

POLYPHOTOINITIATORS AND COMPOSITIONS THEREOF

BACKGROUND OF THE INVENTION

This invention relates to novel free radical generating photoinitiators which are used for curing polymer compositions such as coatings, adhesives, molding compounds or thermoset structural resins. The invention also encompasses processes for making and using the novel initiators and compositions derived therefrom.

The primary function of a photoinitiator is to generate radicals which initiate polymerization when the photoinitiator is irradiated with ultraviolet (UV) light. Photoinitiators are classified into intermolecular H-abstraction and intramolecular photocleavage photoinitiators according to the pathways the effective initiating radicals are generated.

The intermolecular H-abstraction photoinitiators include benzophenone and its dialkyl ketone derivatives such as xanthone, thioxanthone, 4,4'-bis(N,N'-dimethylamino) benzophenone, benzil and quinones. Those photoinitiators require hydrogen-donors, such as amines, thiols or alcohol for generating radicals which are effective in initiating polymerization. The process of H-abstraction is a bimolecular reaction requiring the encounter of a photoinitiator and a hydrogen-donor from diffusion through the matrix of resin.

Examples of the intramolecular photocleavage photoinitiators are benzoin, its derivatives, 2,2-dialkoxyacetophenone and o-acylated- α -dialkoxyacetophenone and α -o-acylated- α -oximinoketones. They are decomposed by UV light directly into radicals which are effective in initiating polymerization. This decomposition process is a unimolecular reaction which is inherently more effective than the bimolecular reaction.

Conventional benzoin type photoinitiators decompose into two fragments of radical species upon being excited by UV light. After initiating the polymerization, the fragmented radical species become ends of polymer chains. The architecture of the resin networks, and consequently the properties of the cured resins, are controlled mainly by the composition of crosslinkers (multifunctional monomers) and prepolymers.

Although the photoinitiators exemplified above are soluble and effective in curing organic resins they often have limited solubility in silicones. Consequently their effectiveness in curing silicones is greatly reduced. To overcome this compatibility difficulty, silicone moieties have been chemically bonded with the photoinitiators.

Direct UV-initiated crosslinking of polysiloxane compositions has also been reported where the polysiloxane resins include methyl, vinyl, alkylmercapto and/or hydrosilyl functionalities. These systems are all believed to involve a hydrogen abstraction mechanism. These compositions have been used for release coatings and electrically resistive circuit board coatings. References describing such systems include Canadian Pat. No. 653,301, to Warrick, 12/4/62; U.S. Pat. No. 3,873,499, to Michael et al., 3/25/75; U.S. Pat. No. 4,064,027, to Gant, 12/20/77; U.S. Pat. No. 4,133,939, to Bokerman et al., 1/9/79; and U.S. Pat. No. 4,052,529, to Bokerman et al., 10/4/77.

A Japanese patent publication, Kokai No. 34,291/76 describes the application of benzophenone derivatives, such as 4-dimethylamino-4'-(trimethoxysilylethyl)dime-thylsilylbenzophenone, in preparing the silicone compatible photoinitiators. The photoinitiators described in

this patent are intermolecular H-abstraction type. The curing time for hardening the resin was around 5 minutes.

Another Japanese patent publication, Kokai No. 71,189/78 describes the application of photoinitiators from the reaction of alkenylsilylbenzophenone and silicones containing silicon-hydrides. Those photoinitiators are intermolecular H-abstraction type which required longer than ten minutes curing time.

Japanese patent publications, Kokai No. 50,067/79 and Kokai Tokkyo Koho No. JP82 09,792 (Chemical Abstracts, 97:23997x, 1982) describe the application of benzoin type photoinitiators attached to the ends of polydimethylsiloxane or to the cyclicsiloxanes through Si—O—C bond. Although these photoinitiators are the intramolecular photocleavage type they are inherently not stable in moisture. The SiOC bond is well known to be hydrolytically unstable and can be decomposed by water to form back silanol and benzoin which has very limited solubility in silicones.

SUMMARY OF THE INVENTION

The novel photoinitiators of the present invention are polyorganosiloxane polymers (silicones) which include a plurality of photoinitiating functional groups attached to the polymer through a carbon-silicon bond. The photoinitiating groups are preferably intramolecular photocleavable molecular fragments. More specifically they are silicones with a plurality of photocleavable benzoin derivatives attached pendently to the polymer backbone by means of carbon-silicon bonds. They may be obtained by reacting α -allylbenzoin ether analogs with a polyorganosiloxane containing a plurality of silicon hydride (—Si—H) groups.

As an alternative to synthesis from



functional silicones hydrolyzable



functional silanes may be reacted with α -allylbenzoin ethers to form silane adducts which can then be polymerized to photoinitiating organosiloxane polymers by hydrolysis. Copolymerization of the allylbenzoin ether-hydrolyzable silane adducts with other hydrolyzable organosilanes permits direct synthesis of polyphotoinitiators with desired physical properties and/or other desired functionalities.

Additional functional groups may also be added to a photoinitiating silicone prepared by either method of this invention by subsequent further randomization polymerization with an appropriately functionalized silane or siloxane using conventional silicone preparation techniques.

The polyorganosiloxane polyphotoinitiators of the invention may be made self curing if free radical curable groups, such as vinyl, mercapto, and methacrylate, are incorporated on the polymer. Alternatively, compositions of the inventive polyphotoinitiators with other