PATENT APPLICATION FORM (CONVENTION AND NON-CONVENTION)

COMMONWEALTH OF AUSTRALIA

Regulation 9

Patents Act 1952

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 12-2-90

APPLICATION FOR A STANDARD PATENT OR A STANDARD PATENT OF ADDITION

505830

(a) Insert full name(s) of applicant(s)

~~I~~/We (a) MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG

(b) Insert address(es) of applicant(s)

of (b) Frankfurter Strasse 250, D-6100 Darmstadt, Germany

(c) Delete as appropriate

(d) Insert title of invention

hereby apply for the grant of a (c) Standard Patent ~~Patent of Addition~~ for an invention entitled (d) "COPOLYMERIZABLE PHOTOINITIATORS IN THE NATURE OF ACRYLIC KETONES"

which is described in the accompanying (c) ~~provisional~~ complete specification.

PATENT OFFICE A.C.T. SUB-OFFICE 08606 2

(e) For a Convention application — details of basic application(s) —

(e) for Convention cases only

NUMBER	COUNTRY	DATE OF APPLICATION
P 35 34 645.0	GERMANY	28 September 1985

(f) For Patents of Addition only.

(f) ~~For Patents of Addition (Section 72):~~

LODGED AT SUB OFFICE - 9 SEP 1986 Sydney

(g) Insert number of 'parent/main' application/or patent as appropriate.

(h) Insert name of applicant/patentee of 'parent/main' application or patent as appropriate.

~~I/We request that the Patent may be granted as a Patent of Addition to the Patent applied for on Application No. (g) .... Patent No. (g) .... in the name of (h) ....~~

~~I/We request that the term of the Patent of Addition be the same as that for the main invention or so much of the term of the patent for the main invention as is unexpired.~~

~~My~~/Our address for service is ARTHUR S. CAVE & CO., Patent and Trade Mark Attorneys, 1 Alfred Street, Sydney, New South Wales, Australia 2000.

(i) Insert day, month and year form signed.

Dated this (i) 8th day of September, 1986.

(j) Signature of applicant or Australian attorney.

MERCK PATENT GESELLSCHAFT MIT BESCHRANKTER HAFTUNG,
By Its Patent Attorneys,
(j) ARTHUR S. CAVE & CO.
(Signature)

(k) Seal, if any. (k)

To:

Commissioner of Patents

JAMES G. SIELY. F.I.P.A.A.

AUSTRALIAN PATENT OFFICE LS

ARTHUR S. CAVE & CO.
PATENT AND TRADE MARK ATTORNEYS
SYDNEY

A.S.C. — 1

(Form 8)

PATENT DECLARATION FORM (CONVENTION)
COMMONWEALTH OF AUSTRALIA
Patents Act 1952

Regulation 12(2)

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

To be signed by the applicant(s) or in the case of a body corporate to be signed by a person authorised by the body corporate.

In support of the Convention application made for a patent for an invention entitled

(a) Insert title of invention.

(a) Copolymerizable photoinitiators in the nature of acrylic ketones

(b) Insert full name(s) of declarant(s).

~~I~~/We (b) DR. SCHUETTLER and JURGEN HEUMANN

(c) Insert address(es) of declarant(s).

of (c) 250 Frankfurter Strasse 250, D-6100 Darmstadt

do solemnly and sincerely declare as follows:—

~~1. I am/We are the applicant(s) for the patent~~

(OR, IN THE CASE OF AN APPLICATION BY A BODY CORPORATE.)

1. ~~I am~~/We are authorised by Merck Patent Gesellschaft Mit Beschrankter Haftung the applicant for the patent to make this declaration on its behalf.

2. The basic application~~(s)~~ as defined by Section 141 of the Act was/~~were~~ made in the following country or countries on the following date~~(s)~~ namely:—

(d) Insert country in which basic application(s) was/were filed.
(e) Insert date of basic application(s).
(f) Insert full names of basic applicant(s).

in (d) Germany on (e) September 28, 1985
by (f) Merck Patent Gesellschaft Mit Beschrankter Haftung
in (d) on (e)
by (f)
in (d) on (e)
by (f)

~~3. I am/We are the actual inventor(s) of the invention referred to in the basic application.~~

(OR, WHERE A PERSON OTHER THAN THE INVENTOR IS THE APPLICANT)

(g) Insert full name(s) of actual inventor(s)
(h) Insert address(es) of actual inventor(s).

3. (g) Manfred Kohler, Jorg Ohngemach and Eike Poetsch
all of (h) Frankfurter Strasse 250, D-6100 Darmstadt, GERMANY

~~is~~/are the actual inventor(s) of the invention and the facts upon which the applicant~~(s)~~ is/~~are~~ entitled to make the application are as follows:

(i) Set out how applicant(s) derive(s) title from actual inventor(s) i.e., assignee of the invention from the actual inventor(s).

(i) The company is the Assignee of the said invention from the said inventors.

4. The basic application~~(s)~~ referred to in paragraph 2 of this Declaration was/~~were~~ the first application~~(s)~~ made in a Convention country in respect of the invention the subject of the application.

Attestation or legalization not required.

Declared at Darmstadt this 3rd day of January 1990

MERCK PATENT GMBH

ppa. ppa.

Heumann

Signature of Declarant(s)
Dr. Schüttler

To:

The Commissioner of Patents

ARTHUR S. CAVE & CO.
PATENT AND TRADE MARK ATTORNEYS
SYDNEY

A.S.C.—4

(12) PATENT ABRIDGMENT (11) Document No. AU-B-62470/86
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 595830

(54) Title
ACRYLIC KETONE PHOTOINITIATORS

International Patent Classification(s)
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C07C 069/533

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(71) Applicant(s)
MERCK PATENT GESELLSCHAFT MIT BESCHRANKTER HAFTUNG

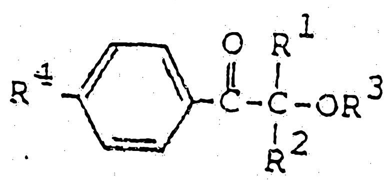
(72) Inventor(s)
MANFRED KOHLER; JORG OHNGEMACH; EIKE POETSCH

(74) Attorney or Agent
ARTHUR S. CAVE & CO.

(56) Prior Art Documents
US 4469774

(57) Claim

1. Compounds of the general formula I



(I)

in which

R^1 and R^2 are each H or C_1-C_6-alkyl

R^3 is H, C_1-C_6-alkyl, C_1-C_6-alkanoyl or the group Z,

R^4 is H, halogen, C_1-C_{12}-alkyl, C_1-C_{12}-alkoxy, C_1-C_{12}-alkylthio or the group $-X[(CH_2-CH_2-O)_n-Z]_m$

and

X is O, S, N or NH,

n is the numbers 0 to 4,

m is the number 1 when X = O, S and NH or the number 2 when X = N

Z is the group -CO-CR=CR'R"

with R, R', R" each being H or CH_3,

always at least one of the radicals R^3 or R^4 containing the group Z.

2. Compounds of the general formula I according to claim 1 when used as copolymerizable photoinitiators for the photopolymerization of ethylenically unsaturated compounds.

COMMONWEALTH OF AUSTRALIA

Form 10
Regulation
13(2)

PATENTS ACT, 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

Short Title:

Int. Cl:

Application Number: 62470/86 595930

Lodged:

Complete Specification-Lodged:
Accepted:
Lapsed:
Published:

Priority:

Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

TO BE COMPLETED BY APPLICANT

Name of Applicant: MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG

Address of Applicant: Frankfurter Strasse 250, D-6100 Darmstadt, Germany

Actual Inventor: 1. MANFRED KÖHLER 2. JÖRG OHNGEMACH
3. EIKE POETSCH

Address for Service: ARTHUR S. CAVE & CO., Patent and Trade Mark Attorneys, 1 Alfred Street, Sydney, New South Wales, Australia, 2000.

Complete Specification for the invention entitled:

"COPOLYMERIZABLE PHOTOINITIATORS IN THE NATURE OF ACRYLIC KETONES"

The following statement is a full description of this invention, including the best method of performing it known to me:-

AUSTRALIA LS PATENT

ASC-49

Merck Patent Gesellschaft
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6100 D a r m s t a d t

Copolymerizable photoinitiators in the nature of acrylic ketones.

The invention relates to copolymerizable photoinitiators for the photopolymerization of ethylenically unsaturated compounds or of systems containing such compounds.

Photochemically induced polymerization reactions have attained great importance in industry, in particular in the rapid hardening of thin films, as for example in the hardening of paint or resin coatings on paper, metal and plastics or in the drying of printing inks, since these processes are distinguished from conventional methods for printing and coating articles by raw material and energy savings and lower environmental pollution. But even the preparation of polymer materials as such by polymerizing appropriate unsaturated monomeric starting materials is frequently effected photochemically, for which customary processes such as solution and emulsion polymerizations can be used.

Since with the reactions mentioned it is generally the case that none of the reactants is capable of absorbing photochemically active radiation to an adequate degree, it is necessary to add so-called photoinitiators which are either capable of absorbing incident high-energy radiation, usually UV light, and of forming active starter radicals which in turn initiate photopolymerization, or are capable of transferring the absorbed energy for free radical formation to one of the polymerizable reactants. The initiators do not normally participate in the actual polymerization reaction.

The initiators used hitherto for photopolymerizing unsaturated compounds have been in the main benzophenone derivatives, benzoin ethers, benzil ketals, dibenzosuberone derivatives, anthraquinones, xanthenones, thioxanthones, α-halogenoactophenone derivatives, dialkoxyacetophenones and hydroxyalkyl phenones.

Essential criteria for the selection of such initiators are, inter alia, the nature of the reactions to be carried out, the ratio of the absorption spectrum of the initiator to the spectral energy distribution of the available source of irradiation, the activity of the initiator, the solubility of the initiator in the reaction mixture, the dark storage life of the reaction system to which the initiator has been added, and the action on the end products by residues remaining therein of the initiator and/or of the products formed therefrom in the course of the photochemical reaction.

As is known, however, the technical feasibility of many of the substances mentioned is restricted, in some instances severely, by a number of disadvantages. These include in particular the frequently too low reactivity in the ability to initiate the photopolymerization of ethylenically unsaturated compounds. In addition to molecule-specific reactivity, the crucial factor is here in many cases the solubility or the ideally uniform incorporability of the photoinitiators in the photopolymerizable systems.

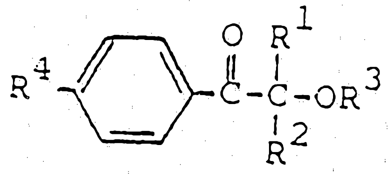
However, owing to their favourable properties, the hydroxyalkylphenones of German Offenlegungsschrift 2,722,264 have proved to be particularly advantageous. This specific class of substances is present at the typical application temperature range in the liquid state; this results in an excellent solubility or homogeneous incorporability in customary photopolymerizable systems. Furthermore, these photoinitiators are of an above-average activity and at the same time the systems to which they are added have a remarkably favourable dark storage life. Nonetheless, hydroxyalkylphenone photoinitiators are still improvable.

Since these, like the other customary photoinitiators, do not participate in the actual photopolymerization, their excess, unreacted residues and their degradation products formed during the photochemical reaction remain in the finished product. Depending on the nature and amount, this can lead to more or less pronounced effects on the properties of the product. In the case of photopolymerized paint coatings, the main field of use for photoinitiators, such residues can, for example, affect the obtainable final hardness of the layer; furthermore, it is possible for undesirable colour changes, for example yellowing, to occur, frequently only after a prolonged period. Initiator residues or their degradation products, owing to their more or less pronounced volatility, can become noticeable through unpleasant odour; their diffusion out of the coating and into surrounding media can create problems, for example where packaging materials with photopolymerized coatings, such as, for example, tins and tubes, are provided for foodstuffs. Especially in this area of use the question of utility is crucially determined by the possible or proven toxicity of the photoiniators and their degradation products.

The prior art discloses certain photoinitiators which have unsaturated substituents besides other types of substituent. They are predominantly benzoin and benzil derivatives. However, apart from the compound α-allylbenzoin, which in its initiator action comes close to the hydroxyalkylphenones, such unsaturated photoinitiators have not become established, since they do not offer any significant advantages with respect to content of unreacted residues and degradation products in the polymer product and otherwise are inferior to the hydroxyalkylphenones.

It is thus an object of the invention to provide photoiniators which, ideally, should be structured in such a way, for example through copolymerizable ethylenically unsaturated substituents, that they participate directly in the photopolymerization reaction and their residues or degradation products are ideally all incorporated in the polymer structure. At the same time, their other properties such as initiator action and compatibility with customary radiation-hardenable systems should at least correspond to the best of the known photoinitiators.

It has now been found, surprisingly, that these requirements are met supremely well by the new compounds of the general formula I



(I)

in which

R^1 and R^2 are each H or C_1-C_6-alkyl

R^3 is H, C_1-C_6-alkyl, C_1-C_6-alkanoyl or the group Z,

R^4 is H, halogen, C_1-C_{12}-alkyl, C_1-C_{12}-alkoxy, C_1-C_{12}-alkylthio or the group - $X[(CH_2-CH_2-O)_n-Z]_m$

and

X is O, S, N or NH,

n is the numbers 0 to 4,

m is the number 1 when X = O, S and NH or the number 2 when X = N

Z is the group -CO-CR=CR'R"
with R, R', R" each being H or CH_3,

always at least one of the radicals R^3 or R^4 containing the group Z.

The invention thus provides the new compounds of the general formula I.

The invention also provides the use of the compounds of the formula I as copolymerizable photoinitiators for photopolymerizing ethylenically unsaturated compounds or systems containing such compounds.

The invention further provides a process for photopolymerizing ethylenically unsaturated compounds or systems containing such compounds, in which the mixture to be polymerized has added to it, before the initiation of the photopolymerization, at least one compound of the formula I as copolymerizable photoinitiator.

The invention additionally provides photopolymerizable systems containing at least one ethylenically unsaturated photopolymerizable compound and, where appropriate, further known and customary additives, these systems containing at least one compound of the formula I as a copolymerizable photoinitiator.

The novel compounds of the formula I are structurally derived from hydroxyalkylphenone photoinitiators, but, unlike the latter, contain ethylenically unsaturated groups of the acryloyl type.

In accordance with the definitions given above for the formula I, at least one of the radicals R^3 or R^4 always is or contains the group Z of the structure -CO-CR=CR'R". Therein R, R' and R" can each be hydrogen or methyl, and the group Z is preferably acryloyl or methacryloyl.

When in the formula I only the radical R^3 is the group Z, the corresponding compounds are esterification products of hydroxylalkylphenones with acrylic acid or acrylic acid derivatives. R^1 and R^2 can then each be hydrogen, C_{1-6}-alkyl or phenyl, and R^4 can be hydrogen, halogen, C_{1-12}-alkyl, -alkoxy or -alkylthio.

Preferred compounds are those in which R^1 and R^2 are methyl.

Corresponding photoinitiators are for example:
phenyl 2-acryloyloxy-2-propyl kentone
phenyl 2-methacryloyloxy-2-propyl ketone
4-isopropylphenyl 2-acryloyloxy-2-propyl ketore
4-chlorophenyl 2-acryloyloxy-2-propyl ketone
4-dodecylphenyl 2-acryloyloxy-2-propyl ketone
4-methoxyphenyl 2-acryloyloxy-2-propyl ketone.

When in the formula I the radical R^4 contains the group Z, the result is hydroxyalkylphenone derivatives which, in the para-position of the phenyl ring, carry unsaturated radicals of the acryloyl type. These radicals can be bonded to the phenyl ring via an oxygen, sulphur or nitrogen atom and/or via one or more oxyethylene bridges. The bonding via an oxyethylene bridge is preferred.

The other substituents can be freely chosen in accordance with the definitions given. Preferred photoinitiators are those in which R^1 and R^2 are methyl and

R^3 is hydrogen.

The corresponding compounds are for example:
4-acryloyloxyphenyl 2-hydroxy-2-propyl ketone
4-methacryloyloxyphenyl 2-hydroxy-2-propyl ketone
4-(2-acryloyloxyethoxy)-phenyl 2-hydroxy-2-propyl ketone
4-(2-acryloyloxydiethoxy)-phenyl 2-hydroxy-2-propyl ketone
4-(2-acryloyloxyethoxy)-benzoin
4-(2-acryloyloxyethylthio)-phenyl 2-hydroxy-2-propyl ketone
4-N,N'-bis-(2-acryloyloxyethyl)-aminophenyl 2-hydroxy-2-propyl ketone.

However, it is also advantageous when, in the formula I, not only the substituent R^3 but also the substituent R^4 contains unsaturated radicals of the acryloyl type. The result is then hydroxyalkylphenone derivatives whose hydroxyl groups are on the one hand esterified with acrylic acid or acrylic acid derivatives, but which on the other, in para-position, carry acryloyl radicals on the phenyl ring via oxygen, sulphur, nitrogen and/or one or more oxyethylene bridges.

Here too preference is given to those compounds of which the other substituents R^1 and R^2 are methyl. Corresponding photoinitiators are for example:
4-acryloyloxyphenyl 2-acryloyloxy-2-propyl ketone
4-methacryloyloxyphenyl 2-methacryloyloxy-2-propyl ketone
4-(2-acryloyloxyethoxy)-phenyl 2-acryloyloxy-2-propyl ketone
4-(2-acryloyloxydiethoxy)-phenyl 2-acryloyloxy-2-propyl ketone.

Particularly preferred photoinitiators according to the invention are the compounds:
phenyl 2-acryloyloxy-2-propyl ketone
4-acryloyloxyphenyl 2-hydroxy-2-propyl ketone
4-acryloyloxyphenyl 2-acryloyloxy-2-propyl ketone
4-(2-acryloyloxy)-phenyl 2-hydroxy-2-propyl ketone
4-(2-acryloyloxyethoxy)-phenyl 2-acryloyloxy-2-propyl ketone.

The compounds of the general formula I can be prepared by standard processes of organic chemistry.

The reaction conditions therein can be taken from the standard works of preparative organic chemistry, for example HOUBEN-WEYL, Methoden der organischen Chemie [Methods of organic chemistry], Georg-Thieme Verlag, Stuttgart, or ORGANIC SYNTHESIS, J. Wiley, New York London Sydney.

In general, it is advantageous to prepare the photoinitiators according to the invention, or their precursors, by the proven methods of synthesis which are customary for the known hydroxyalkylphenone photoinitiators. These methods are described in detail in German Offenlegungsschrift 2,722,264. Compounds of the formula I in which the radical R^3 is the unsaturated group Z can be obtained in a simple manner from commercially available or conventionally prepared hydroxyalkylphenones by esterification, for example with acryloyl halide and a customary esterification catalyst, preferably a tertiary amine. For instance, the novel initiator phenyl 2-acryloyloxy-2-propyl ketone can be prepared from phenyl 2-hydroxy-2-propyl ketone (phenyl-2-hydroxy-2-methylpropan-1-one; Daracur® 1173, E. Merck) by esterification with acryloyl chloride/triethylamine.

Compounds of the formula I in which R^4 contains the unsaturated group Z can be obtained for example by subjecting suitable phenyl derivatives which contain Z or a grouping into which Z is easily introducible to a Friedel-Crafts acylation with an appropriate carbonyl halide to introduce the photoinitiator active structure or a precursor thereof.

Examples of phenyl derivatives which are suitable for use as starting materials are phenol, 4-thiophenol, 4-aminophenol and monoethoxylated or polyethoxylated phenol such as 2-hydroxyethyl phenyl ether.

For the Friedel-Crafts acylation it is advisable to protect the terminal functional groups by means of suitable, subsequently redetachable protective groups, for example by acylation in the case of the OH group. After introduction of the photoinitiator active structure the terminal OH group can then be esterified in conventional manner, for example with acrylic acid.

Phenyl derivatives which already contain the unsaturated group Z, however, can also be phenyl acrylate, phenyl methacrylate or terminally acrylated, monoethoxylated or polyethoxylated phenol such as acryloyloxyethyl phenyl ether. With these starting materials, however, there does exist a danger of a premature polymerization during the subsequent reactions.

To produce the photoinitiator active structure of the hydroxyalkylphenone type, it is possible to acylate for example with isobutyroyl halide or α-chloroisobutyroyl halide and subsquently to introduce the hydroxyl, alkoxy or alkanoyloxy grouping.
For instance, the Friedel-Crafts acylation of acylated 2-hydroxyethyl phenyl ether with isobutyroyl chloride and a subsequent bromination and hydrolysis on the tertiary C atom leads to the compound 4-(2-hydroxyethoxy)phenyl 2-hydroxy-2-propyl ketone. From this compound it is possible to obtain, for example by selective esterification with acryloyl chloride/tertiary amines, the novel initiator 4-(2-acryloyloxyethoxy)-phenyl 2-hydroxy-2-propyl ketone and, by esterification of both OH groups, the novel initiator 4-(2-acryloyloxyethoxy)-phenyl 2-acryloyloxy-2-propyl ketone.

When the bonding of the unsaturated radical R^4 to the aromatic is effected by sulphur (X = S), substitution of appropriate 4-halogenoaryl ketones with thiols such as 2-mercaptoethanol under basic conditions is possible. N,N-disubstituted anilines (X = N) can be acylated under Vilsmeier conditions for example with N,N-dimethylisobutyramide and phosphorus oxychloride. Esterification of the OH groups with unsaturated acid chlorides gives the corresponding copolymerizable photoinitiators.

The compounds of the general formula I are highly active photoinitiators and can in general be used in photopolymerizable systems, provided the latter contain ethylenically unsaturated, photopolymerizable compounds.

The photoinitiators according to the invention, owing to the specific, unsaturated substituent(s) Z, have the property that they or their degradation products formed in the photoinitiator reaction can function as copolymerizable comonomers in the photopolymerization reaction. This, as the experiment reproduced within the framework of the examples below, surprisingly leads to an unexpectedly high degree of incorporation of unreacted photoinitiators and of photoinitiator degradation products in the polymer product eventually obtained. This is consequently a very effective way of reducing or wholly eliminating undesirable influences on the properties of the end product. It has further been found that practically no loss of activity occurs on introducing the unsaturated substituents Z in the hydroxyalkylphenone photoinitiator structure.

The compounds of the general formula I can be used according to the invention as photoinitiators for photopolymerizing ethylenically unsaturated compounds and/or for hardening photopolymerizable systems which contain such compounds, and in particular also as UV hardeners for printing inks and in the irradiation hardening of aqueous prepolymer dispersions. This use is effected in conventional manner. The compounds to be used according to the invention are added the systems to be polymerized in general in amounts of 0.1 to 20% by weight, preferably 0.5 to 12% by weight.

This addition generally takes the form of simple dissolving and stirring, since most of the photoinitiators to be used according to the invention are liquid or at least readily soluble in the systems to be polymerized. A system to be polymerized is to be understood as meaning a mixture of monofunctional or polyfunctional ethylenically unsaturated monomers, oligomers, prepolymers, polymers or mixtures of these oligomers, prepolymers and polymers with unsaturated monomers, which is initiatable by free radicals and which, if necessary or desired, can contain further additives such as, for example, antioxidants, light stabilizers, dyes, pigments, but also further known photoinitiators and also reaction accelerants. Suitable unsaturated compounds are all those whose C=C double bonds are activated by, for example, halogen atoms, carbonyl, cyano, carboxyl, ester, amide, ether or aryl groups or by conjugated further double or triple bonds. Examples of such compounds are vinyl chloride, vinylidene chloride, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, methyl, ethyl, n- or tert.-butyl, cyclohexyl, 2-ethylhexyl, benzyl, phenyloxyethyl, hydroxyethyl, hydroxypropyl, lower alkoxyethyl, tetrahydrofurfuryl acrylate or methacrylate, vinyl acetate, propionate, acrylate, succinate, N-vinylpyrrolidone, N-vinylcarbazol, styrene, divinylbenzene, substituted styrenes, and also mixtures of such unsaturated compounds. Even polyunsaturated compounds such as, for example, ethylene diacrylate, 1,6-hexanediol diacrylate, propoxylated bisphenol A diacrylate and dimethacrylate, trimethylolpropane diacrylate and pentaerythritol triacrylate can be polymerized with the photoinitiators used according to the invention. Further photopolymerizable compounds are unsaturated oligomers, prepolymers or polymers and their mixtures with unsaturated monomers. These include for example unsaturated polyesters, unsaturated acrylic materials, epoxy materials, urethanes, silicones, aminopolyamide resins and in particular acrylated resins such as acrylated silicone oil, acrylated polyesters, acrylated urethanes, acrylated polyamides, acrylated soya bean oil, acrylated epoxy resin, acrylated acrylic resin, preferably in mixture with one or more acrylates of a mono-, di- or polyalcohol.

The photopolymerizable compounds or systems can be stabilized by adding known thermal inhibitors and antioxidants, such as, for example, hydroquinone or hydroquinone derivatives, pyrogallol, thiophenols, nitro compounds, β-naphthylamines or β-naphthols, in the customary amounts without significantly impairing the initiator action of the photoinitiators accordi[illegible] to the invention. The main purpose of such additions is [illegible] prevent premature polymerization during the preparati[illegible] [illegible]ystems by mixing of the components.

It is also possible to add [illegible] [illegible]ight stabilizers, such as, for example, benzophenone derivatives, benzotriazole derivatives, tetraalkylpiperidines or phenyl salicylates.

To exclude the inhibiting action of air oxygen, photopolymerizable systems frequently also have added to them paraffin or similar waxy substances. As a consequence of insufficient solubility in the polymer, they float out at the start of the polymerization and form a transparent surface layer which prevents the access of air. Air oxygen can also be deactivated, for example by introducing autoxidizable groups, such as, for example, allyl groups, in the system to be hardened.

The photoinitiators according to the invention can also be used in combination with known free radical initiators, such as, for example, peroxides, hydroperoxides, ketone peroxides or percarboxylic acid esters. Furthermore, they can contain pigments or dyes of the type customary, for example, in photochemically hardening printing inks. In this case, the amount of photoinitiator is chosen to be higher, for example 6 to 12% by weight, while 0.1 to 5% by weight is in most cases fully sufficient for colourless photopolymerizable products. Depending on the intended use, it is possible to add fillers, such as talcum, gypsum or silica, fibres, organic additives such as thixotroping agents, flow control agents, binders, lubricants, matting agents, plasticizers, wetting agents, silicones for improving the constitution of the surface, antiflotation agents or minor amounts of solvents.

Examples of known photoinitiators which, where appropriate, are usable together with the initiators according to the invention are benzophenones such as, for example, Michler's ketone [4,4'-bis(dimethylamino)-benzophenone], 4,4'-bis(diethylamino)benzophenone, p-dimethylaminobenzophenone, p-chlorobenzophenone, benzophenone; anthraquinones such as, for example, anthraquinone, 2-chloroanthraquinone, 2-alkylanthraquinones; xanthones, such as, for example, 2-halogenoxanthones or 2-alkylxanthones; thioxanthones such as 2-chlorothioxanthones, 2-alkylthioxanthones; acridanones such as, for example, 2-alkylacridanones or N-substituted acridanones; benzoins such as, for example, p-dimethylaminobenzoin and alkyl ethers of benzoin; benzil ketals, α-halogenoketones, dialkoxyacetophenones, α-hydroxyalkylphenones and α-aminoalkylphenones as described, for example in German Offenlegungsschrift 2,722,264 and European Offenlegungsschrift 3,002, and also for example fluorenones, dibenzosuberones, phenanthrenquinones, benzoic acid esters such as, for example, hydroxypropyl benzoate, benzoyl benzoate acrylate.

Mixtures with known initiators contain the copolymerizable photoinitiators to be used according to the invention in general in amounts of at least 10% by weight, preferably of 50 to 95% by weight, relative to the total amount of initiator mixture used.

It is advantageous to use in the photopolymerizable systems, in addition to the copolymerizable photoinitiators according to the invention, reaction accelerants.

Examples of reaction accelerants which can be added are organic amines, phosphines, alcohols and/or thiols which all have at least one CH groups which is in the α-position relative to the hetero atom. Suitable are for example primary, secondary and tertiary aliphatic, aromatic, araliphatic or heterocyclic amines as described, for example, in US Patent 3,759,807. Examples of such amines are butylamine, dibutylamine, tributylamine, cyclohexylamine, benzyldimethylamine, dicyclohexylamine, triethanolamine, N-methyldiethanolamine, phenyldiethanolamine, piperidine, piperazine, morpholine, pyridine, quinoline, ethyl p-dimethylaminobenzoate, butyl p-dimethylaminobenzoate, 4,4'-bis(dimethylamino)benzophenone (Michler's ketone) or 4,4'-bis(diethylamino)benzophenone. Particularly preferred are tertiary amines such as, for example, trimethylamine, triisopropylamine, tributytlamine, octyldimethylamine, dodecyldimethylamine, triethanolamine, N-methyldiethanolamine, N-butyldiethanolamine, tris-(hydroxypropyl)amine, alkyl dimethylamino-benzoates. Other suitable reaction accelerants are for example trialkylphosphines, secondary alcohols and thiols. The addition of such reaction accelerants can vary within their customary amounts.

Photopolymerizable systems which additionally contain a tertiary organic amine as a reaction accelerant are a particularly preferred form of the present invention.

The expression "photopolymerization of ethylenically unsaturated compounds" is to be understood in the widest sense. It also covers, for example, the further polymerizing or the crosslinking of polymeric materials, for example of prepolymers, the homopolymerization, copolymerization and terpolymerization of simple monomers, and even the combination of the types of the reaction mentioned.

By exposing the photopolymerizable systems containing the copolymerizable photoinitiators according to the invention to the action of high-energy radiation, preferably UV light, the photopolymerization can be initiated. The photopolymerization is effected in accordance with methods known per se, namely by irradiating with light or UV radiation of the wavelength range of 250-500 nm, preferably of 300-400 nm. The sources of radiation used can be sunlight or artificial radiators. Advantageous are for example mercury vapour high-pressure, medium-pressure or low-pressure lamps and also xenon and tungsten lamps.

The photopolymerization using the photoinitiators according to the invention can be carried out not only batchwise but also continuously. The irradiation time depends on the way the photopolymerization is carried out, on the nature and concentration of the polymerizable materials used, on the nature and amount of the photoinitiators used and on the intensity of the light source and, as for example in the radiation hardening of coatings, can be within the range from a few seconds to minutes, but in the case of large batches, as for example, in mass polymerization, can also be of the order of hours.

The compounds of the formula I are preferable used as photoinitiators in the UV hardening of thin films such as, for example, surface coatings on all customary materials and supports. These can be, chiefly, paper, wood, textile base materials, plastic and metal. An important field of use is also the drying and/or hardening of printing inks and screen printing materials, of which the latter are preferably used in the surface coating and design of, for example, tins, tubes and metallic closure caps. Owing to the very substantial or complete absence of free initiator residues after photopolymerization from the systems containing copolymerizable photoinitiators according to the invention, these systems are particularly suitable for use in fields of application where any diffusion of such residues into media surrounding corresponding end products is to be ruled out, for example when packaging materials with photopolymerized coatings come into contact with foodstuffs.

Examples 1-5 below describe the preparation of copolymerizable photoinitiators according to the invention.

Example 1

Phenyl 2-acryloyloxy-2-propyl ketone

TO 5.0 g (0.03 mol) of commercially available phenyl 2-hydroxy-2-propyl ketone in 40 ml of dioxane are added under inert gas protection 5.4 g (0.06 mol) of acryloyl chloride and then, dropwise with stirring, a mixture of 6.1 g (0.06 mol) of triethylamine and 5 ml of dioxane. This is followed by refluxing for one hour and, after cooling down, discharge of the reaction mixture into 300 ml of ice-water. Extraction with ethyl acetate, removal of the solvent and recrystallization from methyl t-butyl ether gave 3.2 g of the photoinitiator with a melting point of 89°C.

Prepared analogously: phenyl 2-methacryloyloxy-2-propyl ketone.

Example 2

4-(2-Acryloyloxyethoxy)-phenyl 2-hydroxy-2-propyl ketone

a) To 880 g (6.6 mol) of anhydrous aluminium chloride in 480 ml of dichloromethane are added dropwise with stirring at -5 to 0°C 336 g (3.2 mol) of isobutyrol chloride in the course of 40 minutes. At the same temperature 540 g (3.0 mol) of 2-phenoxyethyl acetate are then added dropwise in the course of 2 hours. The dropwise addition is followed by stirring at the stated temperature for a further 2 hours and subsequent discharge of the reaction mixture into a mixture of 1.8 l of concentrated hydrochloric acid and 5 kg of ice. The organic phase is separated off, and the aqueous layer is extracted with dichloromethane. The combined organic phases are washed with water, dried and concentrated, and the residue is distilled in vacuo. This gives 740 g of 4-(2-acetoxyethoxy)-phenyl 2-propyl ketone having a boiling point of 145-152°C/ 0.3-0.5 torr.

b) 250 g (1.0 mol) of 4-(2-acetoxyethyloxy)-phenyl 2-propyl ketone are dissolved in 200 ml of glacial acetic acid, and 192 g (1.2 mol) of bromine are added at 25°C with stirring in the course of 2 hours. This is followed by about 10 hours of stirring and subsequent discharge in 3 l of glacial acetic acid. The product is extracted with ethyl acetate. The combined extracts are dried, and concentrating gives 365 g of a viscous oil. This oil is dissolved in 1 l of ethanol, and 380 g of 32% strength sodium hydroxide solution are then added at 25°C with stirring in the course of 20 minutes. This is followed by 10 minutes of stirring and the subsequent removal of ethanol. The oily residue is discharged into 3 l of ice-water, and this mixture is extracted repeatedly with a total of 1.5 l of ethyl acetate. Drying, filtering and concentrating of the solution gives 250 g of isolated oily crude product. Recrystallization from acetone/ petroleum ether and/or chromatographic purification gives 145 g of 4-(2-hydroxyethoxy)-phenyl 2-hydroxy-2-propyl ketone in the form of a colourless solid substance having a melting point of 88-90°C.

c) 27.0 g (0.12 mol) of 4-(2-hydroxyethoxy)-phenyl

2-hydroxy-2-propyl ketone are dissolved in 240 ml of dioxane. 12.0 g (0.132 mol) of acryloyl chloride in 20 ml of dioxane are then added dropwise at room temperature with stirring, followed by 16.8 g (0.132 mol) of quinoline in 20 ml of dioxane. This is followed by stirring at 50°C for 1 h, cooling down and discharge onto 1 l of ice-water. The mixture is extracted 3 times with 250 ml of ethyl acetate each time. Drying and concentrating of the organic phase gives 20.8 g of the photoinitiator in the form of a viscous oil.

^{1}H-NMR ($CDCl_3$): δ 1.6 (s, 6 H, 2 CH_3), 4.3 (m, 2 H, CH_2), 4.6 (m, 2 H CH_2), 5.3 (s, 1H, OH), 5.9-6.5 (m, 3 olefinic H), 7.0 (m, 2 aromatic H), 8.1 (m, 2 aromatic H) ppm.

IR: ν 1710 (CO): 3500 (OH) cm^{-1}.

Prepared analogously:

4-(2-Methacryloyloxyethoxy)-phenyl 2-hydroxy-2-propylketone

^{1}H-NMR ($CDCl_3$): δ 1,6 (s, 6 H, 2 CH_3); 2,0 (s, 3 H, CH_3); 4,3 (t, 2 H, CH_2); 4,5 (t, 2 H, CH_2), 5,6 (s, 1 olef. H); 6,2 (s, 1 olef. H); 7,0 (d, 2 arom.H); 8,1 (d, 2 arom. H) ppm.

4-(2-Acryloyloxyethylthio)-phenyl 2-hydroxy-2-propylketone

^{1}H-NMR (($CDCl_3$): δ 1,6 (s, 6 H, 2 CH_3); 3,3 (t, 2 H, CH_2); 4,4 (t, 2 H CH_2); 5,8 bis 6,4 (m, 3 olef. H); 7,4 (d, 2 arom. H); 8,0 (d, 2 arom. H) ppm.

Example 3

4-(2-Acryloyloxyethoxy)-phenyl 2-acryloyloxy-2-propyl ketone

27.0 g (0.12 mol) of the 4-(2-hydroxyethoxy)-phenyl 2-hydroxy-2-propyl ketone obtained in Example 2a are esterified with 24.0 g (0.264 mol) of acryloyl chloride and 26.4 g (0.264 mol) of triethylamine. Corresponding working up gives 22.8 g of the photoinitiator with a melting point of 71°C.

Example 4

4-Acryloxyphenyl 2-hydroxy-2-propyl ketone

To a solution of 2.2 g (0.012 mol) of 4-hydroxyphenyl 2-hydroxy-2-propyl ketone in 20 ml of anhydrous tetrahydrofuran are added at room temperature with stirring and a little at a time 0.4 g (0.013 mol) of sodium hydride (80% strength in paraffin oil). 15 min later, 1.2 g (0.013 mol) of acryloyl chloride in 5 ml of anhydrous tetrahydrofuran are added dropwise in 10 min, which is followed by stirring for a further 1 hour. Working up (see Example 2 c) gives 2.5 g of a viscous, colourless oil.

^{1}H-NMR ($CDCl_3$): δ 1.5 (S, 6 H, 2 CH_3), 6.0 to 6.6 (m, 3 olefinic H), 7.1 (m, 2 aromatic H), 8.0 (m, 2 aromatic H) ppm.

Prepared analogously: 4-methacryloyloxyphenyl 2-hydroxy-2-propyl ketone.

^{1}H-NMR ($CDCl_3$): δ 1,6 (s, 6 H, 2 CH_3); 2,1 (s, 3 H, CH_3); 5,8 (s, 1 olef. H); 7,3 (d, 2 arom. H); 8,1 (d, 2 arom. H) ppm.

Example 5

4-acryloyloxyphenyl 2-acryloyloxy-2-propyl ketone

2.2 g (0.012 mol) of 4-hydroxyphenyl 2-hydroxy-2-propyl ketone, 2.4 g (0.027 mol) of acryloyl chloride and 2.7 g (0.027 mol) of triethylamine are reacted in 30 ml of dioxane, and worked up, as in Example 3. This gives 3.6 g of a white, crystalline product having a melting point of 90-93°C (recrystallized from cyclohexane).

Prepared analogously: 4-methacryloyloxyphenyl-2-methacryloyloxy-2-propyl ketone.

^{1}H-NMR ($CDCl_3$): 1,8 (s, 6 H, 2 CH_3); 5,8 bis 6,7 (m, 6 olef. H); 7,2 (d, 2 arom. H); 8,1 (d, 2 arom. H) ppm.

Examples 6-9 below describe the use of the copolymerizable photoinitiators according to the invention in radiation-hardenable binder systems.

Example 6

A UV-hardenable binder system which consists of 75 parts by weight of an oligomeric epoxy acrylate (Laromer® LR 8555 from BASF) and 25 parts by weight of hexanediol diacrylate has added to it 5 parts by weight of phenyl 2-acryloyloxy-2-propyl ketone (initiator according to Example 1).

The ready-to-use formulation is applied to degreased glass plates (10 x 10 cm) with spiral wires in a thickness of 50 µm. The coatings are then hardened in an irradiator ("Mini-Cure" from Primarc Ltd.) underneath a mercury medium-pressure lamp (lamp power 80 watt/cm) at a belt speed of 10 m/min. The exposure gap is about 10 cm.

The fully hardened coatings obtained are completely odourfree and exhibit no yellowing.

An analogous method is used to obtain similar results with the initiators of Example 2-5.

Example 7

A UV-hardenable binder system consisting of 60 parts by weight of an acrylated polyurethane prepolymer (Prepolymer VPS 1748, from Degussa AG), 40 parts by weight of hexanediol diacrylate, 15 parts by weight of pentaerythritol triacrylate and 5 parts by weight of 4-(2-acryloyloxyethoxy)-phenyl 2-hydroxy-2-propyl ketone (initiator according to Example 2) is processed into 50 µm thick coatings and hardened at a belt speed of 30 /min, analogously to Example 6. The fully hardened coatings obtained are completely odourfree and colourless.

The corresponding use of the initiators according to Example 1 and 3-5 gives similar results.

Example 8

63.5 parts of an epoxy acrylate resin (Laromer® 8555 from BASF, Ludwigshafen) are ground up on a three-roll mill together with 36.5 parts of butanediol diacrylate and 20 parts of Heliogen Blue. 5 parts of 4-(2-acryloyloxyethoxy)-phenyl 2-hydroxy-2-propyl ketone (initiator according to Example 2) are stirred into the suspension within 10 minutes. The printing ink thus obtained is printed onto glazed paper in a 1 µm film thickness and is hardened with a radiation output of 160 W/cm at a belt speed of 50 m/min. The odourfree printed sheets obtained are immediately stackable. According to the colour differance measurement, the blue print shows no shift in colour due to yellowing.

The method of Example 8 is also suitable for using the photoinitiator mentioned in Example 1 and 3-5 as UV hardeners for printing inks.

Example 9

63.5 parts by weight of a urethane acrylate resin (Uvimer® 530 from Bayer, Leverkusen) are porcelain ball milled together with 36.5 parts of butanediol diacrylate and 100 parts of titanium dioxide (anatase). 5 parts by weight of 4-acryloyloxyphenyl 2-hydroxy-2-propyl ketone (initiator according to Example 4) and 3 parts by weight of N-methyldiethanolamine are then stirred in. The paint applied to glass plates in a film thickness of 10 µm can be hardened at a belt speed of 50 m/min and with a radiation output of 160 W/cm to give an odourless, yellowing-free film.

The method of Example 9 is also suitable for incorporating the compounds mentioned in Examples 1 to 3 and 5 as photoinitiators in a pigmented lacquer.

The test reproduced in Example 10 below shows the advantages of the copolymerizable photoinitiators according to the invention over known photoinitiators with respect to residual content of initiator in the photopolymerized layer under optimal conditions for the final hardness of the layer.

Example 10

Test

A UV-hardenable binder system was prepared to consist of

75% by weight of a prepolymer based on an acrylated epoxy resin (Laromer® EA 81, BASF AG),

25% by weight of hexanediol diacrylate.

To identical portions of this binder system were added in each case 5% by weight of the following photoinitiators:

No. 1 4-(2-acryloyloxyethoxy)-phenyl 2-hydroxy-2-propyl ketone (initiator according to the invention and Example 2)

No. 2 Phenyl 2-hydroxy-2-propyl ketone (Darocur® 1173, E. Merck; for comparison)

No. 3 α-allylbenzoin (for comparison)

No. 4 α-allylbezoin allyl ether (for comparison).

Samples of the homogeneous, ready-to-use UV coatings were applied in a known manner with a spiral wire to glass plates (10 x 10) in a film thickness of 50 µm. In preliminary tests the optimal hardening conditions for these surface coatings were initially determined. To this end, the coated plates were passed in a UV laboratory dryer (Beltrolux, from Beltron) on a variable speed conveyor belt (2.5 to 40 m/min) at a distance of about 1 cm and past underneath 2 mercury medium pressure lamps each of 50 watt radiation output/cm. On the day after the UV hardening the layer hardness obtained in each case was determined by determining the König pendulum hardness (DIN 53157).

The hardness determination in accordance with this standard is based on the fact that the damping of the swing of a pendulum which rests on the layer increases with the softness of the layer. The pendulum hardness is deemed to be measured by the time span in seconds in which the deflection of the swinging pendulum decreases from 6^{o} to 3^{o} relative to the vertical. The longer the damping time, the harder the layer.

The coatings produced with the present UV-hardenable binder systems were found to have, as obtainable final hardness, a pendulum hardness of 210 seconds, which was obtainable in the case of initiators No. 1 (initiator according to the invention) and No. 2 at a maximum belt speed of 10 m/min (corresponds to a minimum exposure time of 6 s/m) and in the case of initiators No. 3 and No. 4 at 5 m/min (12 s/m).

To determine the proportions of unreacted initiator still present in these coatings after the UV hardening, these layers were detached from the base materials, and comminuted, and samples thereof were weighed out accurately into extraction vessels and were each treated for 2 hours in an ultrasonic bath with identical amounts of acetonitrile as extractant.
The solutions obtained were then analysed by means of high pressure liquid chromatography for their initiator content.

Table 1 below shows, for the coatings obtained with the respective photoinitiators (pendulum hardness 210 s) the respectively extractable amount of initiator (amount of initiator used in the unhardened binder system = 100%).

Table 1

Initiator No.	UV hardening belt speed	Extractable amount of initiator
1	10 m/min	6.5%
2	10 m/min	66 %
3	5 m/min	40 %
4	5 m/min	26 %

Result

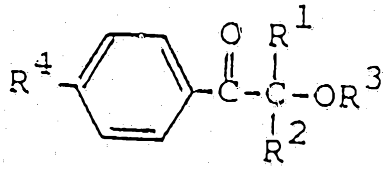
It is found that, in the case of UV hardening under optimal conditions, the amounts of initiator extractable out of the coatings obtained with the known initiators (Nos. 2, 3 and 4) are higher by a factor of 4 to 10 than in the case of hardening with the copolymerizable initiator according to the invention (No. 1.).

From this it is possible to infer that the initiator according to the invention is virtually completely incorporated in the polymer material by copolymerization, which is evidently not the case with the known initiators, including in particular the unsaturated allylbenzoin derivatives.

It is also found that the initiator according to the invention is comparable in its activity with the known hydroxyalkylphenone initiator.

The claims defining the invention are as follows:

1. Compounds of the general formula I



(I)

in which

R^1 and R^2 are each H or C_1-C_6-alkyl

R^3 is H, C_1-C_6-alkyl, C_1-C_6-alkanoyl or the group Z,

R^4 is H, halogen, C_1-C_{12}-alkyl, C_1-C_{12}-alkoxy, C_1-C_{12}-alkylthio or the group $-X[(CH_2-CH_2-O)_n-Z]_m$

and

X is O, S, N or NH,

n is the numbers 0 to 4,

m is the number 1 when X = O, S and NH or the number 2 when X = N

Z is the group -CO-CR=CR'R"

with R, R', R" each being H or CH_3,

always at least one of the radicals R^3 or R^4 containing the group Z.

2. Compounds of the general formula I according to claim 1 when used as copolymerizable photoinitiators for the photopolymerization of ethylenically unsaturated compounds.

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3. Compounds of the general formula I according to claim 1, where appropriate together with known photoinitiators and/or sensitizers, when used as copolymerizable photoinitiators for the photopolymerization of ethylenically unsaturated compounds or systems containing such compounds.

4. Compounds of the general formula I according to claim 1, when used in UV-hardening printing inks.

5. Compounds of the general formula I according to claim 1, when used in the radiation

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hardening of aqueous prepolymer dispersions.

6. Process for photopolymerizing ethylenically unsaturated compounds or systems containing such compounds, characterized in that at least one compound of the formula I is added as a copolymerizable photoinitiator to the mixture to be polymerized, before initiation of the photopolymerization.

7. Process according to Claim 6, characterized in that 0.1 to 20% by weight of a compound of the formula I is added to the mixture to be polymerized, before initiation of the photopolymerization.

8. Photopolymerizable systems containing at least one ethylenically unsaturated photopolymerizable compound and, where appropriate, further known and customary additives, characterized in that they contain at least one compound of the formula I as a copolymerizable photoinitiator.

9. Photopolymerizable system according to Claim 8, characterized in that it contains 0.1 to 20% by weight of a compound of the formula I.

DATED this 8th day of September, 1986.

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By Its Patent Attorneys,
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