

1

3,434,833

STABLE FREE RADICALS AS ACTIVATORS FOR PHOTOCONDUCTIVE AND PHOTOHARDENABLE POLYMER LIGHT-SENSITIVE SYSTEMS

Charles J. Fox, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed July 26, 1965, Ser. No. 474,963

Int. Cl. G03g 5/06

U.S. Cl. 96—1.5

17 Claims

ABSTRACT OF THE DISCLOSURE

Stable free radicals are used as sensitizers to increase the photoresponsive characteristics of photoconductive insulating compositions and photohardenable polymer compositions.

This invention relates to photography and more particularly to photographic elements comprising novel activators for various photosensitive properties of light-sensitive elements.

In the art of photography may compounds have been proposed as activators for increasing the photographic speed and broadening the special response of light-responsive reactions in various photosensitive systems such as (1) layers comprising a resin which is hardened by chemical crosslinking in response to light, (2) photoconductive electrically insulating layers which undergo change in electrical resistance in response to light, (3) photosensitive coatings comprising silver halides and other metal salts which undergo a change of reducibility by photographic developers in response to photoexposure.

An object of the present invention is to provide improved photosensitive elements comprising a stable free-radical as an activator for improving the particular photo-responsive characteristics of the photosensitive elements. This and other objects and advantages will appear from the following detailed description.

In accordance with the present invention, stable free mono-radicals and di-radicals which are stable under ambient conditions and which can be isolated in pure form, are excellent activators for the photosensitive characteristic of various photosensitive systems. Thus, in accordance with my invention I provide novel photographic elements comprising an activating amount of a stable free radical combined in a photosensitive layer with a photosensitive composition.

Without intending to limit the invention to use of the particular free-radicals named here, the following are mentioned as preferred examples selected from the class of stable free-radicals used as activators in accordance with my invention:

tri-p-tolylaminium perchlorate,
tri-p-tolylaminium picrate,
triphenylaminium perchlorate,
triphenylaminium picrate,
N,N'-dibenzyl-4,4'-dipyridyl diradical,
tetra-p-tolylhydrazinium perchlorate,
di-p-anisylnitrogen oxide,
2,6,3',5'-tetra-t-butyl-4'-phenoxy-4-methylene-2,5-cyclohexadiene-1-one radical,
2,6,3',5',3'',5''-hexa-t-butyl-4',4''-diphenoxy-4-methylene-2,5-cyclohexadiene-1-one diradical.

Numerous examples of stable mono-radicals and di-radicals have been described in the literature, for example: E. Weitz, *Angew. Chem.*, 66, 658-677 (1954); R. Kuhn, *ibid.*, 66, 678-679 (1954), and E. S. Gould, *Mechanism and structure in Organic Chemistry*, Henry Holt Co., New York (1959), Chapter 16.

2

In order for the activator to be effective, it must be in its free radical state at the time and under the conditions in which the photoexposure occurs. Accordingly, the free radicals useful in my invention are stable in the free-radical state under ordinary atmospheric conditions of temperature and pressure and are stable in the environment of the composition of the photosensitive layer in which they are incorporated. By the term "stable free radical" we means that the radical is capable of remaining essentially in its free radical state, under ordinary circumstances, in the photosensitive layer in which it is intended for use, at least until photoexposure.

The amount of stable free radical needed in the photosensitive layer to produce an activating effect will usually be relatively small with respect to the amount of sensitive material. While the sensitizing amount will vary depending on the particular system in which the activator is used, generally the optimum amount for a given light-sensitive system will be in the range from about 0.1 to about 10 percent by weight of the photosensitive component present in the coated layer with the activator.

Among the advantages obtained by activation of photosensitive systems by stable free radicals is that relatively higher photographic speeds are obtained by means of these materials in a variety of photosensitive systems.

Following are specific examples describing some preferred embodiments of the present invention.

EXAMPLE I

A photohardenable polymer which undergoes crosslinking in response to incident light, consisting of poly (vinyl alcohol) in which hydroxyl groups are substituted to the extent of 12 percent with acetate, 50 percent with azidobenzoate, and 32 percent with dimethyl glutarate-2-urethane was mixed in a 2 percent solution with methyl-ethyl ketone and activated by the addition of 0.2 percent of tri-p-tolylaminium perchlorate. The resulting dope was coated on a film base and the sensitivity of the film to light was determined. The glass factor of the film described above was 50 and the film responded to actinic wavelengths in the range from 270-400 mμ. An unsensitized control sample had a glass factor of 25 and the actinic wavelengths to which this sample was sensitive ranged from 280-330 mμ.

EXAMPLE II

A photoconductive system was prepared as follows:
A coating solution was made with 0.5 gram of triphenylamine (an organic photoconductor) and 2.0 grams of polystyrene dissolved in 15 ml. of tetrahydrofuran with the addition of 0.025 gram of tri-p-tolylaminium perchlorate. The solution was coated under red safelights onto aluminum foil. After drying, the coating was stored in the dark. The coating was charged under a negative corona and then exposed to light through a photographic negative and then was toned by conventional magnetic brush development. A good image was obtained using exposure time of one second to a tungsten source of 30-ft. candle intensity. With a control sample containing none of the free-radical activator and tested by the same procedure, no image was obtained.

EXAMPLE III

A photoconductive element was prepared and tested as in Example II except that triphenylaminium perchlorate was substituted as an activator instead of tri-p-tolylaminium perchlorate. Also, samples were prepared substituting Vitel PE-101 polyester resin (Goodyear Tire and Rubber Company) for polystyrene. All of the various resin and

activator combinations produced acceptable results using only slightly different exposure times for the various samples.

EXAMPLE IV

Another photoconducting element was prepared as described in Example II except 2,6,3',5'-tetra-t-butyl-4'-phenoxy - 4 - methylene - 2,5 - cyclohexadiene - 1 - one radical was substituted for tri-p-tolylaminium perchlorate. The test results were essentially the same as those described in Examples II and III above.

The examples above demonstrate the versatility of free radicals as activators for various types of photoresponsive systems in which the respective photosensitive responses may be entirely different. Compare for example the photochemical response in Example I and the photoelectric responses in Examples II, III, and IV. My invention is not intended to be restricted to use of free radicals in any particular photosensitive system but is applicable generally to improve photoresponse in photographic elements of various types.

Stable free radical activators of the invention may be used in photohardenable layers of various kinds such as those used for making lithographic plates, for example: photosensitive crosslinking polymer systems and photopolymerizable monomer systems. The activators may be used to improve photoresponse in various photoconductive electrophotographic layers such as zinc oxide in resin systems, organic-photoconductor-in-resin systems, polymeric photoconductor systems, inorganic photoconductive coatings and the like. They may be employed to improve photoresponse in a variety of silver halide photographic systems, and the like. Generally, the activators are useful to improve photoresponse in many different photosensitive systems.

It will be understood that modifications and variations may be made within the scope of the invention as described above and as defined in the following claims.

I claim:

1. A photographic element comprising a support and coated thereon a layer comprising in combination a photosensitive composition selected from the group consisting of photoconductive insulating compositions and photohardenable polymer compositions and an activating amount of a stable free radical as a sensitizer for the photoresponsive property of said photosensitive composition.

2. A photographic element comprising a support and coated thereon a photoconductive insulating layer having dispersed therein a stable free radical as an activator for the photoconductive property of said layer.

3. The photographic element defined in claim 1 wherein said stable free radical is tri-p-tolylaminium perchlorate.

4. The photographic element defined in claim 1 wherein said stable free radical is tri-p-tolylaminium picrate.

5. The photographic element defined in claim 1 wherein said stable free radical is triphenylaminium perchlorate.

6. The photographic element defined in claim 1 wherein said stable free radical is triphenylaminium picrate.

7. The photographic element defined in claim 1 wherein said stable free radical is N,N'-dibenzyl-4,4'-dipyridyl diradical.

8. The photographic element defined in claim 1 wherein said stable free radical is tetra-p-tolylhydrazinium perchlorate.

9. The photographic element defined in claim 1 wherein said stable free radical is di-p-anisylnitrogen oxide.

10. The photographic element defined in claim 1 wherein said stable free radical is 2,6,3',5'-tetra-t-butyl-4'-phenoxy - 4 - methylene - 2,5 - cyclohexadiene - 1 - one radical.

11. The photographic element defined in claim 1 wherein said stable free radical is 2,6,3',5',3'',5''-hexa-t-butyl-4',4'' - diphenoxy - 4 - methylene - 2,5 - cyclohexadiene-1-one diradical.

12. A photoconductive element as defined in claim 3 wherein said photoconductive insulating layer comprises triphenylamine dispersed in an insulating resin binder and said free radical is tri-p-tolylaminium perchlorate.

13. A photoconductive element as defined in claim 3 wherein said photoconductive insulating layer comprises triphenylamine dispersed in an insulating resin binder and said free radical is triphenylaminium perchlorate.

14. A photoconductive element as defined in claim 3 wherein said photoconductive insulating layer comprises triphenylamine dispersed in an insulating resin binder and said free radical is 2,6,3',5'-tetra-t-butyl-4',4''-diphenoxy-4-methylene-2,5-cyclohexadiene-1-one diradical.

15. A photographic element having a photohardenable layer comprising a photocrosslinkable polymer and dispersed therein a stable free radical in a sensitizing amount.

16. A photographic element as defined in claim 15 wherein said polymer is a poly(vinyl alcohol) having substituted azidobenzoate substituted at some hydroxyl positions and said free radical is tri-p-tolylaminium perchlorate.

17. A photoconductive element as defined in claim 3 wherein the photoconductive insulating layer comprises an organic photoconductor dispersed in a binder and the stable free radical is selected from the group consisting of:

tri-p-tolylaminium perchlorate,
tri-p-tolylaminium picrate,
triphenylaminium perchlorate,
triphenylaminium picrate,
N,N'-dibenzyl-4,4'-dipyridyl diradical,
tetra-p-tolylhydrazinium perchlorate,
di-p-anisylnitrogen oxide,
2,6,3',5' - tetra - t - butyl - 4' - phenoxy - 4 - methylene -
2,5-cyclohexadiene-1-one radical and
2,6,3',5',3'',5'' - hexa - t - butyl - 4',4'' - diphenoxy - 4 -
methylene-2,5-cyclohexadiene-1-one diradical.

References Cited

UNITED STATES PATENTS

3,180,730 4/1965 Klupfel et al. _____ 96—1
3,234,280 2/1966 Fox et al. _____ 260—576

NORMAN G. TORCHIN, *Primary Examiner*.

JOHN C. COOPER, *Assistant Examiner*.

U.S. Cl. X.R.

96—115