

PATENT SPECIFICATION

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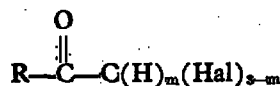


(54) PHOTO-POLYMERISABLE FORMULATIONS

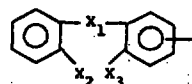
(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to photo-polymerisable formulations and more specifically to such formulations which include a photo-sensitizing agent to initiate and accelerate polymerisation on exposure to light.

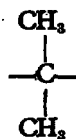
Accordingly, the present invention provides a photo-polymerisable formulation which comprises a photo-polymerisable system in association with a photo-sensitizing amount of a compound of formula I,



wherein R is an unsubstituted or substituted radical of formula a



wherein X₁ is a direct covalent bond or is —O—, —S—, —SO—, —SO₂— or



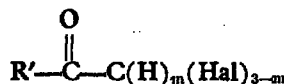
and either X₂ and X₃ are each hydrogen or, when X₁ is a direct covalent bond, X₂ and X₃ together alternatively form one of the bridge members —O—, —S—, —SO— and —SO₂—,

Hal is chlorine or bromine, and m is 0, 1 or 2,

any substituents on the radical of formula a being selected such that the ultraviolet absorption maximum of the resulting compound of formula I lies in the range 250 to 400 nm, especially 270 to 360 nm.

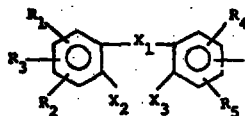
As will be appreciated, the selection of substituents on the radical of formula a forms part of the general knowledge in the photo-sensitizer art.

Preferably, the formulation includes as photo-sensitizing agent a compound of formula Ia



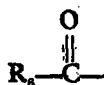
Ia

wherein Hal and m are as defined above
and R' is a radical of formula aa

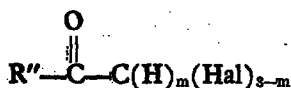


aa

wherein X₁, X₂ and X₃ are as defined above,
each of R₁, R₂, R₄ and R₅, independently, is hydrogen or alkyl (C₁—C₁₈) with a
maximum of 18 carbon atoms in the aggregate of all of the substituents R₁, R₂, R₄
and R₅,
and R₃ is hydrogen, chlorine, bromine, iodine or a radical

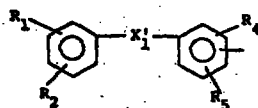


wherein R₆ is —C(H)_m(Hal)_{3-m}
wherein Hal and m are as defined above, furenyl, thienyl, phenyl or phenyl substi-
tuted by an alkyl (C₁—C₄) substituent or 1 or 2 halogen substituents, the or each
halogen substituent being chlorine, bromine or iodine.
More preferably, the formulation includes as photo-sensitizing agent a compound
of formula Ib



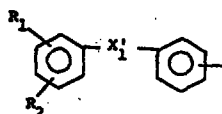
Ib

wherein Hal and m are as defined above
and R'' is a radical of formula ab



ab

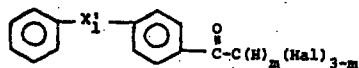
wherein R₁, R₂, R₄ and R₅ are as defined above,
and X₁' is —O— or —S—,
more preferably a radical of formula ab'



ab'

wherein R₁, R₂ and X₁' are as defined above.

In particular, the formulation preferably includes as photo-sensitizing agent a com-
pound of formula Ic



Ic

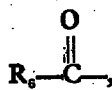
wherein X₁', Hal and m are as defined above.

Of the halogen substituents chlorine, bromine and iodine, chlorine and bromine
are preferred, and chlorine is most preferred.

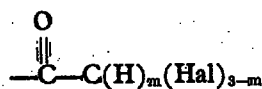
When any of R₁, R₂, R₄ and R₅ are alkyl, this is preferably C₁—C₁₂, more pre-
ferably C₁—C₆, especially C₁—C₃, and in particular C₁—C₄ alkyl, e.g. methyl. Such
alkyl may be straight or branched chain, primary, secondary or tertiary.

Preferably R₄ and R₅ are each hydrogen.

When R₆ is a group



R_6 therein is preferably $-\text{C}(\text{H})_m(\text{Hal})_{3-m}$.
 Preferably R_6 is hydrogen or

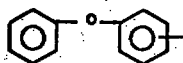


especially hydrogen.

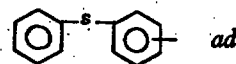
Preferably R_6 , when a substituent, occupies a *para* position in relation to X_1 or, when X_2 forms part of a bridge member, to X_2 .

Preferably the free bond of the radical *a* occupies a *para* position in relation to X_1 or, when X_3 forms part of a bridge member, to X_3 .

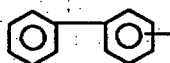
Preferably the unsubstituted or substituted radical of formula *a* has one of the following ring structures, viz.



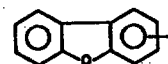
ac



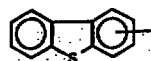
ad



ae



af

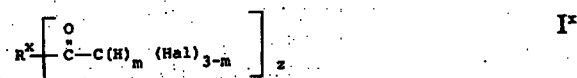


ag

each of which is unsubstituted or substituted, particularly *ac*, *ad*, *ae* and *af*, especially *ac* and *ad*.

Of all the compounds of formula I, 4-dichloroacetyl-, 4-trichloroacetyl-, 4-monochloroacetyl- and 4-dibromoacetyl-diphenyl ether, 4-monochloroacetyl- and 4-dichloroacetyl-diphenyl sulphide, and 4-monochloroacetyl-, 4-dichloroacetyl and 4-trichloroacetyl-diphenyl are the most preferred for the formulations of the present invention.

An interesting class of compounds of formula I for use in the formulations of the present invention is constituted by the compounds of formula I^x,

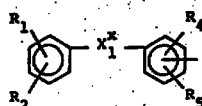


wherein *z* is 1 or 2,

Hal is chlorine or bromine,

m is 0, 1 or 2,

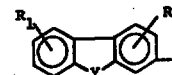
and R^x , when *z* is 1, is a radical of formula



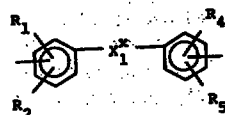
or



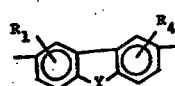
or



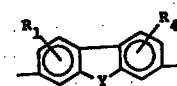
or R^x , when *z* is 2, is a radical of formula



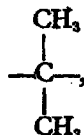
or



or



wherein X_1^2 is a direct covalent bond or is $-O-$, $-S-$, $-SO-$, $-SO_2-$ or



each of R_1 , R_2 , R_4 and R_6 , independently, is hydrogen or alkyl (C_1-C_{18}) with a maximum of 18 carbon atoms in the aggregate of all the substituents R_1 , R_2 , R_4 and R_6 , or R_1 and R_4 , as the case may be,

and Y is $-O-$, $-S-$, $-SO-$ or $-SO_2-$, with the proviso that when X_1^2 is a direct covalent bond, at least one of R_1 and R_2 and at least one of R_4 and R_6 is hydrogen and the free valency (valencies) is (are) on the meta or para position(s) to the point of attachment of the direct covalent bond X_1^2 on the benzene ring(s) to which the valency (valencies) is (are) attached.

The compounds of formula I are generally known. Insofar as they are not known, they may be produced in analogous manner to the processes for producing the known compounds, e.g. by the Friedel-Crafts reaction.

The present invention also provides a method of photo-polymerising a photo-polymerisable system which comprises irradiating said system with ultraviolet light of wave length 250 to 400 nm in the presence of a photo-sensitizing amount of a compound of formula I.

It is to be understood that the terms "photo-polymerising" and "photo-polymerisable" are employed herein in a broad sense to include e.g. cross-linking of polymeric materials, such materials being referred to herein as "prepolymers", as well as simple homo-, co- and terpolymerisation of monomers.

Any of the conventional light sources providing light of wave length 250 to 400 nm may be employed, such as sunlight or actinic light from e.g. a sun ray lamp or mercury arc lamp.

Photo-polymerisable systems suitable for use in the formulations of the present invention are in general known, e.g. in the ultraviolet curable coating and printing ink arts. Such systems are preferably those capable of polymerising by a free radical mechanism and in general the polymerising species is/are unsaturated. The systems may be mono- or multi-component. It is preferred that the system contain at least one multi-functional component, i.e. a component having at least two centres at which polymerisation can occur, to promote photo-initiated cross-linking. In addition, it is preferred that at least one component of the system is an unsaturated carboxylic acid or a derivative thereof, e.g. an ester or acid anhydride, in particular an α,β -unsaturated carboxylic acid such as acrylic or methacrylic acid or a derivative thereof such as an ester or acid anhydride.

Preferably the system is multi-component and more preferably comprises one or more reactive prepolymers selected from unsaturated polyethers, polyesters, polyester-based urethanes and epoxy resins, and saturated or unsaturated such polymers modified by esterification with an unsaturated carboxylic acid, or one or more reactive long chain monomers selected from acryl derivatives of epoxylated unsaturated fatty acids, in association with one or more cross-linking monomers. Preferred reactive prepolymers are acrylated or methacrylated hydroxy-functional polyethers, polyester, polyester-based urethanes and epoxy resins, and unsaturated polyesters. Preferred reactive long chain monomers are acryl derivatives of epoxylated linseed oil. Preferred cross-linking monomers are vinyl and allyl monomers, e.g. styrene, the diallyl ether of trimethylol propane, and vinyl and allyl esters such as vinyl acrylate and diallyl maleate and phthalate, acrylated alcohols, e.g. acrylated phenoxyethyl alcohol, and multi-functional acrylates such as acrylated polyols, e.g. acrylated neopentyl glycol and pentaerythritol.

The photo-polymerisable formulations of the present invention are of particular interest as U.V. curable coatings, e.g. coating lacquers, and printing inks, e.g. offset lithographic printing inks.

For such use, the formulations are preferably of resinous form and contain no or minimal (i.e. less than 1% by weight) non-reactive solvent i.e. solvent which does not react with the constituents of the photo-polymerisable formulation and in which the prepolymer(s) and/or monomer(s) are soluble. In the case of multicomponent systems comprising a reactive prepolymer or long chain monomer and at least one cross-linking monomer, the cross-linking monomer is preferably selected *inter alia* in accordance with the solvent properties thereof to provide the desired viscosity characteristics for the final formulations.

Other agents, e.g. anti-oxidants, pigments and fillers, may also be employed in the above-mentioned formulations.

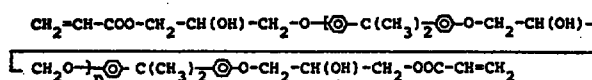
The exact composition of such formulations is not critical and may be varied to suit the intended use.

The amount of photo-sensitizing agent employed in the photo-polymerisable formulations of the invention will vary depending on the proposed use. However, satisfactory results may be obtained when employed in an amount of from 0.01 to 10%, preferably 0.05 to 5%, of the weight of the photopolymerisable system.

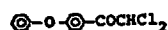
The invention is illustrated by the following Examples wherein parts and percentage are by weight and temperatures are in ° Centigrade.

EXAMPLE 1.

A photo-polymerisable system consisting of 60 g of a prepolymer of the formula



having a viscosity of about 9000 poise at 77°C (cf. U.S. Patent 3,713,864), and 35 g pentaerythritol tetraacrylate and 5 g of a photo-sensitizer of the formula



were applied with a spatula in an amount of 3.5 g/m² to matt art paper and cured in a U.V. Mini-Cure at a belt speed of 71.6 m/min. to give a non-sticky, shiny film.

In analogous manner, the photo-sensitizers set out in the following Tables 1 and 2 are employed.

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TABLE 1

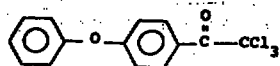
$\text{R}_7\text{-C}_6\text{H}_3\text{-O-C}_6\text{H}_4\text{-C(=O)-C(H)_m(Cl)_{3-m}}$			
Ex. No.	R ₇	R ₈	m
2	H	H	0
3	"	"	2
4	n-C ₆ H ₉	"	0
5	"	"	1
6	CH ₃	CH ₃	0
7	"	"	1
8	"	"	2
9	n-C ₁₂ H ₂₅	"	0
10	"	"	1
11	"	"	2
12	$\text{-C(=O)-C(H)_m(Cl)_{3-m}}$	H	0
13	"	"	1
14	"	"	2
15	Cl	"	1
16	$\text{C}_6\text{H}_5\text{-C(=O)-}$	"	1
17	$\text{C}_6\text{H}_4\text{-C(=O)-}$	"	1
18	$(\text{CH}_3)_3\text{C-C}_6\text{H}_4\text{-C(=O)-}$	"	1
19	$\text{C}_6\text{H}_5\text{-C(=O)-}$	"	1
20	I	"	0
21	"	"	1

TABLE 2

Ex. No.	Formula	Ex. No.	Formula
22		30	
23		31	
24		32	
25		33	
26		34	
27		35	
28		36	
29		37	
		38	
		39	

EXAMPLE 40.

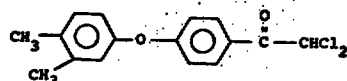
A photo-polymerisable system consisting of 50 parts of the acryl derivative of epoxylated linseed oil (2.9 acryl groups per molecule on average), 20 parts of neopentyl glycol diacrylate and 27 parts of 2-phenoxyethyl acrylate, and 5 parts of a photo-sensitizer of the formula



were applied onto matt art paper and cured in the manner described in Example 1.

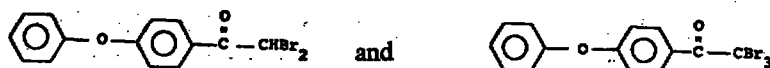
EXAMPLE 41.

100 Parts of a photo-polymerisable system consisting of 67 parts of polyester (produced from maleic anhydride, phthalic anhydride and propane-1,2-diol) and 33 parts styrene, and 3 parts of a photo-sensitizer of the formula



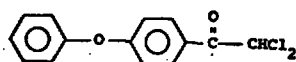
as well as 0.1 parts by weight of paraffin oil, were applied and cured in accordance with the procedure of Example 1.

The Example is repeated employing the photo-sensitizers of the formulae



EXAMPLE 42.

A polymerisable polyester based acrylated urethane system is produced by reacting an hydroxy functional saturated polyester (produced from adipic acid, ethylene glycol and 1,6-hexane-diol) with the reaction product of toluene di-isocyanate and β -hydroxyethyl acrylate. 70 Parts of the resulting system is employed in association with 30 parts of pentaerythritol triacrylate and 3 parts of the photo-sensitizer of the formula



in analogous manner to that described in Example 1.

The Example is repeated employing an unsaturated polyester produced from maleic anhydride, diethylene glycol and 1,3-butylene glycol.

In analogous manner to the procedures described in Examples 40 to 42, the photo-sensitizers of Examples 2 to 39 may be employed.

The compounds employed in the preceding Examples may be produced according to or in analogous manner to the procedure described in Examples A and B below.

EXAMPLE A.

17.0 g of diphenyl ether and 11.3 g chloroacetyl chloride were dissolved in 200 ml of chlorobenzene. To the solution so formed at room temperature and with stirring were added 30 g of aluminium chloride over a period of 2 hours. The reaction mixture was stirred for a further 4 hours at 50°. After cooling, 100 ml of concentrated HCl and 200 ml of ice water were added thereto. The organic phase was separated off, washed with water, and the solvent distilled off. After further washing the compound of Example 3 of Table 1 is obtained. M.P. 55—56°.

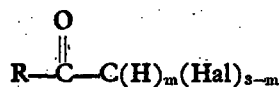
EXAMPLE B.

16.9 g of 4-trichloroacetyl-diphenyl ether were dissolved at 78° in a mixture consisting of 70 ml of acetic acid and 7 ml of water. To the solution so formed, still at 78°, were added successively 1.4 ml concentrated H₂SO₄, 2.1 g HIO₃, and 5.7 g iodine. The reaction was allowed to proceed for 3 hours at 78 to 80°. The light brown reaction mixture was added to 400 ml of water whereby a yellowish oil separated out. The separated oil was taken up in 100 ml of toluene and separated from the aqueous phase. The toluene phase was washed neutral, the solvent distilled off, and the residue recrystallized from isopropanol. The compound of Example 20 of Table 1 was obtained in white crystalline form. M.P. 101—103°.

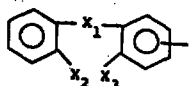
In analogous manner the compound of Example 21 of Table 1 is obtained. M.P. 69—72°.

WHAT WE CLAIM IS:—

1. A photo-polymerisable formulation which comprises a photo-polymerisable system in association with a photo-sensitizing amount of a compound of formula I

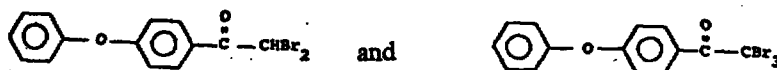


wherein R is an unsubstituted or substituted radical of formula a



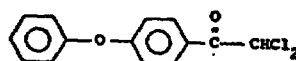
as well as 0.1 parts by weight of paraffin oil, were applied and cured in accordance with the procedure of Example 1.

The Example is repeated employing the photo-sensitizers of the formulae



EXAMPLE 42.

A polymerisable polyester based acrylated urethane system is produced by reacting an hydroxy functional saturated polyester (produced from adipic acid, ethylene glycol and 1,6-hexane-diol) with the reaction product of toluene di-isocyanate and β -hydroxyethyl acrylate. 70 Parts of the resulting system is employed in association with 30 parts of pentaerythritol triacrylate and 3 parts of the photo-sensitizer of the formula



in analogous manner to that described in Example 1.

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In analogous manner to the procedures described in Examples 40 to 42, the photo-sensitizers of Examples 2 to 39 may be employed.

The compounds employed in the preceding Examples may be produced according to or in analogous manner to the procedure described in Examples A and B below.

EXAMPLE A.

17.0 g of diphenyl ether and 11.3 g chloroacetyl chloride were dissolved in 200 ml of chlorobenzene. To the solution so formed at room temperature and with stirring were added 30 g of aluminium chloride over a period of 2 hours. The reaction mixture was stirred for a further 4 hours at 50°. After cooling, 100 ml of concentrated HCl and 200 ml of ice water were added thereto. The organic phase was separated off, washed with water, and the solvent distilled off. After further washing the compound of Example 3 of Table 1 is obtained. M.P. 55—56°.

EXAMPLE B.

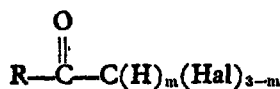
16.9 g of 4-trichloroacetyl-diphenyl ether were dissolved at 78° in a mixture consisting of 70 ml of acetic acid and 7 ml of water. To the solution so formed, still at 78°, were added successively 1.4 ml concentrated H₂SO₄, 2.1 g HIO₃, and 5.7 g iodine. The reaction was allowed to proceed for 3 hours at 78 to 80°. The light brown reaction mixture was added to 400 ml of water whereby a yellowish oil separated out. The separated oil was taken up in 100 ml of toluene and separated from the aqueous phase. The toluene phase was washed neutral, the solvent distilled off, and the residue recrystallized from isopropanol. The compound of Example 20 of Table 1 was obtained in white crystalline form. M.P. 101—103°.

In analogous manner the compound of Example 21 of Table 1 is obtained. M.P. 69—72°.

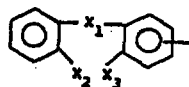
WHAT WE CLAIM IS:—

1. A photo-polymerisable formulation which comprises a photo-polymerisable system in association with a photo-sensitizing amount of a compound of formula I

I



wherein R is an unsubstituted or substituted radical of formula a



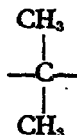


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wherein X_1 is a direct covalent bond or is $-O-$, $-S-$, $-SO-$, $-SO_2-$ or



and either X_2 and X_3 are each hydrogen or, when X_1 is a direct covalent bond, X_2 and X_3 together alternatively form one of the bridge members $-O-$, $-S-$, $-SO-$ and $-SO_2-$,

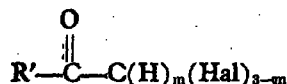
Hal is chlorine or bromine,

and m is 0, 1 or 2,

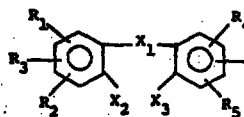
any substituents on the radical of formula a being selected such that the ultraviolet absorption maximum of the resulting compound of formula I lies in the range 250 to 400 nm.

2. A formulation according to Claim 1, comprising a photo-sensitizing amount of a compound of formula Ia

Ia

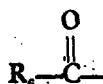


wherein Hal and m are as defined in Claim 1,
and R' is a radical of formula aa



aa

wherein X_1 , X_2 and X_3 are as defined in Claim 1,
each of R_1 , R_2 , R_4 and R_5 , independently, is hydrogen or alkyl(C_1-C_{18}) with a maximum of 18 carbon atoms in the aggregate of all of the substituents R_1 , R_2 , R_4 and R_5
and R_3 is hydrogen, chlorine, bromine, iodine or a radical

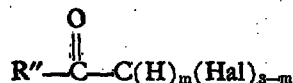


wherein R_6 is $-\text{C}(\text{H})_m(\text{Hal})_{s-m}$

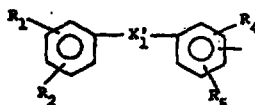
wherein Hal and m are as defined in Claim 1, furenyl, thienyl, phenyl or phenyl substituted by an alkyl(C_1-C_4) substituent or 1 or 2 halogen substituents, the or each halogen substituent being chlorine, bromine or iodine.

3. A formulation according to Claim 2 comprising a photo-sensitizing amount of a compound of formula Ib

Ib



wherein Hal and m are as defined in Claim 2 and R'' is a radical of formula ab



ab

wherein R_1 , R_2 , R_4 and R_5 are as defined in Claim 2 and X_1' is $-O-$ or $-S-$.

4. A formulation according to Claim 3 wherein the radical of formula ab is of formula ab'

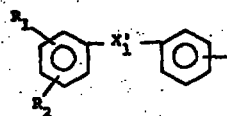
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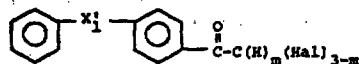


ab'

wherein R_1 , R_2 and X_1' are as defined in Claim 3.

5. A formulation according to Claim 4 comprising a photo-sensitizing amount of a compound of formula Ic

5

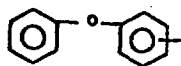


Ic

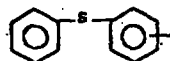
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wherein X_1' is as defined in Claim 4 and Hal and m are as defined in Claim 3.

6. A formulation according to Claim 1 wherein the unsubstituted or substituted radical of formula *a* has one of the ring structures

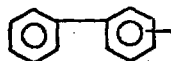


ac

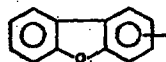


ad

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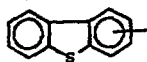
ae



af

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and

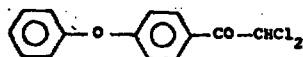


ag

each of which is unsubstituted or substituted.

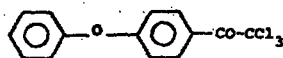
7. A formulation according to Claim 5 comprising a photo-sensitizing amount of a compound of the formula

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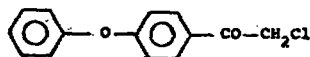
8. A formulation according to Claim 5 comprising a photo-sensitizing amount of a compound of the formula



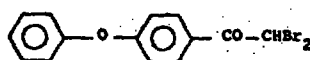
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9. A formulation according to Claim 5 comprising a photo-sensitizing amount of a compound of the formula

20



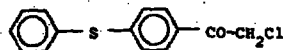
10. A formulation according to Claim 5 comprising a photo-sensitizing amount of a compound of the formula



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11. A formulation according to Claim 5 comprising a photo-sensitizing amount of a compound of the formula

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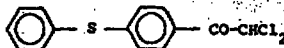
* C L N S *

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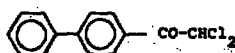
12. A formulation according to Claim 5 comprising a photo-sensitizing amount of a compound of the formula



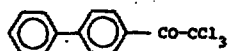
13. A formulation according to Claim 2 comprising a photo-sensitizing amount of a compound of the formula



14. A formulation according to Claim 2 comprising a photo-sensitizing amount of a compound of the formula



15. A formulation according to Claim 2 comprising a photo-sensitizing amount of a compound of the formula



16. A formulation according to any preceding claim, in which the photo-polymerisable system comprises at least one multi-functional component to promote photo-initiated cross-linking.

17. A formulation according to any preceding claim, in which at least one of the components of the photo-polymerisable system comprises an unsaturated carboxylic acid or a derivative thereof.

18. A formulation according to Claim 17, in which the unsaturated carboxylic acid or derivative thereof is acrylic or methacrylic acid or a derivative thereof.

19. A formulation according to any preceding claim, in which the polymerisable system comprises one or more reactive prepolymers selected from unsaturated polyethers, polyesters, polyester-based urethanes and epoxy resins, and saturated or unsaturated such polymers modified by esterification with an unsaturated carboxylic acid, or one or more reactive long chain monomers selected from acryl derivatives of epoxylated unsaturated fatty acids, in association with one or more cross-linking monomers.

20. A formulation according to Claim 19, in which the reactive prepolymers are selected from acrylated or methacrylated hydroxy-functional polyethers, polyesters, polyester-based urethanes, polyester-based epoxy resins and unsaturated polyesters.

21. A formulation according to Claim 19 or Claim 20, in which the reactive long chain monomers are selected from acryl derivatives of epoxylated linseed oil.

22. A formulation according to any one of Claims 19 to 21, in which the cross-linking monomers are selected from vinyl and allyl monomers, acrylated alcohols and multi-functional acrylates.

23. A formulation according to Claim 22, in which the cross-linking monomers are selected from styrene, the diallyl ether of trimethylol propane, vinyl acrylate, diallyl maleate, diallyl phthalate, acrylated phenoxyethyl alcohol, acrylated neopentyl glycol and acrylated pentaerythritol.

24. A formulation according to any preceding claim in the form of an ultraviolet curable coating or printing ink resin containing no or less than 1% by weight of non-reactive solvent.

25. A formulation according to any preceding claim, in which the amount of the compound of formula I present is from 0.01 to 10% of the weight of the photo-polymerisable system.

26. A formulation according to Claim 25, in which the amount is from 0.05 to 5% of the weight of the photo-polymerisable system.

27. A formulation according to Claim 1, substantially as described herein with reference to any one of Examples 1 to 42.

28. A method of photo-polymerising a photo-polymerisable system which comprises irradiating said system with ultraviolet light of wave-length 250 to 400 nm in the presence of a photo-sensitizing amount of a compound of formula I as defined in Claim 1.



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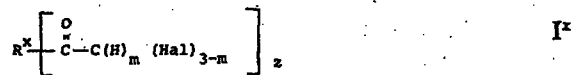
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29. A method according to Claim 28 substantially as described herein with reference to any one of Examples 1 to 42.

30. A polymer whenever produced by the method of Claim 28 or Claim 29.

31. A formulation according to Claim 1 comprising a photo-sensitizing amount of a compound of formula I^x,

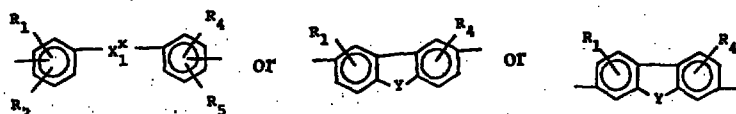


wherein z is 1 or 2,

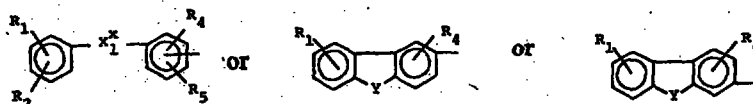
Hal is chlorine or bromine,

m is 0, 1 or 2,

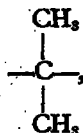
and R^x, when z is 1, is a radical of formula



or R^x, when z is 2, is a radical of formula



wherein X₁^x is a direct covalent bond or is —O—, —S—, —SO—, —SO₂— or



each of R₁, R₂, R₄ and R₅, independently, is hydrogen or alkyl(C₁—C₁₈) with a maximum of 18 carbon atoms in the aggregate of all the substituents R₁, R₂, R₄ and R₅, or R₁ and R₅, as the case may be,

and Y is —O—, —S—, —SO— or —SO₂—, with the proviso that when X₁^x is a direct covalent bond, at least one of R₁ and R₂ and at least one of R₄ and R₅ is hydrogen and the free valency (valencies) is (are) on the meta or para position(s) to the point of attachment of the direct covalent bond X₁^x on the benzene ring(s) to which the valency (valencies) is (are) attached.

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