

0.1 grams of N-cyclohexylmaleimide(1%) was dissolved 9.9 grams of lauryl acrylate. An 100 µm thick film was prepared on a glass plate and irradiated under nitrogen with a total dose of 1J/cm². The irradiated
30 liquid formulation was dissolved in CDCl₃ and the acrylate double bond conversion was analysed by means

of 200MHz ^1H -NMR. The acrylate double bond conversions using different lamps are: Fusion F600 H-bulb: 23%; Fusion F600 D-bulb: 12%; Fusion VIP 308: 17%

Experiment III and comparative example D clearly show that the highest degree of conversion employing the same dose is obtained by using the combination of an aliphatic maleimide and a tertiary amine.

10 Experiment IV

Preparation and curing of a coating composition based on ethoxylated TMPTA containing an aliphatic maleimide and an aliphatic tertiary amine

0.2 grams of N-cyclohexylmaleimide (2%) and 0.2 grams of N,N-dimethylethanolamine (2%) were dissolved in 9.6 grams of ethoxylated trimethylol propane trisacrylate (Mw=607).

A 100- μm -thick film was applied on a glass plate and subsequently cured with a total dose of 1 J/cm² under nitrogen using a Fusion VIP 308 as lamp. After irradiation a cured coating was obtained as indicated with the acetone double rub test. The cured film could withstand 100 acetone double rubs without being affected.

25

Comparative example E

Preparation and curing of a coating composition based on ethoxylated TMPTA containing an aliphatic maleimide without a tertiary amine.

0.2 grams of N-cyclohexylmaleimide (2%) was dissolved in 9.8 grams of ethoxylated trimethylol

propane trisacrylate (Mw=607).

A 100- μ m-thick film was applied on a glass plate and subsequently cured with a total dose of 1 J/cm² under nitrogen using a Fusion VIP 308 as lamp. After

- 5 irradiation the coating was not fully cured as indicated with the acetone double rub test. The coating was completely removed from the glassplate after 60 acetone double rubs.

10 Experiment V

Preparation and curing of a coating composition based on Ebercryl 80 containing an aliphatic maleimide and an aliphatic tertiary amine.

- 0.2 grams of N-cyclohexylmaleimide (2%) and
15 0.2 grams of N,N-dimethylethanolamine (2%) were dissolved in 9.6 grams of Ebercryl 80 (UCB).

A 100- μ m-thick film was applied on a glass plate and subsequently cured with a total dose of 1 J/cm² under nitrogen using a Fusion VIP 308 as lamp. After

- 20 irradiation a cured coating was obtained as indicated with the acetone double rub test. The cured film could withstand 100 acetone double rubs without being affected.

25 Comparative example F

Preparation and curing of a coating composition based on Ebercryl 80 containing an aliphatic maleimide without a tertiary amine.

- 0.2 grams of N-cyclohexylmaleimide (2%) was
30 dissolved in 9.8 grams of Ebercryl 80.

A 100- μ m-thick film was applied on a glass plate and

subsequently cured with a total dose of 1 J/cm^2 under nitrogen using a Fusion VIP 308 as lamp. After irradiation the coating was not fully cured as indicated with the acetone double rub test. The coating was completely removed from the glassplate after 72 acetone double rubs.

Experiment IV and comparative example E as well as Experiment V and comparative example F clearly show that a cured coating is obtained employing the same dose by using the combination of an aliphatic maleimide and a tertiary amine.

Experiment VI

Preparation and curing of a coating composition based on Ebercryl 80 containing an aliphatic maleimide an aliphatic tertiary amine and benzophenone

0.1 grams of N-cyclohexylmaleimide (1%), 0.1 grams of benzophenone (1%) and 0.2 grams of N,N-dimethylethanolamine (2%) were dissolved in 9.6 grams of Ebercryl 80 (UCB).

A 100- μm -thick film was applied on a glass plate and subsequently cured with a total dose of 1 J/cm^2 under nitrogen using a Fusion VIP 308 as lamp. After irradiation a cured coating was obtained as indicated with the acetone double rub test. The cured film could withstand 100 acetone double rubs without being affected.

This example clearly shows that the maleimide/tertiary amine combination can be used in combination with sensitisers like benzophenone.

C L A I M S

1. Radiation-curable coating composition containing a
5 radiation-curable resin composition and an
aliphatic maleimide, characterised in that it also
contains a tertiary amine.
2. Composition according to Claim 1, characterised in
that the amount of aliphatic maleimide in the
10 radiation-curable coating composition is between
0.1 and 15 wt.%, relative to the radiation-curable
resin composition.
3. Composition according to Claim 1 or Claim 2,
characterised in that the amount of tertiary amine
15 in this radiation-curable coating composition is
between 0.1 and 15 wt.%, relative to the
radiation-curable resin composition.
4. Composition according to any one of Claims 1-3,
characterised in that the aliphatic maleimide is
20 an aliphatic maleimide with a hydroxy, ether,
ester or urethane functionality.
5. Composition according to any one of Claims 1-3,
characterised in that the aliphatic maleimide is
an aliphatic maleimide with more than one
25 maleimide functionality.
6. Composition according to any one of Claims 1-3,
characterised in that the aliphatic maleimide is
an aliphatic maleimide with more than one
maleimide group and a hydroxy, ether, ester or
30 urethane functionality or a combination of these
functionalities.

7. Composition according to any one of Claims 1-6, characterised in that the tertiary amine in this radiation-curable coating composition is an aliphatic tertiary amine.
- 5 8. Composition according to any one of Claims 1-6, characterised in that the tertiary amine in the radiation-curable coating composition is an aromatic tertiary amine.
9. Composition according to any of the Claims 1-8
10 characterised in that the maleimid/tertiary amine combination is sensithised with benzophenone, xanthone, thioxanthone and derivatives thereof.
10. Entirely or partly coated substrate, characterised
15 in that the radiation-curable coating composition according to any one of Claims 1-9 has been used as the coating.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 98/00382

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09D4/02 C08F222/40

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 025 409 A (MCGINNISS VINCENT DANIEL) 24 May 1977 see column 6, line 14 - line 33; claims; examples 1,5,7,11 ---	1-3,5,7, 9,10
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 201 (C-1188), 8 April 1994 & JP 06 001944 A (HITACHI CHEM CO LTD), 11 January 1994 see abstract ---	1-10
A	PATENT ABSTRACTS OF JAPAN vol. 005, no. 168 (C-077), 27 October 1981 & JP 56 098245 A (MITSUBISHI GAS CHEM CO INC), 7 August 1981 see abstract --- -/-	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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.

"&" document member of the same patent family

Date of the actual completion of the international search

7 October 1998

Date of mailing of the international search report

19/10/1998

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INTERNATIONAL SEARCH REPORT

Inter nal Application No

PCT/NL 98/00382

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 3 855 180 A (SCHROETER S) 17 December 1974 see claims</p> <p>-----</p>	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 98/00382

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4025409 A	24-05-1977	US 4066523 A US 4035272 A	03-01-1978 12-07-1977
US 3855180 A	17-12-1974	US 3742089 A	26-06-1973