1 580 968

PATENT SPECIFICATION

(11) 1 580 968

(21) Application No. 15288/77 (22) Filed 13 April 1977
(61) Patent of Addition to No. 1431224 dated 27 June 1973
(31) Convention Application No. 2616408
(32) Filed 14 April 1976 in
(33) Federal Republic of Germany (DE)
(44) Complete Specification published 10 Dec. 1980
(51) INT CL^3 C08F 2/50
(52) Index at acceptance
C3P 406 408 414 528 538 540 544 HL
C3W 201 215 225 228
C3Y B240 B241 B390 B391 B393 F530 H660 H670

(19) THE PATENT OFFICE LONDON

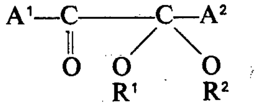
(54) COMPOSITIONS POLYMERIZABLE BY UV IRRADIATION

(71) We, BASF AKTIENGESELLSHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, 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:—

Our UK Patent Specification No. 1,431,224 describes and claims compositions, polymerizable by UV irradiation, comprising one or more compounds having at least one polymerizable carbon-carbon multiple bond, or of mixtures containing such compounds, and a photoinitiator, with or without conventional additives, wherein the photoinitiator is a cyclic monoketal of an aromatic 1,2-diketone. The use of symmetrical non-cyclic ketals of aromatic diketones as photoinitiators for such a purpose is also disclosed in UK Patent Specification No. 1,406,467.

We have now found new non-cyclic unsymmetrical monoketals of aromatic 1,2-diketones which are easily manufactured and are sufficiently stable in polymerizable mixtures or compositions under conventional processing and storage conditions, but exhibit a high reactivity when the compositions are cured by irradiation, and at the same time cause exceptionally little yellowing of the compositions.

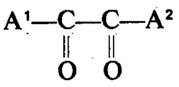
Accordingly, the present invention provides a composition polymerizable by UV irradiation, of (a) a photopolymerizable compound with at least one polymerizable carbon-carbon double bond, or a mixture of two or more such compounds, and (b) a photoinitiator which is a monoketal of an aromatic 1,2-diketone, wherein the monoketal of an aromatic 1,2-diketone is a non-cyclic unsymmetrical monoketal of the formula (I)



$$\mathrm{A^1-\underset{\underset{O}{\|}}{C}-\underset{O R^1\quad O R^2}{C}-A^2} \qquad (I)$$

where A^1 and A^2 are identical or different aromatic radicals which may or may not be substituted, and R^1 and R^2 are different radicals selected as defined below.

Non-cyclic unsymmetrical monoketals of aromatic 1,2-diketones of this type have not previously been explicitly disclosed. The new photoinitiators contains in the present compositions can be manufactured in a simple and advantageous manner (as described and claimed in our copending UK Patent Application No. 1,5287/77) by reacting the aromatic 1,2-diketones on which they are based (formula II)



$$\mathrm{A^1-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-A^2} \qquad (II)$$

in an organic solvent, with an alkylating agent $(R^1)_nX$ and an alcoholate $(R^2O)_mMe$, where R^1 and R^2 have the meanings given below, n and m are integers from 1 to 3, X is a monobasic, dibasic or tribasic acid radical and Me is a non-transition metal from group 1, 2 or 3 of the periodic table of the elements.

Particularly suitable aromatic diketones of the formula II are those where A^1 and A^2 are substituted benzene radicals, suitable substituents being, above all, hydrocarbon radicals of 1 to 10 carbon atoms, e.g. alkyl or phenyl, alkoxyalkyl of 2 to 10 carbon atoms, alkoxy of 1 to 10 carbon atoms, alkylthio of 1 to 6 carbon atoms or halogen.

Examples of aromatic 1,2-diketones from which a monoketal of the formula I may be derived are benzil and substituted benzils e.g. 4,4'-dimethylbenzil, 4,4'-diisopropylbenzil, 4,4'-diphenylbenzil, 2,2'-dimethyoxybenzil, 4,4'-dimethoxybenzil, 4-methylbenzil, 3-methoxybenzil, 2,2'-dimethylbenzil, 4-chloro-4'-phenylbenzil 4,4'-dichlorobenzil, 3,3'-dibromobenzil, 2,4,2',4'-tetramethylbenzil, 2,4,6-trimethylbenzil and 2,4-dichloro-4'-methylbenzil. The manufacture of these benzil derivatives is described in the literature and may be effected, for example, by oxidizing the corresponding benzoins.

Suitable alkylating agents for the manufacture of the unsymmetrical monoketals have the above formula $(R^1)_nX$ and are esters of monobasic, dibasic or tribasic acids, especially of acids containing a sulfur atom, a phosphorus atom or a halogen atom. Examples are the esters of sulfuric acid, of sulfurous acid, of phosphoric acid and of phosphorous acid, R^1 halides, e.g. the chlorides, bromides and iodides (which can be considered to be esters of hydrohalic acids), and esters of the aliphatic and aromatic sulfonic acids, e.g. the mesylates, tosylates, brosylates and benzenesulfonates. The sulfates, halides and sulfonates are particularly suitable, and amongst these the sulfates and bromides are used preferentially. Specific examples of alkylating agents are dimethyl sulfate, diallyl sulfate, dicrotyl sulfate, benzyl bromide or allyl bromide.

The radical R^1 in the monoketals to be used in the compositions according to the invention and consequently in the alkylating agents used for their manufacture is selected from alkyl of 1 to 6 carbon atoms, aralkyl of 7 to 9 carbon atoms, alkenyl of 3 to 5 carbon atoms, aralkenyl of 9 or 11 carbon atoms, $Z—(CHR^3—CHR^4)_p—$ and $Z—(CHR^3)_p—$, where p is a number from 1 to 3, R^3 and R^4 are H or CH_3 and Z is halogen, OR^5, SR^5, OAr or SAr where R^5 is alkyl of 1 to 4 carbon atoms or alkoxyalkyl of up to 5 carbon atoms and Ar is phenyl.

The radical R^2 in the monoketals to be used in the compositions according to the invention and consequently in the alcoholates $(R^2O)_mMe$ used for their manufacture does not correspond to, i.e. is different from, the radical R^1 in the alkylating agent used, and moreover R^1 and R^2 are not simultaneously both selected from alkyl of 1 to 6 carbon atoms, $R^5O—(CHR^3—CHR^4)_p—$ and $R^5O—(CHR^3)_p$ where R^3, R^4, R^5 and p have the above meanings. Thus, for example, sodium methylate is used as an alcoholate when using benzyl or allyl bromide as an alkylating agent. In other respects, the above statement regarding the nature of the radical R^1 applies to the nature of the radical R^2, i.e. the two radicals are selected from the same list of alternatives. The alcoholates of sodium and potassium are preferred.

Examples of organic solvents for the manufacture of the monoketals are aromatic solvents, e.g. benzene or toluene, and especially dimethylformamide and dioxane.

Theoretically, to manufacture the monoketals, 1/n mole of alkylating agent of the above formula $(R^1)_nX$ is reacted with 1 mole of 1,2-diketone and 1/m mole of alcoholate of the above formula $(R^2O)_mMe$, with n and m in the fractions corresponding to the numbers n and m, respectively, in the formulae of the alkylating agent and alcoholate used, in order to produce the unsymmetrical monoacetals of the aromatic 1,2-diketones. In general it is however preferred to use some of the reactants in excess in order to achieve complete conversion. Thus, from 1/n to 10/n mole or more, preferably from 1/n to 4/n mole, of alkylating agent, and from 1/m to 10/m mole or more, preferably from 1/m to 4/m mole, of alcoholate can be used per mole of 1,2-diketone. A particularly preferred possible method of working up the reaction solution is to remove the solvent from the reaction mixture, after addition of water, by azeotropic distillation. After this distillation the water-insoluble monoketal separates out, especially on cooling, as a crystalline substance or as an oil, often in an analytically pure or virtually analytically pure form.

Compositions within the invention advantageously contain from 0.01 to 10, and preferably from 0.05 to 4% by weight, based on the photopolymerizable compound(s), or its or their mixtures with compatible polymeric binder(s), of the said monoketal of a 1,2-diketone.

All compounds, possessing at least one carbon-carbon double bond, which, when mixed with the photoinitiator, can be caused to undergo polymerization with UV radiation, may be used in the present compositions. Compounds and materials possessing carbon-carbon double bonds, which are activated by, for example, aryl, carbonyl, amide, ester, carboxyl or cyanide groups, halogen atoms or other carbon-carbon double bonds, or carbon-carbon triple bonds, are very suitable. Examples include styrene, vinyltoluene, acrylic acid and methacrylic acid, and their esters, cyanides or amides, e.g. acrylamide, N-methylolacrylamide, diethers obtained from 1 mole of glycol and 2 moles of N-methylolacrylamide, methyl methacrylate, methylene-bis-acrylamide, m-phenylene-bis-acrylamide or m-xylylene-bis-acrylamide, as well as diurethanes with at least two acrylic or methacrylic groups.

To the photopolymerizable compounds, the choice of which, for each particular application of the compositions, is readily made by those skilled in the art, may be added in the conventional way, compatible unsaturated and/or saturated polymers as binder and/or conventional additives, such as thermal polymerization inhibitors, e.g. hydroquinone or tert.-butylhydroquinone, skin-forming materials, e.g. paraffin, flow control agents, e.g. silicone oil, fillers and/or pigments or dyes, in the conventional amounts. Such mixtures are known to those skilled in the art, and the nature and amount of the additives depend in particular on the manner in which the mixtures are to be used.

The new photoinitiators have proved of particular value in unsaturated polyester resins for the manufacture of coatings curable by UV radiation. Suitable compositions based on unsaturated polyester resins comprise, for example, a mixture of (1) from 40 to 85 percent by weight of a conventional unsaturated polyester, (2) from 60 to 15 percent by weight of one or more copolymerizable olefinically unsaturated monomers and (3) from 0.5 to 5 percent by weight, based on the amount of (1) and (2) of the said monoketals of the 1,2-diketones as photoinitiator, and optionally (4) further conventional additives.

Suitable unsaturated polyesters (1) are the conventional polycondensation products of polybasic, especially dibasic, carboxylic acids, linked by ester bonds to polyhydric, especially dihydric, alcohols; these polyester binders may in addition contain radicals of monobasic carboxylic acids and/or radicals of monohydric alcohols and/or radicals of hydroxycarboxylic acids.

Suitable olefinically unsaturated monomeric compounds (2) for the unsaturated polyester resins are all conventional monomeric compounds copolymerizable with unsaturated polyesters, especially vinyl-aromatics, e.g. styrene, and esters of acrylic acid or methacrylic acid with alkanols of 1 to 8 carbon atoms, e.g. tert.-butyl acrylate or methyl methacrylate, as well as mixtures of these monomers. The preferentially used mixtures contain from 60 to 15, preferably from 50 to 25, percent by weight of component (2), the percentage being, based on the sum of the amounts of components (1) and (2).

The new photoinitiators may also be used with advantage in photopolymerizable compositions which are used for the manufacture of optical information-fixing systems, especially for the manufacture of photopolymer printing plates or of photo-resist coating. For use in the manufacture of an optical information-fixing system, compositions are particularly suitable which comprise in addition to the photoinitiator at least one monomer having at least two photopolymerizable carbon-carbon double bonds or a mixture of compounds which have at least one photopolymerizable carbon-carbon double bond which mixture contains at least 50 percent by weight based on the mixture, of one or more monomers having at least two photopolymerizable carbon-carbon double bonds, and a compatible polymer.

For these purposes, suitable compositions with compounds with at least one polymerizable carbon-carbon double bond are mixtures of (a) from about 10 to 60, preferably from 15 to 35, percent by weight of monomers having predominantly (as explained in the preceding sentence) at least two photopolymerizable carbon-carbon double bonds, e.g. diacrylates or dimethacrylates of aliphatic diols, bis-acrylamides and bis-methacrylamides of aliphatic or aromatic diamines of 2 to 8 carbon atoms, or monomers which in addition to at least two acrylic or methacrylic groups contain ester, amide, urethane or urea groups, with (b) from 90 to 40, preferably from 85 to 65, percent by weight of compatible polymers which are soluble in an organic solvent, e.g. an alcohol, ketone or ether, the percentages being based on the total weight of monomer and compatible polymer. Examples of compatible polymers suitable as binders are copolyamides, e.g. those obtained from ε-caprolactam, hexamethylenediammonium adipate and p,p'-diaminodicyclohexylmethane adipate, as well as soluble polyurethanes, polyureas, butadiene or isoprene copolymers, including block copolymers such as the polystyrene-polyisoprene-polystyrene block copolymers, or cellulose derivatives soluble in organic or alkaline aqueous solvents.

Further information regarding the choice of suitable monomers and/or polymers and/or mixtures, and regarding their processing, is adequately provided, for those skilled in the art, in the published patent literature.

Particularly advantageous radiation sources for the light which initiates the photopolymerization or photocrosslinking of the mixtures are those which emit light having a wavelength of from 230 to 450 nm. Above all, radiation sources with emission maxima in the range of from 300 to 380 nm, or sources which emit a sufficiently high proportion of their light in this wavelength range, may be used. Mercury medium pressure lamps are particularly suitable, but mercury high pressure and low pressure lamps and superactinic fluorescent tubes may also be used. The said lamps may or may not be doped.

Compositions within the invention, containing the new photoinitiators, may be used for the production of coatings, especially coatings based on polyester resins, inter alia for the manufacture of photopolymer printing plates, the manufacture of holograms, photoresist coatings and poromer hides, for information-fixing in general, and for UV-curable printing inks. Compared to compositions containing symmetrical benzil monoketals of the type of benzil dimethylketals the present compositions are distinguished by less yellowing of the cured compositions.

In the Examples which follow, parts and percentages are by weight. Parts by volume bear the same relation to parts as that of the liter to the kilogram.

EXAMPLE 1

21.6 parts of sodium methylate are added in portions in the course of 3 hours to a solution of 52.5 parts of benzil and 68.4 parts of benzyl bromide in 400 parts by volume of dimethylformamide at room temperature, whilst stirring. The reaction mixture is then stirred for 30 minutes at room temperature, after which it is stirred into 2,000 parts by volume of water. The precipitate which separates out is filtered off, washed with water and dried. It is then suspended in 150 parts by volume of petroleum ether, filtered off, washed once with petroleum ether and dried. 62.0 parts of benzil methyl-benzyl-monoketal of melting point 83—84°C are obtained.

EXAMPLE 2

48 parts of sodium methylate are added in portions, in the course of 2.5 hours, to a solution of 105 parts of benzil and 121 parts of allyl bromide in 500 parts by volume of dimethylformamide at room temperature, whilst stirring. After adding 2,000 parts by volume of water, the reaction mixture is extracted with four times 100 parts by volume of chloroform and the combined chloroform extracts are then washed with three times 200 parts by volume of water. The chloroform phase is concentrated on a rotary evaporator and the residue is then distilled under reduced pressure. 115 parts of benzil methyl-allyl-monoketal, boiling at 135—136°C/0.3 mm Hg. are obtained.

EXAMPLE 3

Benzil methyl-crotyl-monoketal of boiling point 140—145°C/0.3 mm Hg, is prepared by the method described in Example 2. Yield: 119 parts (80% of theory).

EXAMPLE 4

An unsaturated polyester is prepared by esterifying 431 parts of maleic anhydride and 325 parts of phthalic anhydride with 525 parts of 1,2-propylene glycol. After adding 0.01% of hydroquinone, a 66% strength solution of the polyester in styrene is prepared (solution A).

3 parts of photoinitiator are added to 97 parts of solution A (giving solution B). The shelf life (gel time) of this mixture is determined at 60°C, in the absence of light. For the photo-curing experiments, 10 parts of a 1% strength solution of paraffin (softening range 50—52°C) in styrene are added to 100 parts of solution B and the resin is applied, by means of a film spreader (500 μm gap width) onto hard fiberboard coated with photographic paper. After being allowed to evaporate in air for about 2 minutes, the films are exposed to fluorescent lamps (emitting a high

proportion of UV light), placed at a distance of 4 cm. The rate of curing is determined by measuring the König pendulum hardness (DIN 53,157) and is summarized in Table 1 together with the color measurements obtained on the cured films.

TABLE 1

Photoinitiator	Pendulum hardness after minutes 4	8	10	Color measurement of the films: yellowness index after exposure	Shelf life at 60°C (hours)
benzil methyl-benzyl-monoketal	90	104	108	18.5	78
benzil methyl-allyl-monoketal	62	92	99	13.8	56—71
benzil methyl-crotyl-monoketal	74	98	104	11.6	not measured
benzil dimethyl-monoketal	92	105	108	21.1	80—105

EXAMPLE 5

A reaction product of 1 mole of bisphenol-A diglycidyl ether with 2 moles of acrylic acid is dissolved in butanediol diacrylate to give a 65% strength solution. 3 percent by weight of the photoinitiators listed in Table 2 and 3 are added to this solution. 80 μm thick layers of the clear finishes are knife-coated onto white photographic paper and irradiated by means of a mercury high pressure lamp having an output of 80 watt/cm of arc length. The distance between the lamp and the surface-coating film is 10 cm. The samples are caused to travel under the UV lamp on a conveyor belt of continuously variable speed. The speed of travel of the conveyor belt (in m/min) at which scratch-resistant curing of the surface-coating films is just still attainable, is determined.

Scratch-resistant curing means that vigorously rubbing the surface of the coating with a fingernail does not break the film surface. The degree of whiteness of samples which have been cured whilst travelling at 11 m/min is also determined, by Berger's method.

TABLE 2

Photoinitiator	Maximum curing speed (m/min)	Whiteness x) (by Berger's method)
benzoin n-butyl ether	16	93.3
p-tert.butyl-trichloro-acetophenone	16	94.0
benzil dimethyl-ketal	24	92.7
benzil methyl-benzyl-ketal	24	94.0

x) higher values indicate less yellowing.

After 5 days' storage at 20°C and 65°C, the clear finishes, mixed with photoinitiators, are retested (see Table 3)

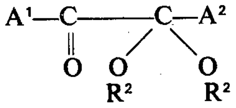
TABLE 3

Photoinitiator	Maximum curing speed in m/min after 5 days' storage at 20°C	65°C
benzoin n-butyl ether	14	prematurely polymerized
p-tert.butyl-trichloro-acetophenone	16	no curing
benzil dimethyl-ketal	24	24
benzil methyl-benzyl-ketal	24	24

WHAT WE CLAIM IS:—

1. A composition capable of being polymerized by UV irradiation which composition comprises a photopolymerizable compound having at least one

polymerizable carbon-carbon double bond or a mixture of two or more such compounds and a photoinitiator which is a monoketal of an aromatic 1,2-diketone wherein the photoinitiator is a non-cyclic unsymmetrical monoketal of the formula



where A^1 and A^2 are identical or different aromatic radicals which are optionally substituted and R^1 and R^2 are different radicals one of which is selected from aralkyl of 7 to 9 carbon atoms, alkenyl of 3 to 5 carbon atoms, aralkenyl of 9 or 11 carbon atoms, $Z—(CHR^3—CHR^4)_p—$ and $Z—(CHR^3)_p—$ where p is a number from 1 to 3, R^3 and R^4 are H or CH_3 and Z is halogen, SR^5, OAr or SAr, R^5 being alkyl of 1 to 4 carbon atoms or alkoxyalkyl of up to 5 carbon atoms and Ar being phenyl, and the other of which is selected from any of the above radicals, alkyl of 1 to 6 carbon atoms and $Z—(CHR^3—CHR^4)_p—$ and $Z—(CHR^3)_p—$ where Z is OR^5 and p, R^3, R^4 and R^5 have the above meanings.

2. A composition as claimed in claim 1, wherein, in the formula of the monoketal, A^1 and A^2 are identical or different benzene radicals substituted by one or more substituents selected from hydrocarbon radicals of 1 to 10 carbon atoms, alkoxyalkyl radicals of up to 10 carbon atoms, alkoxy of 1 to 10 carbon atoms, alkylthio of 1 to 6 carbon atoms or halogen.

3. A composition as claimed in claim 1 or 2, wherein the monoketal is benzyl methyl-benzyl-monoketal, benzyl methyl-alkyl-monoketal or benzyl methyl-crotyl-monoketal.

4. A composition as claimed in any of claims 1 to 3, wherein the monoketal is present in an amount of 0.01% to 10% by weight based on the weight of the photopolymerizable compound(s) or its or their mixtures with polymeric binder(s).

5. A composition as claimed in any of claims 1 to 3, wherein the monoketal is present in an amount of from 0.05% to 4% by weight based on the weight of the photopolymerizable compound(s) or its or their mixtures with polymeric binder(s).

6. A composition as claimed in any of claims 1 to 5 for use in the manufacture of an optical information-fixing system, also including (1) at least one monomer having at least two photopolymerizable carbon-carbon double bonds or a mixture of compounds which have at least one photopolymerizable carbon-carbon double bond which mixture contains at least 50% by weight based on the mixture of one or more monomers having at least two photopolymerizable carbon-carbon double bonds, and (2) a compatible polymer.

7. A composition as claimed in claim 6, comprising from 10 to 60% by weight of monomer material having at least two double bonds and from 90 to 40% by weight of compatible polymer material soluble in an organic solvent, based on the total weight of monomer and compatible polymer.

8. A composition as claimed in any of claims 1 to 5, for use as a coating composition curable by UV radiation also including an unsaturated polyester and a copolymerizable monomer having at least one polymerizable carbon-carbon double bond.

9. A composition as claimed in claim 11 when appendant to any one of claims 1 to 4, comprising (a) of from 40% to 85% by weight of an unsaturated polyester, (b) 60% to 15% by weight of one or more copolymerizable olefinially unsaturated monomers and from 0.5% to 5% by weight, based on the amounts of the mixture of (a) and (b), of the photoinitiator.

10. A composition as claimed in claim 1 and substantially as hereinbefore described in the foregoing Example 4 or 5.

11. A pre-sensitized plate for use in preparing a photopolymer printing plate and comprising a substrate having on a surface thereof a layer of a photopolymerizable composition as claimed in claim 6 or 7.

12. A photopolymer printing plate or photoresist coated material made by a process in which a composition as claimed in claim 6 or 7 is employed as photopolymerizable composition.

J. Y. & G. W. JOHNSON,
Furnival House,
14—18 High Holborn,
London, WC1V 6DE,
Chartered Patent Agent,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.