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54 **Use of esters or amides of benzoylbenzoic acids as photoinitiators and photopolymerisable composition containing them.**

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Use of esters or amides of benzoylbenzoic acids as photoinitiators and photopolymerisable composition containing them

This invention relates to photopolymerizable compositions and to a method employing same. More particularly, this invention relates to the use of certain benzoyl benzoates as photoinitiators for ethylenically unsaturated compounds.

5 Photopolymerization of unsaturated compositions wherein a photoinitiating compound is included in the polymerizable mass is well known in the art. The process has many advantages over thermal polymerization and is particularly useful where long holding life combined with rapid hardening at low temperature is desirable. Photoinitiating compounds must absorb light and utilize the energy so acquired to initiate polymerization.

10 A large number of compounds have been found useful as photoinitiators for the polymerization of unsaturated compounds. Among those heretofore in most common usage in industry are the benzoin ethers of primary and secondary alcohols such as methyl alcohol, ethyl alcohol and isobutyl alcohol.

15 While particular industrial applications often dictate certain requisite characteristics, the primary determinants of universal application in the selection of a suitable photoinitiating compound are its level of reactivity and its effect upon storage stability when combined with the photopolymerizable medium wherein it is to function. This latter characteristic is significant in view of the desirability of one-component systems which will not gel prior to use.

20 While compounds in common use as photoinitiators do effect rates of polymerization which are industrially acceptable and render photopolymerization superior to thermal polymerization in various applications, methods of achieving increased polymerization rates with increased stability are constantly being sought. Improved photoinitiators are particularly desirable since photopolymerization techniques are gaining increasingly widespread acceptance due to the inherently lower equipment costs, reduction of volatile emissions and reduced energy consumption which attend their use.

25 Thus, the ethers of benzoin, which are widely used as photoinitiating compounds, are not wholly satisfactory with regard to the one-component system storage stability factor. Any unsaturated system to which a benzoin ether is added has considerably diminished dark storage stability and will gel prematurely. Various attempts have been made to remedy this deficiency of the benzoin compounds by including stabilizing additives in the polymerization system. Thus, U.S. Patent 3,819,495 discloses the addition of organic chlorine containing compounds and copper compounds as a stabilization system while U.S. Patent 3,819,496 teaches the use of organic chlorine compounds with iron and/or manganese 30 compounds for that purpose. Many other stabilizers have been suggested and ; while some improvements have been achieved in the stability of unsaturated systems containing benzoin-type photoinitiators, the necessity of incorporating stabilizing additives raises the cost of such systems appreciably while the results are still not wholly satisfactory.

35 Thus, various aromatic compounds have been proposed as photoinitiators for unsaturated compounds. For example, U.S. Patent No. 3,715,293 teaches the use of acetophenone compounds such as 2,2-diethoxyacetophenone, while a series of patents including U.S. Patents 3,404,998 ; 3,926,638 ; 3,926,639 ; 3,926,640 ; 3,926,641 ; 4,022,674 ; 4,004,998 ; 4,008,138 and 4,028,204 describe complex compounds derived from benzophenone. As an example of the benzophenone-derived materials, U.S. Patent 3,404,998 describes photoinitiators made by reacting carboxy-substituted benzophenones with hydroxyl-containing polyethylenically unsaturated esters, while U.S. Patent 3,404,998 describes photoinitiators made by reacting carboxy-substituted benzophenones with hydroxyl-containing polyethylenically unsaturated esters, while U.S. Patents 3,926,639 and 4,028,204 describe a benzophenone substituted with a carboxy group and an ester group which is reacted with certain resins, such as alkyds, polyesters, polyethers, polyamides and epoxides, to provide the photoinitiator.

45 Another approach is disclosed in U.S. Patent No. 3,759,807 where certain benzophenones which must be used with activators are disclosed. Also representative of benzophenone systems is Brit. Patent 1,223,463 which teaches the addition of diketones such as m-benzoylbenzophenone, ethylene glycol bis (p-benzoylbenzoate) or diethylene glycol bis (p-benzoylbenzoate) to nylon to give photosensitive materials suitable for the preparation of printing plates.

50 In U.S. Patent No. 4,017,652, ethyl benzoylbenzoate is disclosed as a photosensitizer which must be used in connection with a photoinitiator such as a benzoin ether.

With regard to rate of polymerization and the dark storage stability of the uncured system, none of the most widely used photoinitiating compounds is wholly acceptable in unsaturated systems.

55 Now it has been found in accordance with this invention that certain benzoyl benzoates and benzamides are excellent photoinitiators for ethylenically unsaturated compounds. These photoinitiators provide polymerizable systems not subject to premature gelation. Furthermore, these photoinitiators are reactive in many different systems based on ethylenically unsaturated compounds.

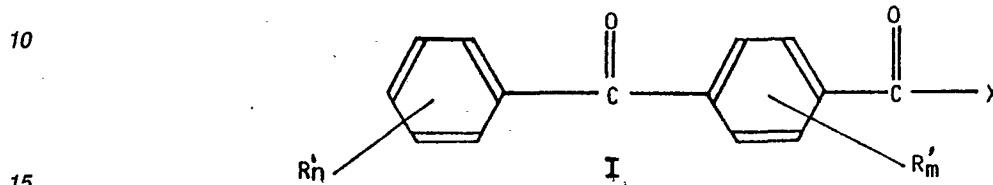
Summary of the invention

60 The photopolymerizable composition of this invention comprises an ethylenically unsaturated compound and a p-benzoyl benzoate or a p-benzoyl benzamide. After applying the compositions to the

desired substrate, curing is effected by exposure to actinic radiation.

Detailed description of the invention

More in detail, the photopolymerizable composition of this invention comprises an ethylenically unsaturated compound and a photoinitiating amount of a photoinitiator, characterised in that said photoinitiator is a *p*-benzoyl benzoate or benzamide of the formula :



wherein X is OR, NHR or NRR ; R is an independently selected hydrocarbon of 1 to 30 carbon atoms, alkoxy-substituted alkyl of 2 to 12 carbon atoms or aminosubstituted alkyl of 2 to 12 carbon atoms ; R' is an independently selected halogen or X ; and n and m are independently selected integers from 0 to 3.

In the foregoing definition, the term « hydrocarbon of from 1 to 30 carbon atoms » refers to straight and branched chain acyclic hydrocarbon groups which may contain unsaturated carbon-to-carbon bonds.

Preferred compositions are characterized in that X is OR and R is an alkyl of 1 to 15, especially 1 to 13 carbon atoms, an alkenyl of 3 to 5 carbon atoms, an alkoxy-substituted alkyl of 2 to 4 carbon atoms or an amino-substituted alkyl of 2 to 5 carbon atoms, or are characterized in that X is the group NHR or NRR and R is an alkyl of 1 to 4 carbon atoms.

Illustrative compounds I include, but are not limited to, methyl-*p*-benzoylbenzoate ; tridecyl-*p*-benzoylbenzoate ; (2-propenyl)-*p*-benzoylbenzoate ; (3-pentenyl)-*p*-benzoylbenzoate ; methoxymethyl-*p*-benzoylbenzoate ; (2-ethoxyethyl)-*p*-benzoylbenzoate ; aminoethyl-*p*-benzoylbenzoate ; (2-amino-propyl)-*p*-benzoylbenzoate ; (dimethylaminopropyl)-*p*-benzoylbenzoate ; N-methyl-*p*-benzoylbenzamide ; N-tridecyl-*p*-benzoylbenzamide ; N-(2-propenyl)-*p*-benzoylbenzamide ; N-(3-pentenyl)-*p*-benzoylbenzamide ; N-methoxymethyl-*p*-benzoylbenzamide ; N-(2-ethoxyethyl)-*p*-benzoylbenzamide ; N-aminoethyl-*p*-benzoylbenzamide ; N-(2-aminopropyl)-*p*-benzoylbenzamide ; N-(dimethylaminopropyl)-*p*-benzoylbenzamide ; 4-butoxycarbonyl-4'-fluorobenzophenone ; 4-butoxycarbonyl-3-bromobenzophenone, 4-ethoxycarbonyl-3,4,4'-trichlorobenzophenone and 4-butoxycarbonyl-4'-ethoxycarbonylbenzophenone.

The benzoyl benzoates and benzamides I are known compounds, some of which are commercially available. Alternately, they are readily prepared by methods described in the literature. Thus, for example, they can be prepared by the techniques described in *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, J. March ed., McGraw Hill, New York (1968). The esters can also be prepared by the procedure of D. Bichan and M. Winnik, *Tetrahedron Letters*, 3857 (1974).

The compositions curable by actinic radiation according to the invention can contain a photopolymerizable polymer in a reactive ethylenically unsaturated monomeric medium, a reactive polymer alone, a reactive monomer alone, or any of these combined with an inert solvent. Additionally, the polymerizable composition can contain any of the pigments commonly used in photopolymerization techniques.

Polymerizable ethylenically unsaturated compounds which are useful in practicing the invention are acrylic, α -alkacrylic and α -chloroacrylic acid compounds such as esters, amides and nitriles. Examples of such compounds are acrylonitrile, methacrylonitrile, methyl acrylate, ethyl acrylate, methyl methacrylate, isobutyl methacrylate, 2-ethylhexyl acrylate, methacrylamide and methyl α -chloroacrylate. Also useful, although not preferred due to their slower rates of reactivity, are vinyl and vinylidene esters, ethers and ketones. Additionally, compounds having more than one terminal unsaturation can be used. Examples of these include diallyl phthalate, diallyl maleate, diallyl fumarate, triallyl cyanurate, triallyl phosphate, ethylene glycol dimethacrylate, glycerol trimethacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, trimethylolpropane triacrylate, methacrylic anhydride and allyl ethers of monohydroxy or polyhydroxy compounds such as ethylene glycol diallylether and pentaerythritol tetraallyl ether tetraallyl. Nonterminally unsaturated compounds such as diethyl fumarate can similarly be used.

The acrylic acid derivatives are particularly well suited to the practice of the invention and are consequently preferred components as monomers in monomer-containing polymerizable systems and as reactive centers in polymerizable polymers. While monomeric styrene can be used in the practice of the invention, it is not a preferred constituent of systems polymerizable thereby due to its slow rate of reaction.

Additionally, the photopolymerizable composition can contain a sensitizer capable of enhancing the photoinitiating reactivity of the photoinitiating compound of the invention by triplet sensitization. Examples of sensitizers useful in the practice of the invention are such compounds as biphenyl, xanthone, thioxanthone and acetophenone. These are typically added in amounts ranging from 0,1 to 6 weight percent. The techniques whereby such sensitizers are selected for use in conjunction with

particular photoinitiators are well known in the art. See, for example, MUROV, Handbook of Photochemistry, Marcel Dekker, Inc., New York (1973).

Additionally polymerization promoters such as organic amines can be used to accelerate cure rates, either alone or in combination with a sensitizer. Such amines can be primary, secondary, or preferably, tertiary, and can be represented by the general formula :



wherein R^1 and R^2 are independently selected hydrogen, straight chain or branched alkyl having from 1 to about 12 carbon atoms, straight chain or branched alkenyl having from 2 to about 12 carbon atoms, cycloalkyl having from 3 to about 10 ring carbon atoms, cycloalkenyl having from 3 to about 10 ring atoms, aryl having from 6 to about 12 ring carbon atoms, alkaryl having 6 to about 12 ring carbon atoms ; R^3 has the same meaning as R^1 and R^2 with the exception that it cannot be hydrogen and that it cannot be aryl when both R^1 and R^2 are aryl. Also, when taken together R^2 and R^3 can be divalent alkylene groups having from 2 to about 12 carbon atoms, a divalent alkenylene group having from 3 to about 10 carbon atoms, a divalent alkadienylene group having from 5 to about 10 carbon atoms, a divalent alkatrienylene group having from 5 to about 10 carbon atoms, a divalent alkyleneoxyalkylene group having a total of from 4 to about 12 carbon atoms, or a divalent alkyleneaminoalkylene group having a total of from 4 to about 12 carbon atoms. As previously indicated, the amines can be substituted with other groups ; thus, the R^1 , R^2 and R^3 variables, whether taken singly or together, can contain one or more substituents thereon. The nature of such substituents is generally not of significant importance and any substituent group can be present that does not exert a pronounced deterrent effect on the ultraviolet crosslinking reaction.

Exemplary suitable organic amines are methylamine, dimethylamine, triethylamine, isopropylamine, triisopropylamine, tributylamine, t-butylamine, 2-methylbutylamine, N-methyl-N-butylamine, di-2-methylbutylamine, tri-2-ethylhexylamine, dodecylamine, tri-2-chloroethylamine, di-2-bromoethylamine, methanolamine, triethanolamine, methyldiethanolamine, propanolamine, triisopropanolamine, butylethanolamine, dihexanolamine, 2-methoxyethylamine, 2-hydroxyethylisopropylamine, allylamine, cyclohexylamine, trimethylcyclohexylamine, bis-methylcyclopentylamine, tricyclohexadienylamine, N-methyl-N-cyclohexylamine, N-2-ethylhexyl-N-cyclohexylamine, diphenylamine, methylphenylamine, trixylylamine, tribenzylamine, triphenethylamine, benzyldimethylamine, N-methylethylenimine, N-cyclohexylethylenimine, piperidine, N-ethylpiperidine, 1,2,3,4-tetrahydropyridine, 2-, 3- and 4-picoline, morpholine, N-methyl morpholine, N-2-hydroxyethylmorpholine, piperazine, N,N' dimethylpiperazine and 2,2-dimethyl-1,3-bis [3(N-morpholinyl)propionyloxy]-propane. The preferred organic amines are the tertiary amines, with the alkanol amines being most preferred.

Thus is seen that the constitution of photopolymerizable compositions which can be used in the practice of the invention is widely variable. However, the compounds enumerated above are purely illustrative. Materials subject to polymerization by actinic radiation as well as permissible variations and substitutions of equivalent components within particular types of compositions are well known to those skilled in the art.

The photoinitiators of the invention can be utilized in amounts ranging from 0.01 to 30 percent by weight based on the photopolymerizable composition. However, preferable amounts of the compounds are between 1.0 and 10.0 weight percent.

The process can be carried out by mixing a quantity of a photoinitiating compound of the invention with a photopolymerizable composition and exposing the resultant mixture to actinic radiation. Alternatively, a one-component system comprising the photopolymerizable composition, the photoinitiator of the invention and, if desired, pigmentation, can be stored in the dark for a prolonged period of time prior to use without fear of gelation.

A preferred manner of practicing the invention is by the use of photopolymerizable molding and coating compositions which consist of mixtures of unsaturated polymeric compounds and monomeric compounds copolymerizable therewith. The polymeric compounds can be conventional polyesters prepared from unsaturated polycarboxylic acids such as maleic acid, fumaric acid, glutaconic acid, itaconic acid, citraconic acid and mesaconic acid, and polyhydric alcohols such as ethylene glycol, diethylene glycol, glycerol, propylene glycol, 1,2-butanediol, 1,4-butanediol, pentaerythritol and trimethylolpropane. The carboxylic acid content can also contain saturated components. The inclusion of a monobasic fatty acid content, either as such or in the form of a triglyceride or oil, in the photopolymerizable polyester composition to comprise an alkyd resin is also acceptable. These resins can, in turn, be modified by silicones, epoxides or isocyanates, by known techniques.

The compositions of the instant invention after being prepared in the ratios as set out above can be applied to the material to be coated by conventional means, including brushing, spraying, dipping, and roll coating techniques, and may, if desired, be dried under ambient or elevated conditions to provide coatings on the substrate. The substrate can be of any composition, including but not limited to plastic, fiber, ceramic, glass, etc.

After the composition is applied to the desired substrate, it is exposed to light radiation having wave lengths of above about 2 000 Angstrom units, preferably from about 2 000 up to about 8 000 Angstroms

and most preferably between about 2 400 Angstroms and 5 400 Angstroms. Exposure should be from a source located about 2.54 to 12.70 cm from the coating for a time sufficient to cause crosslinking of the composition.

5 The light radiation can be ultraviolet light generated from low, medium, and high pressure mercury lamps. This equipment is readily available and its use is well known to those skilled in the art. Other sources could include electron beam radiation, plasma arc and laser beams.

While any of the compounds having the formula I can be used in the practice of this invention, preferred are those compounds where m and n are 0 ; R is alkyl of 1 to 12 carbon atoms, alkenyl of 3 to 5 carbon atoms, alkoxy-substituted alkyl of 2 to 4 carbon atoms or aminosubstituted alkyl of 2 to 5 carbon atoms. Particularly preferred are the *p*-benzoylbenzoates, i.e., compounds I where X is OR.

10 In the following examples, which will serve to illustrate the practice of this invention, all parts and percentages are by weight unless otherwise specified.

15 Example 1

To a magnetically stirred solution of 5.0 grams (0.022 mole) of *p*-benzoylbenzoic acid in benzene was added 5.0 grams (0.24 mole) of phosphorus pentachloride. After heating under reflux all volatile components were removed on a rotary evaporator. To the residual solid *p*-benzoyl benzoic acid chloride 20 was added methanol and the mixture was warmed briefly to cause dissolution. All volatiles were once again removed on a rotary evaporator to provide 5.2 grams of a white solid, representing a 98 % yield of methyl-*p*-benzoylbenzoate. The infrared spectrum showed carbonyl bands at 1 650 and 1 715 cm^{-1} and the absence of a carboxylic acid band at 3 300-2 000 cm^{-1} , confirming the formation of methyl-*p*-benzoylbenzoate.

25 To a standard test solution consisting of 42 % by weight of trimethylolpropane triacrylate, 17 % by weight of ethylhexyl acrylate and 41 % by weight of ACTOMER X.80 ® Resin, an unsaturated long chain linseed oil alkyd resin, available from Union Carbide Corporation, was added 4.0 % by weight of methyl *p*-benzoylbenzoate.

Cure rates were determined in air using as a source of actinic light a PPG Model QC 1202 AN UV 30 Processor manufactured by PPG Industries, Inc. The radiation source for this apparatus consists of two high intensity medium pressure quartz mercury lamps 30.5 cm in length and each operating at a linear power density of about 200 watts per 2.54 cm or 2 400 watts per lamp. The lamps are housed in an elliptical reflector above a variable speed conveyor belt and each lamp provides a 5.08 cm band of high flux actinic radiation on the conveyor. This 5.08 cm exposure area is bordered on both sides by an additional 5.08 cm area of medium flux energy for a total radiation area of 15.24 cm for each lamp. In the 35 curing data presented below, cure rate of the polymerizable composition is presented in cm-per-minute-per-lamp (cm/min/lamp). Thus, a conveyor belt speed of 30.5 cm/min will, with a 30.5 cm exposure area for the two lamps, provide 60 seconds of exposure or a cure rate of 15.24 cm/min/lamp. Similarly, a belt speed of 305 cm/min will provide 6 seconds of exposure or a rate of 15.24 cm/min/lamp while a speed of 40 610 cm/min will give 3 seconds exposure or a rate of 305 cm/min/lamp, etc.

The composition had a cure rate of 610 cm/min/lamp.

45 Example 2

To a mechanically stirred solution of 1 000 grams (7.12 moles) of benzoyl chloride in 6 000 grams of toluene was added 1 000 grams (7.50 moles) of anhydrous aluminum chloride over a 20-30 minutes period. The temperature of the reaction mixture rose to near the boiling point during the addition, and heating at reflux was maintained for three additional hours. After cooling, 1 200 milliliters of water were 50 added, slowly at first, followed by 1 000 milliliters of concentrated hydrochloric acid. The organic layer was separated ; washed twice with hot water and concentrated on a rotary evaporator. Vacuum distillation of the residual oil provided 1 300 grams (93 % yield) of white, semi-solid methyl benzophenone ; (b.p. 180-200 °C, 10-15 mm Hg ; m.p. 50 °C). The infrared spectrum revealed a carbonyl band at 1 665 cm^{-1} .

55 The amount of 1 300 grams (6.65 moles) of methyl benzophenone was then melted and heated to 170-180 °C in a 2 liters two necked round bottom flask with magnetic stirring. Chlorine gas was introduced through a gas dispersion tube immersed below the liquid at a rate such that the characteristic greenish color of chlorine was not detectable in the exiting stream of hydrogen chloride. After 12 hours, the hot melt was poured into 8 liters of isopropyl alcohol. This mixture was chilled to - 5 to 0 °C and the precipitated solid removed by suction filtration to provide 1 600 grams (81 % yield) of 4-(trichloromethyl) 60 benzophenone, mp 109-111 °C. A carbonyl band at 1 670 cm^{-1} was noted in the infrared spectrum.

A mixture of 1 600 grams (5.35 moles) of the 4-(trichloromethyl) benzophenone, 4 000 milliliters of *n*-butanol and 2 400 milliliters of 19 % by weight aqueous hydrochloric acid was mechanically stirred at the reflux temperature for three hours. Then three liters of water was added. The upper organic layer was 65 separated and stirred with 4 000 milliliters of 10 % aqueous sodium carbonate solution. The organic layer

was again separated and washed twice with hot water. Removal of volatile components under reduced pressure produced 1 400 grams (93 % yield) of semi-solid, off-white *n*-butyl-*p*-benzoylbenzoate, m.p. 50-60 °C. Carbonyl bands in the infrared spectrum at 1 670 and 1 730 cm^{-1} confirmed the structure of the product.

5 Varying concentrations of the *n*-butyl-*p*-benzoylbenzoate were added to samples of the standard test solution described in Example 1 ; the cure data is presented below. Where ranges for cure rates are indicated, several samples were tested, with purer esters giving the faster rates.

10	Sample	Concentration (% Wt.) of <i>n</i> -butyl- <i>p</i> -benzoylbenzoate	Cure rate (Cm./Min./Lamp)
	1	2	228.8-305
	2	4	457.5-610
15	3	6	610
	4	8	915-1 067.5
	5	10	915

20 Example 3

The amount of 4 % by weight of the *n*-butyl-*p*-benzoylbenzoate prepared in Example 2 was added to resin samples comprising 50 % by weight of EPOCYRL® Resin DRH-303, a diacrylate ester of Bisphenol A epoxy resin available from Shell Chemical Company, and 50 % by weight of 1,6-hexanediol diacrylate available from Celanese Corporation. A cure rate ranging from 915 to 1 220 cm/min/lamp was obtained for several samples.

30 Comparative examples

In order to demonstrate the efficacy of the *para* esters of this invention, the *ortho* and *meta* isomers of the ester of Example 2 were prepared and tested. The *n*-butyl-*p*-benzoylbenzoate was prepared by the acid-catalyzed esterification of *o*-benzoyl benzoic acid. The *n*-butyl-*m*-benzoylbenzoate was prepared following the procedure and employing the ingredients described in Example 2 but substituting *m*-toluyl chloride for benzoyl chloride and benzene for toluene. The cure data for 4 % by weight loading is presented below.

40	Ester	Cure rate	(Cm./Min./Lamp)
		TMPTA/EHA actomer X.80® (1)	Epocryl resin DRH-303/HDDA (2)
	<i>n</i> -butyl- <i>o</i> -benzoylbenzoate	152.5-228.8	0
45	<i>n</i> -butyl- <i>m</i> -benzoylbenzoate	152.5	305

(1) 42 % by weight of trimethylolpropane triacrylate, 17 % by weight of ethylhexyl acrylate and 41 % by weight of Actomer X.80® Resin, an unsaturated long chain linseed oil alkyd resin, available from Union Carbide Corporation.

50 (2) 50 % by weight of Epocryl® Resin DRH-303, a diacrylate ester of Bisphenol A epoxy resin available from Shell Chemical Company, 50 % by weight 1,6-hexanediol diacrylate available from Celunese Corporation.

Example 4

55 Following the procedure of Example 1, but employing 4-methylpentanol instead of methanol, the ester (4-methyl penty)-*p*-benzoylbenzoate was prepared. The structure was confirmed by the presence of carbonyl bands at 1 670 and 1 730 cm^{-1} in the infrared spectrum. When this ester was added at a level of 4 % by weight to the test solution of Example 1, a cure rate of 457.5 cm/min/lamp was obtained.

60 Example 5

65 A solution of 5.0 g (0.020 mole) of *p*-benzoylbenzoic acid chloride made as described in Example 1, in 75 ml of pyridine was magnetically stirred at ambient temperature and treated at once with excess *n*-pentanol (5-10 milliliters). After 30 minutes, cold dilute hydrochloric acid and ether was added. The

organic layer was separated, washed with dilute hydrochloric acid until the washing was acidic to litmus paper and dried over anhydrous magnesium sulfate. Gravity filtration and concentration on a rotary evaporator produced a greenish-yellow colored oil. The excess alcohol was removed under vacuum with warming to afford an essentially quantitative yield of *n*-pentyl-*p*-benzoyl benzoate showing carbonyl absorption bands in the infrared spectrum at 1 725 and 1 670 cm^{-1} . A cure rate of 610 $\text{cm}/\text{min}/\text{lamp}$ was obtained at a 4 % by weight loading in the test solution of Example 1.

In order to demonstrate the dark-storage stability of this compound, 4 % by weight was added to another sample of the test solution. A glass jar was filled to greater than 90 % by volume with the composition, which was then stored in the dark at 65 °C. The composition had not gelled when inspected after 3 months storage.

Example 6

n-Octyl-*p*-benzoylbenzoate was prepared by reacting *p*-benzoylbenzoic acid chloride with *n*-octanol. The presence of carbonyl bands at 1 725 and 1 670 cm^{-1} in the infrared spectrum confirmed that the product had been obtained. The test solution of Example 1 was employed and the ester was added at a level of 4 % by weight ; a cure rate of 533.8 $\text{cm}/\text{min}/\text{lamp}$ was obtained.

20

Example 7

Tridecyl-*p*-benzoylbenzoate was prepared from *para* benzoylbenzoic acid chloride and tridecanol. The infrared spectrum revealed carbonyl bands at 1 725 and 1 670 cm^{-1} . A cure rate of 457.5/ min/lamp was obtained at a 4 % by weight loading in the test solution of Example 1.

25

Example 8

(2-Ethoxyethyl)-*p*-benzoylbenzoate was prepared from *para*-benzoyl benzoic acid chloride and 2-ethoxyethanol. The structure of the product was confirmed by the presence of carbonyl bands in the infrared spectrum at 1 670 and 1 730 cm^{-1} . When added at 4 % by weight loading to the solution described in Example 1, a cure rate of 457.5 $\text{cm}/\text{min}/\text{lamp}$ was obtained. A sample in the same test solution was stable after three months storage following the procedure described in Example 5.

30

35

Example 9

(2-Dimethylaminoethyl)-*p*-benzoylbenzoate was prepared from *para*-benzoylbenzoic acid chloride and 2-dimethylaminoethanol. The structure of the product was confirmed by the presence of carbonyl absorption bands in the infrared spectrum at 1 670 and 1 725 cm^{-1} . When added at 4 % by weight loading to the test solution described in Example 3, a cure rate of 1 220 $\text{cm}/\text{min}/\text{lamp}$ was observed.

45

Example 10

3-(Dimethylaminopropyl)-*p*-benzoylbenzoate was prepared from *para*-benzoylbenzoic acid chloride and 3-dimethylaminopropanol. The structure of the product was confirmed by the presence of carbonyl bands in the infrared spectrum at 1 670 and 1 730 cm^{-1} . At a 4 % by wight loading, this ester resulted in a cure rate of 457.5 $\text{cm}/\text{min}/\text{lamp}$ in the test solution of Example 1 and a cure rate of 1 525 $\text{cm}/\text{min}/\text{lamp}$ in the test solution of Example 3.

55

Example 11

A mixture of 10.0 grams (0.044 mole) of *p*-benzoylbenzoic acid, 100 milliliters of *n*-propanol and 0.25 milliliters of concentrated sulfuric acid was stirred under reflux for 5 hours. Aqueous sodium bicarbonate solution was then added. The organic layer was separated, dried over anhydrous magnesium sulfate and filtered. Volatiles were removed under vacuum with warming to provide 9.0 grams (76.3 % yield) of *n*-propyl-*p*-benzoylbenzoate. The infrared spectrum revealed carbonyl absorption bands at 1 670 and 1 730 cm^{-1} .

At a loading of 4 % by weight in the test solution of Example 3, this ester exhibited a cure rate of 762.5 $\text{cm}/\text{min}/\text{lamp}$.

65

Example 12

Following the procedure of Example 2, iso-butyl-*p*-benzoylbenzoate was prepared from 20 grams of *p*-benzoyl benzotrichloride, 50 milliliters of iso-butanol and 30 milliliters of 19 per cent by weight aqueous hydrochloric acid. When added at a loading of 4 % by weight to the test solution described in Example 3, a cure rate of 915-1 067.5 cm/min/lamp was observed for several samples.

Example 13

Following the procedure of Example 6, (4-pentenyl)-*p*-benzoylbenzoate was prepared from *p*-benzoylbenzoic acid chloride and 4-pentenol. The structure of the product was confirmed by the presence of carbonyl bands in the infrared spectrum at 1 670 and 1 730 cm^{-1} . At a loading of 4 % by weight, a cure rate of 457.5 cm/min/lamp was obtained in the test solution described in Example 1.

Example 14

N,N-diethyl-*p*-benzoyl benzamide was prepared by reacting *p*-benzoylbenzoic acid chloride with diethylamine. At a 4 % by weight loading in the test solution described in Example 1 a cure rate of 228.8-305 cm/min/lamp was observed for several samples.

Example 15

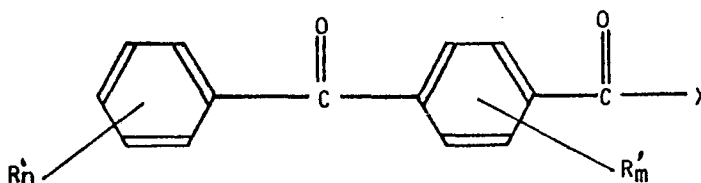
N-iso-butylamine was reacted with *p*-benzoylbenzoic acid chloride to provide N-iso-butyl-*p*-benzoyl benzoic benzamide. At a 4 % by weight loading in the test solution described in Example 1, a cure rate of 228.8-305 cm/min/lamp was observed for several samples.

Example 16

N,N-di-n-butyl-*p*-benzoyl benzamide was prepared from *p*-benzoylbenzoic acid chloride and di-*n*-butylamine. A cure rate of 305 cm/min/lamp was observed at a 4 % by weight loading in the test solution described in Example 1. A rate of 152.5 cm/min/lamp was observed at the same loading in the test solution described in Example 3.

Claims

1. A photopolymerizable composition comprising an ethylenically unsaturated compound and a photoinitiating amount of a photoinitiator, characterized in that said photoinitiator is a *p*-benzoyl benzoate or benzamide of the formula



wherein X is OR, NHR or NRR ; R is an independently selected hydrocarbon of 1 to 30 carbon atoms, alkoxy-substituted alkyl of 2 to 12 carbon atoms or aminosubstituted alkyl of 2 to 12 carbon atoms ; R' is an independently selected halogen or X ; and n and m are independently selected integers from 0 to 3.

2. The composition of Claim 1 where said benzoyl benzoate comprises between 0.01 to 30 percent by weight of said compositions.

3. The composition of one of the Claims 1 or 2 further including an organic amine as a promoter.

4. The composition of one of the Claims 1 through 3, characterized in that m and n each are zero.

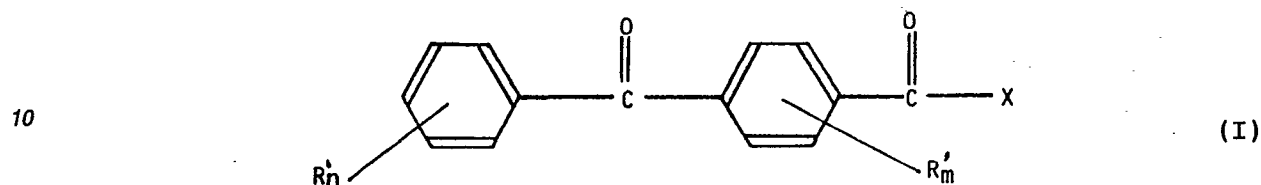
5. The composition of one of the Claims 1 through 4, characterized in that X is OR and R is an alkyl of 1 to 15, especially 1 to 13 carbon atoms, an alkenyl of 3 to 5 carbon atoms, an alkoxy-substituted alkyl of 2 to 4 carbon atoms or an amino-substituted alkyl of 2 to 5 carbon atoms.

6. The composition of one of the Claims 1 through 4, characterized in that X is the group NHR or NRR and R is an alkyl of 1 to 4 carbon atoms.

7. The use of a benzoyl benzoate and/or of a benzoyl benzamide as defined in the general formula I of Claim 1 or in one of the Claims 4 through 6 as a photoinitiator in the method of photopolymerizing an ethylenically unsaturated compound by exposure to an actinic radiation.

Ansprüche

1. Photopolymerisierbare Masse, enthaltend eine ethylenisch ungesättigte Substanz und eine photoinitierende Menge eines Photoinitiators, dadurch gekennzeichnet, daß der Photoinitiator ein p-Benzoylbenzoat oder ein Benzamid der Formel

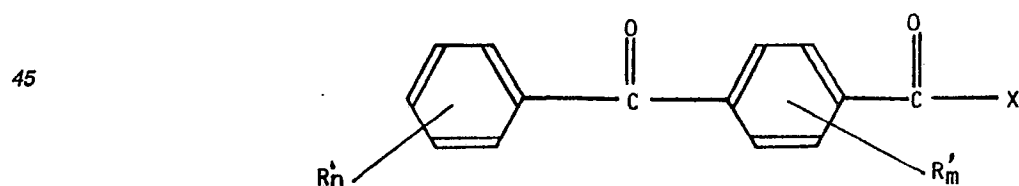


- 15 ist, in der X OR, NHR oder NRR ist, wobei R ein unabhängig gewählter Kohlenwasserstoffrest mit 1 bis 30 Kohlenstoffatomen, ein alkoxy-substituierter Alkylrest mit 2 bis 12 Kohlenstoffatomen oder ein amino-substituierter Alkylrest mit 2 bis 12 Kohlenstoffatomen ist, in der R' ein unabhängig gewähltes Halogenatom oder der Rest X ist, und in der n und m unabhängig gewählte ganze Zahlen von Null bis 3 sind.
- 20 2. Masse nach Anspruch 1, dadurch gekennzeichnet, daß die Masse 0,01 bis 30 Gew.-% Benzoylbenzoat, bezogen auf das Gewicht der Masse, enthält.
3. Masse nach einem der Ansprüche 1 oder 2, dadurch gekennzeichnet, daß die Masse zusätzlich ein organisches Amin als Beschleuniger enthält.
- 25 4. Masse nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß sowohl m als auch n Null sind.
5. Masse nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß X die Bedeutung OR hat und R ein Alkylrest mit 1 bis 15, insbesondere 1 bis 13 Kohlenstoffatomen, ein Alkenylrest mit 3 bis 5 Kohlenstoffatomen, ein alkoxy-substituierter Alkylrest mit 2 bis 4 Kohlenstoffatomen oder ein amino-substituierter Alkylrest mit 2 bis 5 Kohlenstoffatomen ist.
- 30 6. Masse nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß X den Rest NHR oder NRR bedeutet und R ein Alkylrest mit 1 bis 4 Kohlenstoffatomen ist.
7. Verwendung eines Benzoylbenzoats und/oder eines Benzoylbenzamids der allgemeinen Formel I nach Anspruch 1 oder einem der Ansprüche 4 bis 6 als Photoinitiator zum Photopolymerisieren einer ethylenisch ungesättigten Substanz durch Belichten mit einer aktinischen Strahlung.

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Revendications

- 40 1. Composition photopolymérisable renfermant un composé à insaturation éthylenique et une quantité efficace d'un photoinitiateur, caractérisée en ce que ledit photoinitiateur est un para-benzoylbenzoate ou -benzamide de formule générale :



dans laquelle :

- X est un groupe OR, NHR ou NRR ; les radicaux R sont, indépendamment l'un de l'autre, des groupes hydrocarbonés comportant 1 à 30 atomes de carbone, des groupes alkyles alkoxylés comportant 2 à 12 atomes de carbone ou des groupes alkyles aminés comportant 2 à 12 atomes de carbone ; les radicaux R sont, indépendamment l'un de l'autre, des atomes d'halogène ou des groupes X ; m et n sont, indépendamment l'un de l'autre, des nombres entiers compris entre 0 et 3 ; toutes les limites s'entendent bornes comprises.
- 55 2. Composition selon la revendication 1, caractérisée en ce que ledit benzoylbenzoate constitue 0,01 à 30 % du poids de la composition.
- 60 3. Composition selon la revendication 1 ou 2, caractérisée en ce qu'elle renferme en outre une amine organique en tant que promoteur ou adjuvant.
4. Composition selon l'une quelconque des revendications 1 à 3, caractérisée en ce que m et n sont tous deux égaux à zéro.
5. Composition selon l'une quelconque des revendications 1 à 4, caractérisée en ce que X est OR et R est un groupe alkyle comportant 1 à 15 atomes de carbone et plus particulièrement 1 à 13 atomes de
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carbone, un groupe alkényle comportant 3 à 5 atomes de carbone, un groupe alkoxyalkyle comportant 2 à 4 atomes de carbone ou un groupe aminoalkyle comportant 2 à 5 atomes de carbone.

6. Composition selon l'une quelconque des revendications 1 à 5, caractérisée en ce que X est le groupe NHR ou NRR et en ce que R est un groupe alkyle comportant 1 à 4 atomes de carbone.

5 7. Utilisation d'un benzoylbenzoate ou d'un benzoylbenzamide selon une quelconque des revendications 1 à 6 en tant qu'agent photoinitiateur pour la photopolymérisation de composés à insaturation éthylénique par exposition à un rayonnement actinique.

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