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PHOTOGRAPHY

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This invention relates to the use of photosensitive compositions based on leuco bases of triphenylmethane dyes and more particularly to the fixing of the images obtained when leuco bases of the type indicated are sensitized with organic compounds containing a carbonyl group

(>C=O)

as originally described in United States patent application Serial No. 134,862, filed August 30, 1961, and now U.S. Patent No. 3,121,632, and now described in United States patent application Serial No. 200,664, filed June 7, 1962.

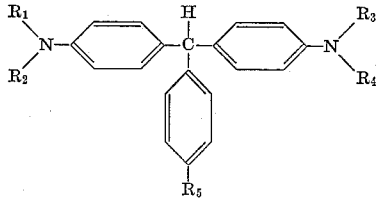
As described in the above identified patent applications, compositions exhibiting enhanced sensitivity to radiation of a suitable wavelength comprise (1) a photosensitive material, (2) an activator for the photosensitive material, and (3) a binder, support or carrier on which the first two ingredients may be supported, or in which they may be dispersed. It has now been found that images obtained when practicing the invention described in the aforesaid patent application are stabilized by contacting the image bearing print with an alkaline material represented by the general formula

wherein R and R_1 and R_2 are each selected from the group consisting of H and lower alkyl, e.g. methyl, ethyl, propyl, isopropyl, n-butyl, and the like; or stabilization may be achieved by incorporating in the photosensitive coating a neutral compound which yields ammonia or an amine on heating after the image-forming exposure, or such a compound may be applied in a separate layer overcoated on the light-sensitive layer.

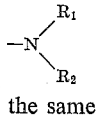
The photosensitive material, activator, carrier and proportions of the constitutents in our photosystem are as follows:

I. THE PHOTOSENSITIVE MATERIAL

The sensitive materials utilized in the present photosystem comprise the leuco bases of triphenylmethane dyes, such as Leucocrystal Violet. The leuco bases of other triphenylmethane dyes may be used including the leuco bases represented by the general formula



wherein R_1, R_2, R_3 and R_4 are each selected from the group consisting of H, alkyl, aralkyl, and aryl and they may be the same or different and R_5 represents a monovalent radical selected from the group consisting of —H and



wherein R_1 and R_2 have the same meaning as above.

II. THE ACTIVATORS

Activators suitable for the present invention are selected from the group of compounds including a >C=O structure, including both aliphatic and aromatic acids, and acid anhydrides of the types exemplified in the examples in the aforesaid patent applications.

III. THE CARRIER

Both the leuco base and the activator are preferably placed in solution, for the purpose of applying them as a coating to a suitable base such as plastic, paper, or other material. Furthermore, a binder, preferably a film-forming binder, is included in the coating formulation, although it will be appreciated that compositions comprising the leuco base and the activator, both in solution, in solvents which may be the same or which are compatible with one another, may be applied to absorbent substrates such as paper, without any additional binder.

Ethyl cellulose is the binder preferred by us but other film-forming synthetic polymers and cellulose derivatives and the like may also be used. The synthetic polymers found useful as carriers for the remaining constituents include polyester, e.g. polyethylene terephthalates (Mylar) and polycarbonates and polymers of vinylidene or vinyl monomers and include both homopolymers, e.g. polystyrene, and heteropolymers or copolymers, e.g. polyvinylidene chloride-polyvinyl chloride copolymers, as well as mixtures of such polymers. Cellulose derivatives suitable for the same purpose include methyl, ethyl and butyl cellulose and cellulose esters.

IV. PROPORTIONS

The addition of small amounts of one or more activators of the types described above to leuco bases of triphenylmethane dyes imparts an increased sensitivity to the leuco base, as is indicated by the increase in density of the visible image obtained when such compositions are exposed to suitable radiation—as compared with the density of an image obtained by similar exposure of the leuco base without the added carbonyl compound.

The relative proportions of activator to leuco base depend to some extent upon the specific materials. In general appproximately 8 parts of carbonyl compound to 1 part of leuco base appeared to produce optimum activation (image intensification). Between 0.5 and 24 parts by weight of activator per 1 part by weight of leuco base appears to represent a desirable working range for exposure intervals between 2 and 30 seconds, to suitable radiation.

The following examples are illustrative of a preferred method of practicing the invention and are not to be construed as limitative thereof.

Example 1

The photocomposition was made as follows:

COMPOUNDS		
(*a*) Leuco Opal Blue	gram	0.5
(*b*) 2,4-dichlorophenoxyacetic acid	do	0.4
(*c*) 10% solution of polystyrene in benzene	cc	10.0
(*d*) Acetone	cc	5.0

Compounds (*a*) and (*b*) were dissolved in a mixture of (*c*) and (*d*), and the solution was coated .0015-inch wet-thickness with a Bird applicator bar on a sheet of unsubbed 500–D Mylar (terephthalate polyester). The coating was air-dried for at least fifteen minutes.

The coated Mylar sheet was exposed under a negative in a standard printing frame to three General Electric sunlamps at a distance of 12 inches from the bottom of the lamp to glass in the printing frame. A fan was used to keep the glass in the printing frame cool.

Exposure in the above fashion under an Eastman step tablet for five minutes gave a maximum density of 1.3 and 10 steps. As a result of the exposure, a distinct blue image was visible in the exposed areas, the unexposed areas remaining clear.

The print was stabilized by use of the following mixture:

28% ammonium hydroxide	cc.. 200
Acetone	cc.. 100

The print was taped to a sheet of glass, which was then placed over a container of the stabilizing solution at a distance of approximately 1½ inches. The print was thus kept in the vapors for fifteen minutes, which deactivated the sensitizing acid component and at the same time bleached the image. In three to five minutes after removal from exposure to the alkaline vapor the image color returned to full maximum density in the print which was now stabilized.

A second method of stabilization consisted of immersing the print for 60 seconds in the ammonium hydroxide-acetone stabilizing solution, rinsing in water, and blotting dry. Any blush present could be removed by a short heat treatment at 100° C. in a convection oven.

Example 2

Light sensitive coatings were prepared and exposed in the same fashion as in Example 1. After exposure, the image was stabilized by exposing for three minutes to the vapor of the following organic amines:

CH_3NH_2
$(CH_3)_2NH$
$C_2H_5NH_2$
$(C_2H_5)_2NH$
$(C_2H_5)_3N$

Satisfactory stabilization was obtained with ethylamine, methylamine and dimethylamine. Diethylamine was slightly less effective, and triethylamine had undesirable side effects.

Example 3

Coatings were prepared in the same fashion as in Example 1, using leuco Crystal Violet in place of leuco Opal Blue. Exposure was made similarly, and the exposed image-bearing material was fixed by exposure to ammonia vapor for 15 minutes. Re-exposure of the fixed coating to the sunlamp for 60 seconds produced only a trace of fog, indicative of satisfactory stabilization.

Example 4

Coatings were prepared and exposed in the same fashion as Example 1, using leuco Methyl Violet in place of the leuco Opal Blue. The exposed coatings were stabilized with NH_4OH-acetone mixture by the second method of Example 1. The fixed material was stable to 60 seconds re-exposure to sunlamp.

Example 5

A coating mixture was prepared according to the formula given in Example 1, except that 1.0 gram of urea was added to the mixture and the amount of acetone used as solvent was increased to 15 cc. The mixture, coated on Mylar and exposed in the usual way, showed no loss in sensitivity due to the presence of the urea. After exposure, the film was heated at 150° C. for three minutes to release ammonia in the coating through decomposition of the urea, thus stabilizing the coating. Satisfactory stabilization was demonstrated by re-exposure to the sunlamp for 60 seconds, which resulted in only slight fog.

Example 6

Strips coated as in Example 1 were exposed under a line negative for five minutes, stabilized by the second procedure of Example 1, and used as masters for the production of diazo copies. Good quality diazo prints were produced in 20-second exposure to three General Electric sunlamps at twelve-inch distance followed by ammonia development. A portion of the master was re-exposed to the three sunlamps for 60 minutes, resulting in perceptible background fog. However, a satisfactory diazo print could be made from this fogged master with only 30-second exposure. This 60-minute re-exposure would be equivalent to production of at least 120 diazo copies.

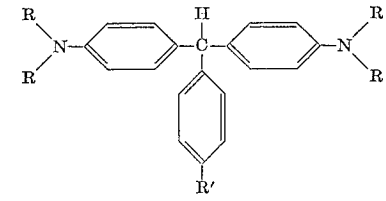
The photosensitive material produced by this invention may be used to prepare photographic prints by either contact or projection printing from a negative, such as microfilm, using suitable light sources. When coated on a transparent base the material may be used for preparation of a positive transparency from which contact prints may be made on diazo paper. The latter procedure is especially useful in the field of engineering drawing retrieval from microfilm, where a positive diazo copy is desired.

Having now described our invention in accordance with the patent statutes, it is not our intention to limit the same except as required by the appended claims.

We claim:

1. A photographic process which comprises: imagewise exposure of a photosensitive mixture coated on a suitable base, said photosensitive mixture consisting essentially of

(1) a leuco base of a triphenylmethane dye represented by the general formula



wherein each R is selected from the group consisting of H, alkyl, aralkyl and aryl and R′ is selected from the group consisting of —H and

wherein each R has the same meaning as above; and

(2) an activator for said leuco base, said activator consisting of a carboxylic compound selected from the group consisting of carboxylic aliphatic acids and carboxylic aromatic acids and carboxylic acid anhydrides; there being between about 0.5 and 24 parts by weight of said activator per part by weight of said leuco base, and thereafter stabilizing the visible image produced as a result of said exposure by contacting the image-bearing exposed material with an alkaline material selected from the group consisting of ammonia and alkyl amines.

2. The process of claim 1 wherein the contacting is effected by immersion of the image-bearing material in a solution of the alkaline material.

3. The process of claim 1 wherein stabilization is effected by contacting the image-bearing material with the alkaline material as a vapor.

4. The process of claim 1 wherein stabilization is effected by incorporating a neutral compound capable of releasing an alkaline material selected from the group consisting of ammonia and alkyl amines on heating into the photosensitive material prior to exposure, and heating the image-bearing material to release said alkaline material and to thereby stabilize the image.

5. The process of claim 1 wherein the leuco triphenylmethane dye is leuco Opal Blue, the carbonyl activator

is 2,4-dichlorophenoxyacetic acid and the alkaline stabilizer is ammonia.

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