

PHOTOINITIATED REACTIONS

This invention relates to photoinitiated reactions, for example curing and polymerisation  
5 reactions, and more particularly to UV curing used in photopolymer technology, as well as to photoinitiated colour forming reactions.

Within the growing realm of UV curing technology, one of the most important applications is in photo-  
10 imaging. Ever since the birth of photography, new and innovative ways of obtaining images by exposure to light have been explored. Even the silver halide process itself, which still forms the core of photography has undergone substantial change, as for  
15 example when the introduction of T-grain emulsions took place.

Although substantial improvements in photopolymer technology have been made over the last 20 years, the sensitivity of the processes is still very limited  
20 compared to the photosensitivity of the silver halide process. One of the major goals in photopolymer science is to approach the sensitivity of silver halide.

Two basic methods of increasing photopolymer  
25 quantum yield beyond unity exist. The first of these is most familiar as the acrylate chemistry used in most commercial free radical U.V. cure systems. The approach here is that of the chain reaction. Any photon which is absorbed and becomes converted by the  
30 initiator into a radical is capable of converting many polymerisable molecules very quickly. Thus the quantum yield for such processes is high, but still not as high as that for silver halide.

The second basic form of photopolymer quantum  
35 yield enhancement is exemplified by the cationic U.V.

curing systems. In this instance, the absorbed photon generates a catalytic monomer species which is capable of catalysing polymerisations, cross-linking, or even molecular cleavage. This technology has been described  
5 as capable of producing "living polymers" which will continue growing as long as substrate monomer molecules are still available. The reactions are, however, relatively slow compared to the chain reactions of the free radical process. Furthermore, although the  
10 quantum yield in terms of reacted molecules is theoretically near infinite, the slow reactions limit spatial resolution by reason of diffusion of active species out of the imaged area.

A limitation in terms of photopolymer imaging has  
15 always been the amount of time needed to deliver an adequate number of photons to the area to be imaged. The delivery of a large amount of random photons is easy. High power lamps, simple reflectors and conveyor belts used in combination enable this aim to  
20 be achieved. For imaging, the light needs to be collimated and delivered in a controlled fashion. To collimate the light output from any lamp involves a substantial loss of intensity. The subsequent use of optical components and even photo tools serves to  
25 reduce the yield of available photons from even a very powerful lamp to a remarkably low level.

It is within this environment that the usage of lasers has developed. Although the amount of energy that a visible or U.V. laser will deliver is relatively  
30 low, the intrinsic collimation and the intensity of photons delivered at a given wavelength make the laser a useful light source. The use of computer guided beam manipulation in combination with mirrors enables one to eliminate photo tool usage, and further enhances the  
35 amount of photons available for the photochemistry.

Nevertheless, these improvements have been only

incremental, and laser imaged photopolymer processes are still slow. The silver halide process achieves extreme quantum efficiency by virtue of the development step. The actual efficiency of the photochemistry is  
5 relatively low compared with chain reaction processes. It is only when the silver halide emulsion is developed that the remarkable autocatalytic development chemistry improves the quantum yield. Wherever silver has been produced, the silver available accelerates the  
10 development reaction, which in turn produces more silver. Thus a single photon can generate a great number of silver atoms and a very high quantum yield is obtained due to the propagation which occurs in the development process.

15 It is an object of this invention to increase significantly the efficiency of photochemical reactions used in particular in photopolymer imaging.

According to one aspect of this invention, there is provided a method of carrying out a photoinitiated  
20 reaction which comprises applying a reactive substrate selected from a polymerisable and crosslinkable composition and a colour changing substance to a support, activating, in selected locations on the support, a latent photoinitiator which contains a  
25 methylene-1,3-dioxolane ring and yields a ketone photoinitiator when activated and which has been applied with the reactive substrate and subsequently exposing the reactive substrate with the resulting ketone photoinitiator therein to photoreaction  
30 conditions wherein actinic radiation causes the substrate to undergo polymerisation or crosslinking or colour change respectively in said selected locations on the support where the latent photoinitiator has been activated.

35 In a second aspect, this invention provides a method of for the photoinitiated polymerization of a

polymerizable substrate applied to a support,  
comprising:

(a) providing a coating on the support, which  
coating comprises the polymerizable substrate and a  
5 latent photoinitiator, wherein the latent  
photoinitiator is a ketone photoinitiator which is  
protected by a methylene 1,3-dioxolane structure;

(b) deprotecting the protected ketone  
photoinitiator in selected locations of the support  
10 thereby to provide an active ketone photoinitiator in  
the coating at said selected locations; and

(c) exposing the coating on the support to a  
source of actinic radiation whereby polymerization of  
the polymerizable material is initiated in said  
15 selected locations on the support where the protected  
ketone photoinitiator has been deprotected in step (b).

An understanding of the above-described concept  
using silver halide emulsions has made it possible to  
establish that a similar approach might be viable in  
20 the field of photopolymer imaging. Although no  
autocatalytic reaction of similar nature has yet been  
commercially exploited, it has been found that a  
similar amplification step can be introduced within the  
photopolymer field.

25 While it is feasible to consider the inventive  
principle as applying also to colour compounds or  
chromophores per se, it is envisaged that the colour  
change will take place during a crosslinking and/or  
polymerisation process to enable areas at which  
30 reaction has taken place to be identified. Leuco  
crystal violet is an important chromophore in this  
respect (latent colour formers are generally termed  
"leuco dyes"). Other leuco dyes to which the inventive  
principle may be applied include leucoanthene and  
35 leucofluorans.

The latent photoinitiator is most commonly to be a  
protected photoinitiator whose protection is removed in

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a reaction which takes place under preliminary  
conditions. Such preliminary conditions preferably  
include the use of a photoinitiator as such which, when  
exposed to actinic radiation, is able to interact with  
5 the latent photoinitiator to cause the latent

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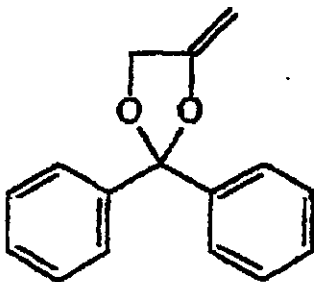
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photoinitiator to be converted to its underlying photoinitiator. The present invention will, unless otherwise indicated, be described with reference to such a mode of activating the latent photoinitiator.

5 There is then overall use of two photoreactions which will need to include application of actinic radiation at two distinct wavelengths. In particular a low energy source of actinic radiation may be employed in a first or preliminary photoreaction, which can be  
10 utilised in achieving an imagewise exposure of the substrate, and a high dosage of actinic radiation is applied as a flood in connection with a second photoreaction in which the substrate is polymerised and/or crosslinked. Preferably, laser direct imaging  
15 is used in applying the low energy source of actinic radiation.

Such method embodying this invention thus uses an amplification step, in which a second photochemical reaction is carried out subsequently to a preliminary,  
20 preferably photochemical reaction. Recent work has indeed been carried out by Bradley et al Journal of Photochemistry and Photobiology A: chemistry 100 (1996) 109-118, having been centred around the development of vinyl-dioxolane based monomers as a more amenable  
25 alternative to vinyl ethers conventionally used as monomers for cationic U.V. curing. Such a material is (2,2'-diphenyl-4-methylene-1,3-dioxolane):-

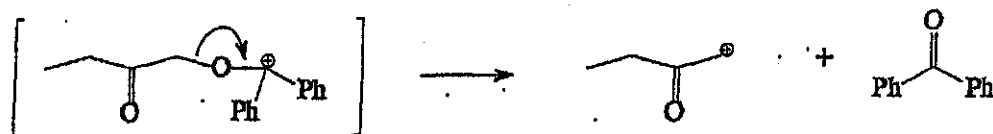
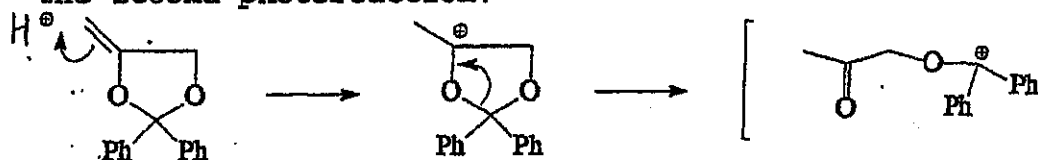


35 The vinyl dioxolane structure can be produced from

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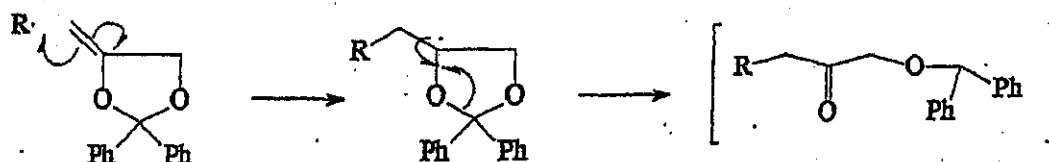
a ketone photoinitiator starting material although other methods are available for the production of such a structure.

Experiments reported in the above reference demonstrated that the acid catalysed photopolymerisation using a cationic species and such vinyl-dioxolane does not proceed via a simple cationic polymerisation but rather occurs via a ROMP-like (Ring Opening Metathesis Polymerisation) process in which a ketone is produced which is to act as photoinitiator in the second photoreaction.

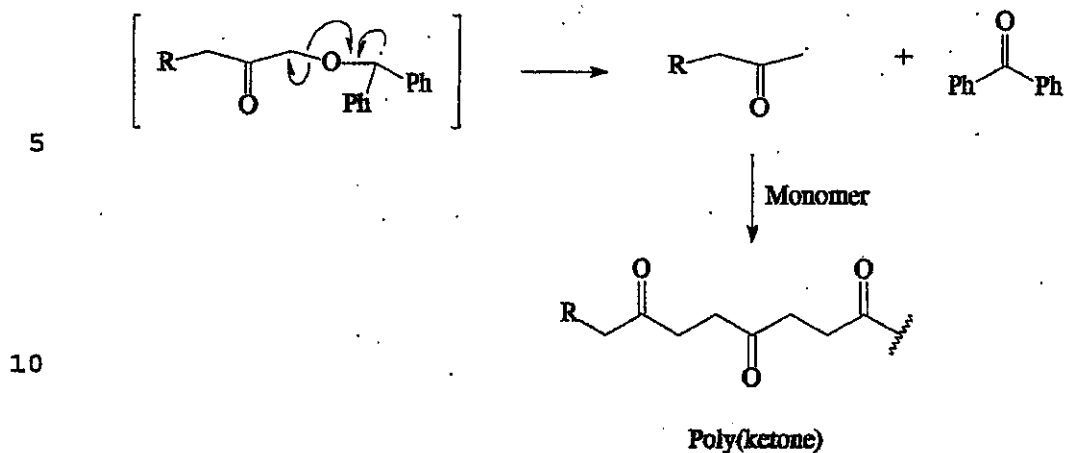


The vinyl-dioxolane behaves as a ketal-protected carbonyl compound and the process generates a polyketone as the dioxolane ring is opened, generating the theoretical parent ketone for the dioxolane ring. In the reported experiments, the ketone used was benzophenone, a well known photoinitiator of acrylate polymerisation.

It has similarly been found that the free radical polymerisation of the same compound results in the photogeneration of the theoretical parent ketone.



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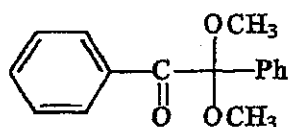


15        The dioxolane ring opening reaction is applicable to formation of a whole range of ketonic functional initiator and co-initiator species ranging from such simple well known materials as benzil dimethyl ketal through to exotic materials such as di-iodo butoxy

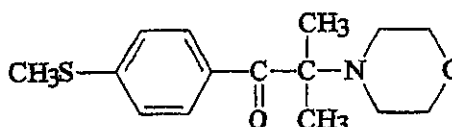
20 fluorone (a visible active photoinitiator used for stereolithography). When made in the form of the required vinyl-dioxolanes, the resulting compounds act as "latent photoinitiators", capable of being activated by low doses of U.V. light on formation of catalytic

25 quantities of acid from cationic initiators or by ongoing radical reactions. Examples of such compounds are:

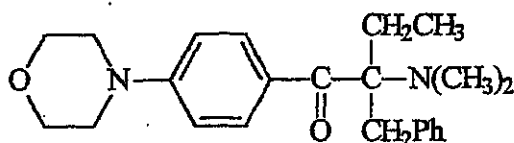
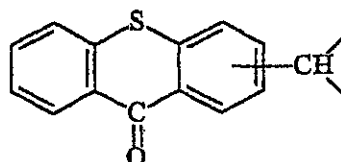
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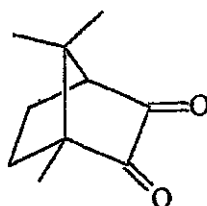
2,2-dimethoxy-2-phenyl acetophenone



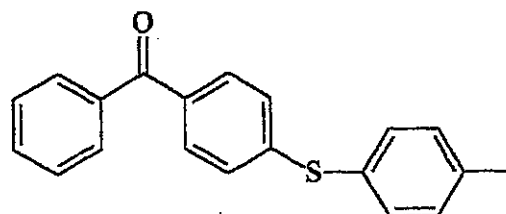
2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one

2-benzyl-2-N,N-dimethylamino  
-1-(4-morpholinophenyl)-1-butanone

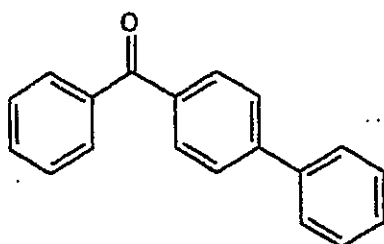
isopropyl thioxanthone



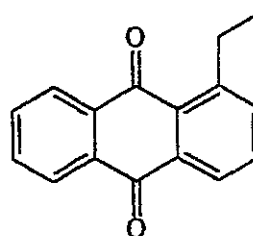
Camphorquinone



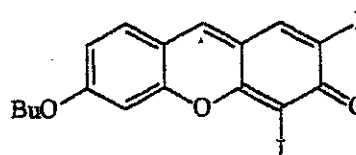
[4-(4-methylphenylthio)phenyl]phenylketone



4-phenyl benzophenone



2-ethyl anthraquinone



Di-iodobutoxy fluorone

Other compounds which can be used are various benzoin ethers, as well as diethoxyacetophenone and 1-hydroxy-cyclohexyl-phenyl ketone, and 2-hydroxy-2-methyl-1-phenyl-propan-1-one and ethers thereof.

5        Such enhanced photopolymerisation method embodying this invention typically involves an initial irradiation of a film containing a cationic (acid producing) photoinitiator, acrylate and vinyl-dioxolane based latent photoinitiator. This irradiation is fast  
10 and efficient, as the polymer formed in this step may be minimal and not cause any viscosity increase, which is a prime limit on reaction rates. Subsequent to the low energy image-wise exposure, the system can be flood irradiated with light of wavelength long enough to  
15 avoid further photolysis of the cationic initiator, but adequate to photolyse the initiator formed from the cleavage of the dioxolane ring. This flood irradiation is not image-wise and therefore can involve far higher dosages of light in a relatively short time. An  
20 application for this example is that of laser direct imaging of photoimageable coatings. The technology eliminates the bottleneck of having to deliver all the polymerisation energy via the laser in an imagewise fashion. An example of this technology is summarised  
25 in the flow scheme of Fig. 1 of the accompanying drawings.

Preferably in general, cationic acid-producing photoinitiators such as sulphonium and iodonium salts and salt-form organometallic compounds are utilised in  
30 achieving conversion of the latent photoinitiator although  $\alpha$ -sulphonyloxy ketones can also be used as cationic acid-producing photoinitiators. These compounds are exemplified by the following compounds:

                  bis[4-(diphenylsulphonio)-phenyl]sulphide,  
35 bis-hexafluorophosphate or bis-hexafluoroantimonate optionally in combination with a mono-or-poly-[4-(

(phenylthiodiphenyl] sulphonium hexafluorophosphate or hexafluoroantimonate

bis[4-(di(4-(2-hydroxyethyl)phenyl)sulphonio-phenyl]sulphide bis-hexafluorophosphate

5 bis[4-(di(4-(2-hydroxyethyl)phenyl)sulphonio)-phenyl]sulphide bis-hexafluoroantimonate

( $\eta^5$ -2,4-(cyclopentadienyl)[(1,2,3,4,5,6- $\eta$ )-(methylethyl)-benzene]-iron(II)hexafluorophosphate

4-isopropyl-4-methyl diphenyliodonium or diphenyl  
10 iodonium hexafluorophosphate or  
tetrakis-(-penta-fluorophenyl)borate, as well as  
2-hydroxy-2-phenyl-3-  
toluenesulphonyloxypropionophenone.

15 A wide range of formulations is possible.  
Generally, for the cationic acid-producing  
photoinitiator, the amount may be in the range of from  
0.25 to 3% by weight of the material to be acted on.  
For the latent initiator, the practical working range  
20 is from 3 to 10% by weight of the material to be acted  
on.

The present invention permits products to be  
obtained which dramatically increase the productivity  
of imaging processes dependent on actinic radiation  
25 curing. Practical experience has shown that it is  
particularly convenient to work in the UV range. With  
vinyl-dioxolane latent photoinitiators and the  
aforementioned acid-producing producing  
photoinitiators, one can use UV-radiation of a  
30 relatively short wavelength in the first photochemical  
reaction and UV-radiator of a longer wavelength in the  
second photochemical reaction, or vice versa.

A second procedure embodying this invention is in  
the field of photoimageable inks for sequential build  
35 up (SBU) technology where cationic systems are to be

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preferred due to their advantageous physical properties. This procedure demonstrates the versatility of the method of this invention. One of the materials which can be made in a dioxolane ring blocked form is isopropylthioxanthone (ITX). Thioxanthenes are particularly suitable as sensitizers for iodonium salts. As the iodonium salts themselves are generators of acid catalysts for cationic polymerisation, the possibility of their being used in a self-sensitising system is apparent and provides a means of increasing quantum yields. Initial irradiation of the iodonium salt directly in an image-wise fashion results in production of a small amount of acid polymerisation catalyst. The resulting film is sensitive to an autoaccelerative reaction when flood irradiated with near visible radiation. This enhanced sensitivity opens the way for using laser direct imaging with photoimageable SBU dielectric. An example of this technology is summarised in the flow scheme of Fig. 2 of the accompanying drawings.

A third example of the same concept relies on the radical cleavage of the dioxolane. If a free radical initiator sensitive only to short wavelength light is formulated together with acrylic monomers, acrylic pre-polymers, and a latent initiator, the latent initiator being sensitive to longer wavelength, the resulting mixture can be exposed to give an autoaccelerating reaction.

Another example of the use of a latent photoinitiator is in the printed circuit board industry. As the volume of boards produced has increased dramatically, so have concerns over the environmental impact of board manufacturing processes, especially with regards to the emission of vapours which are difficult to contain or collect and reprocess. A process responsible for generating

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organic vapour emissions is the application, by various coating methods, of Liquid Photoimageable Solder Masks (LPISM). In this process the PCB is completely coated with a liquid formulation which can be dried in an oven to produce a photosensitive coating. Imagewise exposure of the coating and subsequent developing, either by aqueous carbonate or organic solvent allows formation of openings in the mask for purposes of component or connector placement. This technology is summarised in the flow scheme of Fig. 3 of the accompanying drawings.

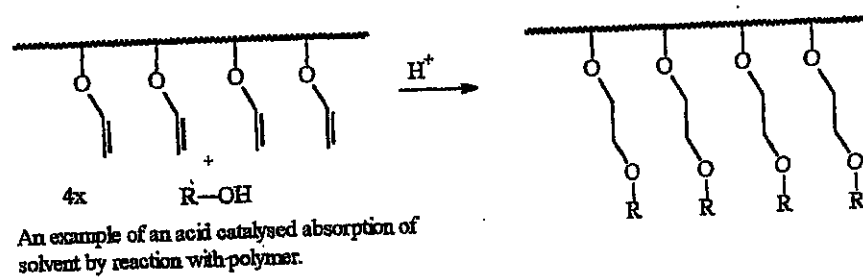
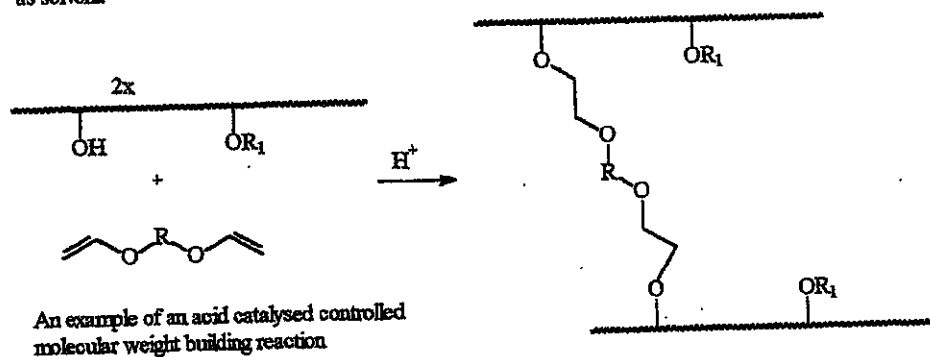
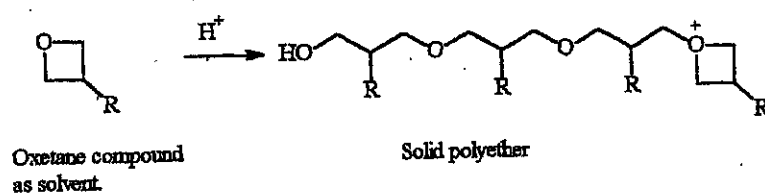
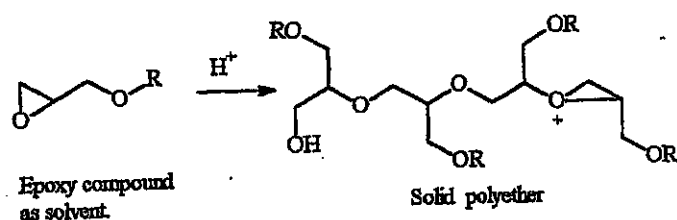
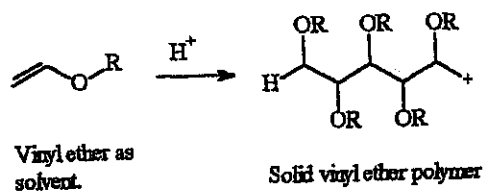
In the face of increasingly stringent regulatory requirements, control technology to reduce or eliminate vapour emissions will become necessary. A few manufacturers have ventured to introduce water reducible LPISMs into the marketplace, but they appear to be technically inferior to traditional solvent based product.

Use of a photoacid generating initiator (cationic initiator) in conjunction with a dioxolane blocked acrylate initiator permits formulation of a 100% solids LPISM. This system has the advantage of producing no emissions. Such a 100% solids formulation which can be made tack-free on exposure to acid catalysis, but remains developable, can be made by following the teaching of the present invention. The LPISM thus produced can be U.V. dried, being heated to complete the solidification process and to ensure complete de-blocking. Subsequently it can be re-exposed to image the formulation and still be developed and finally cured in a fashion familiar to the industry. The use of dioxolane blocked latent photoinitiators preserves the radical initiator during the imaging step whilst the coating is U.V. dried.

A variety of approaches can be used to effect the U.V. drying. Vinyl ethers, cycloaliphatic epoxies and

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5     oxetane compounds can be used as polymerisable solvents. Alternatively, use of such materials as cross linkers for functionalised resins is viable. Use of reactive resins, and building resin molecular weight by cationic reaction can also be used. Finally, it is possible to use a vinyl ether functional resin and react it under cationic conditions with a hydroxy functional solvent, or vice versa. Such technology may be represented by the following:



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The overall use of such LPISM technology is summarised by way of example in the flow scheme of Fig. 4 of the accompanying drawings.

5 Similar, applications are found in the manufacture of flexographic printing plates and other imaged printing systems.

As a further example, the technology can be applied to the field of visible active photoinitiators. The increased usage of these initiators means that many  
10 areas have to be configured as red light zones, these providing an exceedingly difficult environment to work in. Visible active formulations can be made with this technology so that they only become visible sensitive after U.V. irradiation. Substantial production and  
15 handling benefits ensue from this.

Yet another application is in conjunction with high intensity excimer lamp technology. The near monochromatic output of the excimer lamps would be easily capable of photolysing low concentrations of  
20 short-wavelength sensitive cationic initiators in very thick clear films.

A low concentration of any initiator, whilst necessary for controlling optical density in thick coatings, is not normally adequate to effect  
25 polymerisation. Thus the curing of thick films is limited to certain initiators which undergo photobleaching e.g. acylphosphine oxides. With correct formulation, use of a low concentration of cationic initiator in conjunction with a dioxolane blocked free  
30 radical initiator results in the ongoing, in-situ formation of free radical initiator. Thus, because the dioxolanes are blue shifted with respect to their parent initiator, optical density can be controlled, only a small proportion of free radical initiator being  
35 produced at any one time. This, in conjunction with the cold running of these lamps, would enable the use

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of this latent initiator technology in a wide variety of fields.

The latent initiators described here are not confined to being unblocked by photochemical processes yielding acid moieties. Any blocked acid of sufficient strength, for example a blocked toluene sulphonic acid, especially p-toluene sulphonic acid, will, on unblocking, catalyse the breakdown of the dioxolane ring on the latent photoinitiators. Examples of such compounds which can be used are the thermally unblockable blocked superacids produced by King Industries. A thermal unblocking variant on this technology can be useful for a number of the examples given here, especially the 100% solids LPISM and the improved handling for visible initiated processes

In summary, the chemistry outlined here provides for the synthesis of a deactivated photoinitiator by a prescribed synthetic method, for example by reaction of a carbonyl group to form a vinylic functionalised dioxolane ring, for example, by use of a leuco carbonyl group present in the form of a vinyl functionalised dioxolene ring as latent photoinitiator.

The technology is useful in the following applications.

1. Primary and Secondary imaging (PCB industry)
2. U.V. initiated sensitisation of visible initiators
3. Making visible active formulations easy to handle.
4. Controlling the cure of thick films.
5. Improving shelf life of U.V. curing formulations.

The following examples illustrate the preparation of dioxolanes which can be used in the method of this invention:

Example 1**Synthesis of 2-phenyl-2N-[4-(4-methylphenylthio)phenyl]-4-methylene-1,3-dioxolane**

Into an apparatus consisting of a 500ml round  
5 bottomed flask equipped with a Dean and Stark  
apparatus/condenser, were added the following  
materials: 25.37g [4-(4-methylphenylthio)phenyl] phenyl  
ketone, 9.21g (+/-)-3-chloro-1,2-propanediol, 0.25 p-  
toluenesulphonic acid monohydrate and 200ml toluene.  
10 The reaction mixture obtained was heated to reflux  
under atmospheric pressure until the reaction was  
complete (water collected).

The resultant reaction mixture was cooled and  
washed with 200ml molar sodium carbonate solution and  
15 then water. The organic layer was then dried over  
magnesium sulphate, rotary evaporated and distilled  
under reduced pressure.

The purified intermediate was taken and dripped  
into a refluxing solution of potassium t-butoxide (22g)  
20 in tetrahydrofuran (50g) contained in a 250ml two  
necked round bottomed flask fitted with a dropping  
funnel and condenser. After adding the intermediate  
over a period of 1.5 hours the mixture was refluxed for  
a further hour. The resultant reaction mixture was  
25 extracted with ether, washed twice with water, dried  
over magnesium sulphate and rotary evaporated to leave  
a clear oil of the above captioned target substance.

Example 2**Synthesis of Bis-methylene (1,3) dioxolane derivative of camphorquinone**

Into an apparatus consisting of a 500ml round  
bottomed flask equipped with a Dean and Stark  
apparatus/condenser, were added the following  
35 materials: 37.4g camphorquinone, 50g (+/-)-3-chloro-  
1,2-propanediol, 0.2g p-toluenesulphonic acid

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monohydrate and 300ml benzene. The reaction mixture obtained was heated to reflux under atmospheric pressure until the reaction was complete (water collected).

5           The resultant reaction mixture was cooled and washed with 200ml molar sodium hydrogen carbonate solution and then water. The organic layer was then dried over magnesium sulphate, rotary evaporated and distilled under reduced pressure.

10           The purified intermediate was taken and dripped into a refluxing solution of potassium t-butoxide (50g) in tetrahydrofuran (200g) contained in a 500ml two necked round bottomed flask fitted with a dropping funnel and condenser. After adding the intermediate  
15           over a period of 2 hours the mixture was refluxed for a further two hours. The resultant reaction mixture was extracted with ether, washed twice with water, dried over magnesium sulphate and rotary evaporated to leave  
20           a clear oil of the above-captioned target product.

**CLAIMS**

1. A method of carrying out a photoinitiated reaction  
which comprises applying a reactive substrate  
5 selected from a polymerisable and crosslinkable  
composition and a colour changing substance to a  
support, activating, in selected locations on the  
support, a latent photoinitiator which contains a  
methylene-1,3-dioxolane ring and yields a ketone  
10 photoinitiator when activated and which has been  
applied with the reactive substrate and  
subsequently exposing the reactive substrate with  
the resulting ketone photoinitiator therein to  
photoreaction conditions wherein actinic radiation  
15 causes the substrate to undergo polymerisation or  
crosslinking or colour change respectively in said  
selected locations on the support where the latent  
photoinitiator has been activated.
- 20 2. A method according to claim 1, wherein the latent  
photoinitiator is a methylene-1,3-dioxolane  
precursor of diphenyl ketone, 2,2-dimethoxy-2-  
phenyl acetophenone, diethoxyacetophenone, 1-  
hydroxy-cyclohexyl-phenyl ketone, 2-hydroxy-2-  
25 methyl-1-phenyl-propan-1-one, 2-methyl-1-[4-  
(methylthio)phenyl]-2-morpholinopropan-1-one, 2-  
benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-  
1-butanone, isopropyl thioxanthone,  
camphorquinone, [4-(4-methylphenylthio)phenyl]-  
30 phenylketone, 4-phenyl benzophenone, 2-ethyl  
anthraquinone or di-iodobutoxy fluorone.

3. A method according to claim 1 or 2, wherein the latent photoinitiator is employed in an amount of from 3 to 10% by weight of the substrate.
- 5 4. A method according to any preceding claim, wherein the polymerised and/or crosslinked composition attains its distribution by carrying out imagewise exposure of the substrate composition to actinic radiation using a photomask to activate the  
10 photoinitiator in unmasked regions under conditions such that the composition does not undergo polymerisation and/or crosslinking.
5. A method according to any preceding claim, wherein  
15 the latent photoinitiator is a protected photoinitiator and its protection is removed in a photoreaction which takes place under preliminary photoreaction conditions.
- 20 6. A method according to claim 5, wherein the preliminary photoreaction conditions include the presence of a cationic photoinitiator which yields an acid catalyst for the unblocking of the latent photoinitiator.  
25
7. A method according to claim 6, wherein the preliminary set of conditions includes the presence of an iodonium or sulphonium salt or a salt-form organometallic compound or an  $\alpha$ -sulphonyloxyketone.  
30
8. A method according to claim 7, wherein the cationic photoinitiator is selected from;

- 5 bis[4-(diphenylsulphonio)-phenyl]sulphide, bis-hexafluorophosphate or bis-hexafluoroantimonate optionally in combination with a mono-or-poly-[4-(phenylthiodiphenyl] sulphonium hexafluorophosphate or hexafluoroantimonate
- 10 bis[4-(di(4-(2-hydroxyethyl)phenyl)sulphonio)-phenyl]sulphide bis-hexafluorophosphate
- 15  $\eta^5$ -2,4-(cyclopentadienyl) [(1,2,3,4,5,6- $\eta$ )-(methylene)-benzene]-iron(II)hexafluorophosphate
- 4-isopropyl-4-methyl diphenyliodonium or diphenyliodonium hexafluorophosphate or tetrakis(pentafluorophenyl) borate, or
- 20 2'-hydroxy-2-phenyl-3-toluenesulphonyl-propiophenone
9. A method according to claim 6 to 8, wherein the cationic photoinitiator is employed in an amount of
- 25 from 0.25 to 3% by weight of the substrate.
10. A method according to any one of claims 5 to 9, wherein the respective photoreaction conditions include application of actinic radiation at two
- 30 distinct wavelengths.
11. A method according to claim 10, wherein a low energy source of actinic radiation is employed as

part of the preliminary photoreaction conditions in achieving an imagewise exposure and a high dosage of actinic radiation applied as a flood is comprised by the subsequent photoreaction conditions.

12. A method according to claim 11, wherein laser direct imaging is used in applying the low energy source of actinic radiation, to achieve thereby a predetermined distribution of reactive substrate to be polymerised and/or crosslinked in the subsequent photoreaction conditions.

13. A method according to any preceding claim, wherein the actinic radiation is UV-radiation.

14. A method according to any one of claims 1 to 4, wherein the latent photoinitiator is a protected photoinitiator and its protection is thermally removed under preliminary conditions.

15. A method according to claim 14, wherein the preliminary conditions include the presence of an initiator compound which is thermally decomposable to yield an acid catalyst for the unblocking of the latent photoinitiator.

16. A method according to claim 15, wherein said initiator compound is a blocked p-toluene sulphonic acid.

17. A method according to any preceding claim, wherein the substrate is an acrylic substrate.

18. A method for the photoinitiated polymerization of a polymerizable substrate applied to a support, comprising:

5 (a) providing a coating on the support, which coating comprises the polymerizable substrate and a latent photoinitiator, wherein the latent photoinitiator is a ketone photoinitiator which is protected by a methylene 1,3-dioxolane structure;

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(b) deprotecting the protected ketone photoinitiator in selected locations of the support thereby to provide an active ketone photoinitiator in the coating at said selected locations; and

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(c) exposing the coating on the support to a source of actinic radiation whereby polymerization of the polymerizable material is initiated in said selected locations on the support where the protected ketone photoinitiator has been deprotected in step (b).

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19. A method according to claim 18, wherein in step (b), the protected ketone photoinitiator is deprotected by an imagewise exposure of the coating to a source of radiation capable of effecting deprotection of the protected ketone photoinitiator.

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20. A method according to claim 19, wherein the imagewise exposure employs a photomask.

21. A method according to claim 19, wherein the source of radiation used for the imagewise exposure is a low energy source of actinic radiation.
- 5 22. A method according to claim 18, wherein in step (c) the coating is exposed to a high dosage of actinic radiation applied as a flood.
- 10 23. A method according to claim 22, wherein the imagewise exposure is composed of uv radiation of a first wavelength and the flood exposure is composed of a uv radiation of a second wavelength different from the first wavelength.
- 15 24. A method according to claim 18, wherein the coating on the support further includes a cationic acid-producing photoinitiator which on exposure to a source of radiation yields an acid catalyst for the deprotection of the protected photoinitiator.
- 20 25. A method according to claim 24, wherein the cationic acid-producing photoinitiator is a iodonium or sulphonium salt or a salt-form organometallic compound or an  $\alpha$ -sulphonyloxyketone.
- 25 26. A method according to claim 24, wherein the cationic photoinitiator is selected from;
- 30 bis[4-(diphenylsulphonio)-phenyl]sulphide, bis-hexafluorophosphate or bis-hexafluoroantimonate optionally in combination with a mono-or-poly-[4-(phenylthiodiphenyl] sulphonium hexafluoro phosphate or hexafluoroantimonate

bis[4-(di(4-(2-hydroxyethyl)phenyl)sulphonio-phenyl)sulphide bis-hexafluorophosphate

5 bis[4-(di(4-(2-hydroxyethyl)phenyl)sulphonio)-phenyl)sulphide bis-hexafluoroantimonate

$\eta^8$ -2,4-(cyclopentadienyl) [(1,2,3,4,5,6- $\eta$ )-(methylethyl)-benzene]-iron(II)hexafluorophosphate

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4-isopropyl-4-methyl diphenyliodonium or diphenyliodonium hexafluorophosphate or tetrakis(pentafluorophenyl) borate, or

15 2'-hydroxy-2-phenyl-3-toluenesulphonyl-propiophenone

27. A method according to claim 18, wherein the cationic photoinitiator is employed in an amount of  
20 from 0.25 to 3% by weight of the substrate.

28. A method according to claim 18, wherein the deprotected ketone photoinitiator is a sensitizer for the cationic photoinitiator used whereby a  
25 self-sensitizing and auto-accelerating system is obtained.

29. A method according to claim 24, wherein the protected ketone photoinitiator is a protected  
30 thioxanthone and the cationic acid-producing photoinitiator is an iodonium salt.

30. A method according to claim 18, wherein the coating  
on the support further includes a free radical  
initiator which on exposure to a source of  
radiation yields free radicals for the deprotection  
of the protected photoinitiator.
31. A method according to claim 18, wherein the coating  
on the support includes an initiator compound which  
is thermally decomposable to yield an acid catalyst  
for the deprotection of the protected  
photoinitiator.
32. A method according to claim 31, wherein said  
initiator compound is a blocked p-toluene sulphonic  
acid.
33. A method according to claim 18, wherein the  
polymerizable substrate is an acrylic substrate.
34. A method according to claim 18, wherein the ketone  
photoinitiator, after deprotection is selected  
from:
- 2,2-dimethoxy-2-phenyl acetophenone;
- 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-  
one;
- 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-  
butanone;
- isopropyl thioxanthone;
- camphorquinone;

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[4-(4-methylphenylthio)phenyl]phenylketone;

4-phenyl benzophenone;

5

2-ethyl anthraquinone; and

di-iodobutoxy fluorone

10 35. A protected ketone photoinitiator selected from:

2,2-dimethoxy-2-phenyl acetophenone;

15

2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one;

2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone;

20

isopropyl thioxanthone;

camphorquinone;

25

[4-(4-methylphenylthio)phenyl]phenylketone;

4-phenyl benzophenone;

2-ethyl anthraquinone; and

30

di-iodobutoxy fluorone

in which the ketone moiety is protected by a methylene 1,3 dioxolane ring structure.

36. A method as claimed in any one of claims 1 to 34, wherein the support is a printed circuit board and the coating on the support is a liquid photoimageable solder mask.

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37. A printed circuit board (PCB) manufacturing process which includes a step in which a solder mask is formed on a PCB by a method as claimed in claim 36.

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