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3,082,086

FIXING OF PRINT-OUT IMAGES

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This invention relates to compositions suitable for use in a dry photographic process and to the process wherein said compositions are employed.

More particularly it relates to an improvement in the fixing or stabilization of photographic images obtained in photographic systems described in copending patent application Serial No. 787,112, filed January 16, 1959, by Eugene Wainer, and issued as U.S. Patent 3,042,515 on July 3, 1962, and described in other related applications filed subsequently thereto on other aspects of the photo-system disclosed in said application.

Briefly in the aforementioned patent application, photo-systems are described in which a colored image is produced in an originally uniformly colorless clear thin layer containing a suitable originally colorless arylamine and a suitable halogen substituted organic compound.

The photosystems described in the aforesaid Wainer application are usually disposed in a resinous, chemically inert carrier, generally in the form of a thin film or layer, which is supported on paper or other material, or which is self-supporting. Optionally the solution containing the active ingredients may be applied directly to a supporting material, and the resinous chemically inert material may then be omitted from the compositions.

Those photosystems described in the aforementioned Wainer application to which this method of fixing is applicable comprise an initially colorless composition which includes two essential constituents, namely, a colorless secondary arylamine and a colorless organic compound containing at least one trihalogenated methyl group.

The colored image is formed in those areas which have been exposed to an amount of radiant energy, sufficient to produce halogen free radicals from the halogen substituted organic compound. Concurrently with the formation of said free radicals, the secondary arylamine is converted to a triphenylmethane dye in those areas of the layer which have been sufficiently exposed to yield free radicals, while the unexposed areas, or insufficiently exposed areas do not experience a change yielding a colored product.

In these remaining areas of the layer a latent reactivity continues to exist and in the event that a subsequent exposure to a sufficient dose of radiant energy occurs, a colored reaction product is formed and the original image is fogged or obscured in part by the subsequently formed image.

To avoid this, in the photosystems described, it has been customary to bathe the exposed print in a solvent wash to remove the unreacted starting materials from the base or carrier material after the desired first image has been formed. This technique involves the use of a liquid and hence fails to provide the completely dry processing of which the foregoing photosystems have been found to be capable.

One object of this invention is to improve the manner of fixing the photographic materials once the original image has been formed so that the images do not fog as a result of further exposure to radiant energy.

Another object of the invention is to provide photographic compositions which may be fixed or desensitized by a brief exposure to heat, thus avoiding wet fixing heretofore practiced.

These and other objects are accomplished by the in-

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corporation of one or more organic acid anhydrides into the photosensitive compositions of the type indicated and by a short heat treatment of the composition after the desired colored image has been formed.

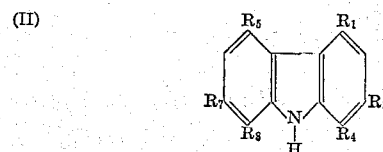
The presence of the anhydride in the light-sensitive coating has no effect on either the keeping qualities or the sensitivity of the coating prior to heat treatment; nor does the presence of the anhydride have any deleterious effect on the stability of the dye image after the exposure. Addition of organic anhydrides to the photosystem therefore furnishes a convenient method of fixing by dry heating in photosystems containing diphenylamine, or other secondary arylamine as the active amine component.

While not wishing to be bound by any specific theory as to the mechanism of the fixing action, it seems probable that the fixing action of the anhydride, on heating the coating, is caused by the acylation of the N-hydrogen atom of the secondary arylamine. It has been found that N-acylation completely deactivates the secondary arylamines. Thus, for example, although diphenylamine mixed with carbon tetrabromide is one of the preferred mixtures for this photoprocess, giving a high yield of a blue triphenylmethane dye on exposing to near ultraviolet light, N-acetyldiphenylamine is completely inert under these conditions.

Amines useful in this photoprocess which are capable of fixation through acylation in this manner may be represented by the following general formulas (I and II below):



wherein R represents a member selected from the group consisting of phenyl, α -naphthyl and β -naphthyl, each of which may be substituted or unsubstituted, and R' represents a member selected from the group consisting of alkyl, aryl and aralkyl groups, each of which may be substituted or unsubstituted.



wherein R₁, R₃, R₄, R₅, R₇, and R₈ each represents a member selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, alkoxy, halogen and dialkylamino groups, and they may be the same or different.

The halogen-containing materials useful in the present invention may be represented by the following general formula:



wherein R represents a member selected from the group consisting of hydrogen, halogen, alkyl, aralkyl and aryl, which may be substituted or unsubstituted, and each X represents a halogen atom selected from the group consisting of chlorine, bromine and iodine and may be the same or different.

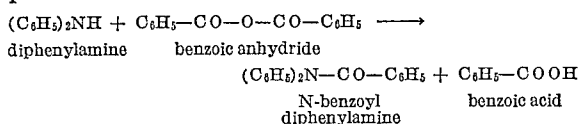
Some of the halogen-containing compounds, which have been utilized in the practice of this invention include:



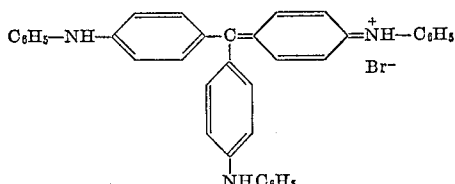
The carboxylic acid anhydrides useful as fixing agents in the photosystems indicated include those normally solid at room temperature, such as benzoic anhydride, phthalic anhydride, maleic anhydride, succinic anhydride, and the

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like. The reaction with diphenylamine, for example, on heating a mixture containing benzoic anhydride is depicted below:



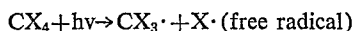
The blue dye formed from diphenylamine and carbon tetrabromide, for example, on exposing to near ultraviolet light, has been identified as a triphenylmethane dye of the following structure:



This identification was accomplished by elemental analysis and spectrophotometric analysis of dye isolated from the photosystem and proof of identity with an authentic specimen of the dye prepared by an unequivocal synthesis by known methods.

It will be noted that the function of the carbon tetrabromide in this reaction is to provide the bridge carbon atom linking the three phenyl groups forming the dye skeleton. The position of attack is para to the activating anilino group. If this group is acylated as in N-benzoyl-diphenylamine, shown above, the activating effect is destroyed and no condensation occurs.

As will be evident from the examples below, the mixture containing the two essential constituents and the organic anhydride fixing agent is applied to a suitable substrate either in the form of a self-sustaining film or by conventional coating techniques, and thereafter the composition is dried. After a thin photosensitive layer has been prepared it is exposed to ultraviolet for up to about 30 seconds, that is, the thin photosensitive layer is exposed to sufficient radiant energy as described more fully in the aforesaid Wainer application, to generate free radicals from the organic halogen compounds present therein, as for example:



A visible colored image is promptly apparent. After the image-producing exposure, the photosensitive layer is fixed or stabilized in accordance with the present invention by the application of heat (90–100° C.) to the image-bearing, fixing-agent-containing photosensitive layer.

With compositions utilizing diphenylamine as the colorless amine, from 1 to 25 parts by weight of anhydride per 5 parts by weight of amine have been found suitable, 1:2 being optimum.

The following examples will serve to further illustrate the novel aspects of the invention and are to be taken as illustrative rather than as limitative.

Example 1

One and four tenths (1.4) cubic centimeters of a 50% solution of maleic anhydride in acetone were added to 10 cc. acetone containing 2.4 g. diphenylamine and 2.8 g. carbon tetrabromide. The mixture was coated on a dense paper, such as is used for Multilith reproductions. When dry, the coated sheet was exposed through a negative to the ultraviolet of a General Electric sunlamp for thirty seconds, then heated for sixty seconds on the surface of a hot plate or under an infrared lamp at a temperature of 95–100° C. This heating cycle sufficiently stabilized the formed image so that two minutes re-exposure to the sunlamp at a lamp-to-subject distance of six inches gave only a trace of fog, and no fog at all when stored for days in normal room light.

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Example 2

One (1.0) cubic centimeter of a 50% solution of maleic anhydride in acetone was added to 10 cc. of acetone containing 6 cc. ethyl acetate, 1.2 g. diphenylamine and 1.4 g. carbon tetrabromide. The mixture was coated on clear cellulose acetate, dried, and exposed through a negative to the ultraviolet light of a sunlamp as in the preceding example. The resulting image was fixed by heating for two minutes at 95–100° C. and did not fog on long storage in room light.

Example 3

To 16 cc. of a 10% solution of nitrocellulose in acetone were added 2.8 g. carbon tetrabromide, 2.4 g. diphenylamine, 0.6 g. hexachloroethane, and 1.0 cc. of a 50% solution of maleic anhydride in acetone. The resulting mixture was coated on dense offset paper. Fixed images were obtained on exposure through a negative to the ultraviolet of a sunlamp as in Example 1, followed by heating for two minutes at 95–100° C. Unexposed samples of this composition retained sensitivity and their ability to be fixed after storage in a sealed polyethylene-lined envelope at 50° C. for several days.

Example 4

Two and four-tenths (2.4) grams of diphenylamine, 2.8 g. carbon tetrabromide, 0.6 g. hexachloroethane, and 1.0 cc. of 50% maleic anhydride solution in acetone were added to 10 cc. of a 10% solution of polyvinylidene chloride in acetone. The mixture was coated on an offset paper, and dried. Exposure to a sunlamp through a negative for thirty seconds, then heating for three minutes at 110–120° C. gave excellent images which did not fog when exposed for long periods to normal room light and gave only a trace of fog on two minutes re-exposure to a sunlamp.

Example 5

Substitution of 5 cc. of a 10% solution of succinic anhydride in acetone for the maleic anhydride solution of Example 4 produced a composition which gave excellent images which did not fog on long exposure to room light.

Example 6

Substitution of 1.0 cc. of a 50% solution of benzoic anhydride in acetone for the maleic anhydride of Example 4 yielded a composition which gave excellent images which did not fog on long exposure to normal room light.

Example 7

Substitution of 5 cc. of a 10% solution of phthalic anhydride in acetone for the maleic anhydride of Example 4 also yielded a composition which gave excellent images which did not fog on long exposure to room light.

Example 8

Two and four-tenths (2.4) grams of trichlorotoluene were dissolved in 16 cc. of a 10% solution of nitrocellulose in acetone containing 2.4 grams of diphenylamine and 1.0 cc. of a 50% maleic anhydride solution in acetone. The mixture was coated on offset paper and dried. Exposure of part of the coating to a sunlamp for ninety seconds gave an intense darkening. The entire coated piece was then heated at 100° C. for two minutes. The unexposed portion showed only a trace of darkening on a two-minute re-exposure to the sunlamp and no darkening at all when exposed for long periods to normal room light.

Example 9

To 16 cc. of a 10% solution of nitrocellulose in acetone were added 2.4 grams of diphenylamine, 1.0 cc. of a 50% maleic anhydride solution in acetone, and 2.0 grams of bromotrichloromethane. The mixture was coated on offset paper and dried. When part of the coating was exposed to a sunlamp for 120 seconds an intense green color was formed. The entire coated piece was heated

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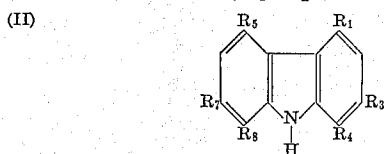
for two minutes at 100° C. When re-exposed to a sun-lamp for two minutes after heating, the unexposed portion showed only a trace of darkening and no darkening at all when exposed to normal room light for hours.

Having now described my invention in accordance with the Patent Statutes, I claim:

1. A process for producing fixed colored images in an originally colorless substrate which comprises preparing as a thin layer, a colorless composition comprising: (1) a colorless arylamine selected from the group consisting of one of amines represented by the following general formulas:



wherein R represents a member selected from the group consisting of phenyl, α -naphthyl and β -naphthyl, and R' represents a member selected from the group consisting of alkyl, aryl and aralkyl groups; and



wherein each of R₁, R₃, R₄, R₅, R₇ and R₈ represents a member selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, alkoxy, halogen and dialkylamino; (2) a colorless halogen-containing compound represented by the formula R—CX₃ wherein R represents a member selected from the group consisting of hydrogen, halogen, alkyl, aralkyl and aryl, and each X represents a halogen atom selected from the group consisting of chlorine, bromine, and iodine, and (3) a normally solid carboxylic acid-anhydride, the proportions of anhydride to amine in said composition being between 1:1 and 25:1 parts by weight; exposing the composition to sufficient light of a suitable wavelength to produce a colored photoreaction product; and fixing the resulting colored product by heating same to a temperature up to about 120° C.

2. The process of claim 1 wherein the amine is diphenylamine.

3. The process of claim 1 wherein the halogen compound is a halogen substituted methane.

4. The composition of claim 1 wherein the acid anhydride is maleic anhydride.

5. The process of claim 1 wherein the heating to fix the colored image is at a temperature between about 80° C. and 120° C.

6. The process of claim 1 wherein the composition is prepared as a solution and is applied to an inert support prior to exposure.

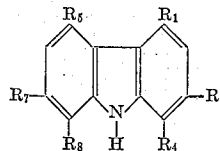
7. The process of claim 1 wherein the proportions of anhydride to amine are between 1:5 and 5:1 parts by weight.

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8. A composition of matter comprising a photosensitive mixture consisting of a colorless arylamine selected from the group consisting of amines represented by the following general formulas



and



wherein R represents a member selected from the group consisting of phenyl, α -naphthyl and β -naphthyl and R' represents a member selected from the group consisting of alkyl, aryl and aralkyl, and each of R₁, R₃, R₄, R₅, R₇ and R₈ represents a member selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, alkoxy, halogen and diamino and a colorless organic halogen-containing compound selected from the group of compounds represented by the formula A—CX₃ wherein A represents a member selected from the group consisting of hydrogen, halogen, alkyl, aralkyl and aryl and each X represents a halogen atom selected from the group consisting of Cl, Br and I; and as a fixing agent for said photosensitive mixture, a carboxylic acid anhydride which is normally solid at room temperature, the proportions of anhydride to amine in said composition being between 1:1 and 25:1 parts by weight.

9. The composition of claim 8 wherein the relative proportions in the photosensitive mixture are between 2:1 and 100:1 parts by weight of amine to organic halogen compound and the amount of fixing agent comprises between 1:5 and 5:1 parts by weight of acid anhydride per part of arylamine.

10. The composition of claim 9 wherein the amine is diphenylamine.

11. The composition of claim 9 wherein the organic halogen compound is a halogen substituted methane.

12. The composition of claim 9 wherein the organic halogen compound is CBr₄.

13. The composition of claim 9 wherein the acid anhydride is maleic anhydride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,072,302 Herrmann et al. ----- Mar. 2, 1937

FOREIGN PATENTS

813,604 Great Britain ----- May 21, 1959