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COLOR PHOTOGRAPHIC MATERIAL

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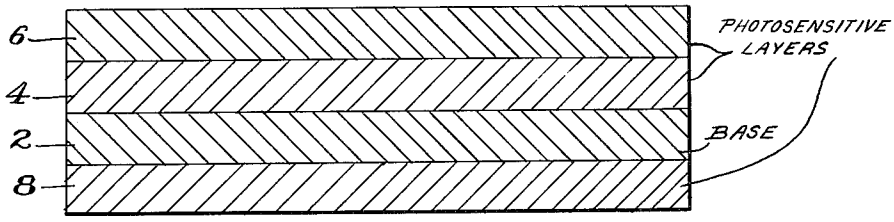

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COLOR PHOTOGRAPHIC MATERIAL

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The present invention relates to a novel photographic color material. More particularly, the invention is concerned with color photographic film comprising a plurality of integral layers of different photosensitivity capable of dry processing.

A large number of photographic color materials and processes exist. A summary of these can be found in "The History of Color Photography" by Friedman. Existing materials and processes suffer from lack of convenience in preparing the final color print. Those materials which produce a color print with a single exposure require wet processing of various degrees of complication. Materials such as the diazo type which can produce color by relatively simple means of development do not have a differential photosensitivity so that prints for each color have to be made on separate films by separate exposures and later combined in the proper registration to produce the finished color print.

From the foregoing, it is apparent that an integral multi-layer film simple to expose and develop which will result in two or three, or possibly more, color transparencies or prints would be highly advantageous and desirable in the present state of the art.

The principal object of the present invention is to provide such an integral multilayer photographic material. A more specific object of the invention is the provision of an integral multilayer photographic film which is capable of being dry processed to give highly desirable plural color transparencies or prints. Other objects will also be hereinafter apparent.

Broadly stated, the photographic material of the invention comprises a suitable film base, coated on one side with (1) leuconitrile color former or the like which upon irradiation by ultraviolet light of short wave length i.e. below 3500A., produces a color image, e.g. magenta, upon exposure; and (2) a photosensitive composition, as described and claimed in copending application Serial No. 623,050 now U.S. Patent 3,032,414, which is sensitive to near ultraviolet light, i.e. ultraviolet light having a wave length in excess of 3500A., and produces a light-scattering image upon heat development; the base being coated on its other side with a second and different leuconitrile color former, or the like, which upon irradiation with short wave length ultraviolet produces a different color, e.g. cyan.

According to the invention, components (1) and (2) above may be combined into a single photosensitive coating or layer on one side of the film base. Alternatively, these components may comprise separate, superimposed photosensitive layers coated on the same side of the film base. Thus, component 1 may comprise a first photosensitive coating directly adjacent the film base with the scatter center-forming layer superimposed thereupon. These layers may also be reversed, if desired.

A preferred form of the invention is illustrated in the accompanying diagrammatic drawing wherein the film

base is designated by the numeral 2, same being coated on one side with a photosensitive layer 4 containing the leuconitrile color former. Typically, layer 4 may comprise a color former such as hydroxyethylate p-rosaniline leuconitrile, which gives a magenta image, in gelatin, The superimposed coating 6 comprises the photosensitive layer which forms light scattering centers upon exposure to ultraviolet light above 3500A., and heat development. Typically, this may comprise a suspension of light sensitive diazonium compound in a thermoplastic polymer carrier such as "Saran" (vinylidene chloride-acrylonitrile copolymer) as described in Serial No. 623,050. The other side of base 2 is coated with the photosensitive layer 8 containing a different leuconitrile color former or the like which gives another color upon exposure. For example, the second dye may be a cyan color-former such as Patent Blue V leuconitrile suspended in gelatin.

It is essential for the success of the invention to utilize a base material which substantially filters out radiation below 3500A. Polyethylene terephthalate film (i.e. Mylar or Cornar) is eminently suitable at the base material. Other film materials suitable for use herein include: glass cellulose triacetate, polystyrene, cellulose acetate, butyrate, etc. The film used herein may have any desired thickness, typically from 3 to 10 mils.

Any leuconitrile color former or other like material may be used herein provided it is responsive only to shorter wave ultraviolet, e.g. radiation below 3500A., to produce a color image. Leuconitrile color formers and photosensitive compositions suitable for use herein are described in the prior art, typically the Chalkley Patents 2,855,303; 2,855,304 and 2,877,169. Thus, for example, suitable leuconitrile color formers include the essentially colorless hydrophilic triphenylmethane dye cyanides of the phenolic and amino type. These color formers form photosensitive combinations with hydrocolloids which are responsive to the indicated shorter wave ultraviolet as described, for example, in 2,855,303. Any of the photosensitive compositions described in the abovementioned patents may be used herein by directly coating same upon the film base in the conventional fashion, the appropriate sides of the base being coated with leuconitrile color formers which give different color images.

As indicated heretofore, the scatter-center component may be combined with the leuconitrile color former on one side of the base. Preferably, however, the scatter-center component constitutes a separate layer or coating superimposed upon a leuconitrile color former layer. Such separate layer may be prepared according to Serial No. 623,050 now U.S. Patent 3,032,414 and may comprise a thermoplastic vehicle, particularly a non-hygroscopic synthetic thermoplastic polymer, having a light decomposable agent substantially uniformly dispersed therein, the agent upon exposure decomposing into products which are chemically non-reactive to said vehicle and which on warming are volatile to form the light scattering discontinuities in the polymer to thereby furnish the desired record.

The light decomposable agent in the scatter-center component should be decomposable upon exposure to ultraviolet light having a wave length in excess of 3500A. Desirably, this decomposable agent is a light sensitive diazonium compound such as p-diazo dimethyl aniline zinc chloride. Other suitable diazonium compounds are

p-diazo diphenylamine sulfate, p-diazo diethylaniline zinc chloride, p-diazo ethyl hydroxyethylaniline zinc chloride, p-diazo methyl aniline zinc chloride, p-diazo diethyl methyl aniline zinc chloride, p-diazo ethyl hydroxyethyl-aniline zinc chloride, 1 diazo-2 oxy naphthaline-4 sulfonate, p-diethyl amino benzene diazonium chloride $ZnCl_2$, 4-benzoylamino-2-5-diethoxy benzene diazonium chloride, p-chlorobenzene-sulfonate of 4-diazo-1-cyclohexylaniline, p-chlorobenzenesulfonate of 4-diazo-2-methoxy-1-cyclohexylamino benzene, tin chloride double salt of 4-N-methyl-cyclohexylamino-benzene diazonium chloride, p-acetamino benzene diazonium chloride, 4-dimethyl-amino benzene diazonium chloride, 3-methyl-4-diethyl amino benzene diazonium chloride, 4-morpholino benzene diazonium chloride, 4-piperidyl 2-5-diethoxy benzene diazonium chloride, 1-dimethyl amino naphthaline-4 diazonium chloride, 4-phenyl amino diazo benzene diazonium chloride.

Other light decomposable agents suitable for use herein include: organic acids such as ferric ammonium citrate and oxalate salts which liberate carbon oxides on exposure to light.

The thermoplastic polymer vehicle for the scatter-center component is desirably Saran (vinylidene chloride-acrylonitrile polymer). However, other suitable vehicles include: polyvinyl chloride, polyvinylidene chloride, copolymers of vinyl chloride and vinylidene chloride, polystyrene, copolymers of styrene and acrylonitrile.

It will be appreciated from the foregoing that the present material consists essentially of four layers of properly differing sensitivity (three layers in the case where the scatter-center component and a leuconitrile color former component are combined into a single layer). The sensitivity of these layers is such that through a proper series of exposures and with a single development, a multi-color image will result. Material such as this greatly simplifies the preparation of multicolor prints, such as those used as visual aids, since such prints can be prepared therefrom using appropriate negatives, one ultraviolet light source and one filter, without requiring wet processing or the registration of separate films.

More particularly, one method of using the above described integral multi-pack material wherein three separate light sensitive layers are used, is to place the appropriate negative in contact with the layer which forms the light-scattering image and to expose ultraviolet light through a filter which substantially blocks radiation having wave lengths below 3500A. Thus, the light-scattering layer is exposed while the leuconitrile color former layer is protected from radiation to which it is sensitive by the filter. The multi-pack material is then subjected to dry heat, for instance, 250° F. for two seconds, so that the light scattering image is developed. A second overall exposure is then made in the same manner, with the filter but without the negative so that the remaining undecomposed sensitizer in the light-scattering emulsion is decomposed to photographically fix the layer and to render it transparent to ultraviolet.

The integral multi-pack layer is then exposed to unfiltered ultraviolet light so that the light passes through the exposed, developed, and fixed light-scattering layer and on to the leuconitrile color former layer immediately beneath the light-scattering layer. An image is developed directly upon exposure without the need for additional energy in the leuconitrile color former layer. This image may be, for example, magenta.

As will be appreciated, the leuconitrile color former layer coated on the other side of the base material is protected from exposure by the base material which acts as a filter to preclude the passage of any substantial amount of radiation below 3500A.

The multi-pack material is then reversed, or turned over, and the second leuconitrile color former layer is exposed to unfiltered ultraviolet light through a suitable negative so that a third image of a different color from

that of the image formed in the first leuconitrile color former layer, e.g. cyan, is directly formed.

The method of exposure and development as described above may also be used when working with two light sensitive layers, i.e. when the light-scattering compound is combined with one of the leuconitrile color formers in a single layer. The finished image in either case appears black, magenta and cyan when projected and, when viewed directly against a dark background, white, magenta and cyan. The leuconitrile dye images are absorption images and will present the same color and general appearance without regard to the viewing conditions while the light-scattering image will appear black when viewed by transmitted light, as upon projection, and will appear white when viewed by reflected light, say against a black background.

Since the leuconitrile images are not fixed against further exposure and development by short wave length ultraviolet, it is desirable, in order to prevent an overall colored fog, to encase the multi-pack material in a jacket which does not permit wave lengths shorter than 3500A. to pass. Alternatively, the material may be over-coated on both sides with a material which performs the same function.

The invention is illustrated, but not limited, by the following examples:

Example I

A photosensitive composition comprising Patent Blue V leuconitrile in aqueous gelatin, prepared in the manner described in Example 15 of 2,855,303, was coated onto a polyethylene terephthalate film (Cronar P42) to a thickness of about 0.8 mil. The Cronar film was 4 mils thick. The coating was set (gelled) by cooling and allowed to dry at room temperature.

The opposite side of the Cronar base was then coated with hydroxyethylated-p-rosaniline leuconitrile (cyanide) in aqueous gelatin, prepared according to Example 13 of U.S. Patent 2,855,303. This coating was also gelled by cooling and air dried at room temperature.

The thus treated film was then coated with a scatter center-forming composition prepared and applied according to Example 1 of Serial No. 623,050, the composition being coated directly upon the dried hydroxyethylated p-rosaniline leuconitrile-gel layer. After drying and curing at 220° F. for about two minutes, the resulting product comprised the Cronar base coated with a first layer of leuconitrile color former and having superimposed thereon a further coating consisting essentially of thermoplastic polymer (Saran) with a light-sensitive diazonium compound, namely, p-diazodimethylaniline zinc chloride salt, dispersed therein, and on the opposite side of the Cronar base a layer of another leuconitrile color former.

The resulting multi-layer, integral product was used as follows to produce a colored record by dry processing:

A negative was placed upon the scatter-center forming, or light-scattering, layer of the material. The negative was then exposed to ultraviolet light using a filter (a polyethylene terephthalate film of 16 mils thickness) so as to prevent substantially the passage of wave lengths below 3500A. Other filters such as cellulose acetate, cellulose acetate butyrate, and cellulose triacetate, could be used in lieu of the polyethylene terephthalate film. The ultraviolet light was obtained from a standard UA–2, 250 watt high pressure mercury lamp kept at about 8 inches from the negative for about 60 seconds. Obviously, other modes of exposure could also be utilized.

After this initial exposure, the material was subjected to heat at 220° F. for two seconds with resulting development of the light scattering image in the top layer, the image being black upon projection. Other developing conditions, e.g. 200 to 250° F. for from 0.5 to 10 seconds, may be utilized.

After heat development, the top layer was given a second overall exposure of 60 seconds using the filter but

without the negative. This decomposed the remaining undecomposed sensitizer in the light-scattering layer thereby fixing the layer and rendering same transparent to ultraviolet.

A negative was again placed on the light-scattering layer and exposed to unfiltered ultraviolet light from the same source. In this instance, light passed through the exposed, developed and fixed light-scattering layer onto the leuconitrile color former layer immediately beneath. This exposure was carried out for 60 seconds although this time may be widely varied, e.g. from 5 to 120 seconds, and the image developed directly upon exposure without the application of any further energy. The resulting image was magenta. The leuconitrile color former layer on the other side of the base material was unaffected.

The material was then turned over and the second leuconitrile color former layer was exposed in like manner to unfiltered ultraviolet light through the negative. A third image, in this case cyan, was immediately formed in this second leuconitrile color former layer.

When projected, the resulting material gave an image which appeared black, magenta and cyan and when viewed directly against a dark background, white, magenta and cyan. To prevent fogging, the developed material was encased in a polyethylene terephthalate jacket. In lieu of this, the material may be overcoated with, for example, 4,4′-dihydroxybenzophenone in a lacquer or other suitable material which prevents substantially the passage of wave lengths shorter than 3500A., as indicated heretofore.

Example II

A photographic color material was prepared in the manner described in Example I except that, the leuconitrile color formers in the first and second leuconitrile layers were, respectively, Erioglaucine leuconitrile (see Example 22 of 2,855,303) and neutral Aurin leuconitrile (Color Index No. 724). Upon exposure, these layers gave cyan and yellow images, respectively.

Example III

The process of Example I was repeated except that the first and second leuconitrile color formers were replaced by Patent Blue V leuconitrile and basic Aurin leuconitrile, respectively, to give cyan and reddish magenta images.

Example IV

The process of Example I was repeated except that the first and second leuconitrile color formers were replaced by p-Rosaniline leuconitrile and Malachite Green leuconitrile, respectively, to give magenta and green images.

Example V

The process of Example I was repeated except that the first and second leuconitrile color formers were replaced by Fast Violet 10B leuconitrile and hydroxyethylated p-Rosaniline leuconitrile, respectively, to give blue and magenta images.

Example VI

Example I was repeated except that instead of forming a separate scatter-center layer, the diazonium compound was dispersed in the first leuconitrile layer. After exposing and developing in the manner of Example I, an essentially equivalent record was obtained showing, on projection, black, magenta and cyan images.

Obviously, various modifications may be made in the invention as described above. Accordingly, the scope of the invention is defined in the following claims wherein:

We claim:

1. A color photographic material comprising a film base coated on one side with a member selected from the group consisting of

(1) a coating comprising a layer (*a*) which comprises a first leuconitrile color former which is sensitive only to light having a wave length below 3500 Angstrom units and upon irradiation with said light produces a colored image and superimposed thereon a layer of a photo sensitive coating composition (*b*) comprising a record furnishing material capable of furnishing a record solely in the form of radiation scattering discontinuities formed within an otherwise optically substantially homogeneous vehicle, said record furnishing material comprising a dry, water-resistant film having uniformly dispersed therein a light decomposable agent which is sensitive to light having a wave length above 3500 Angstrom units and which is decomposed by said light of wave length above 3500 Angstrom units to form a product which is substantially non-reactive to said vehicle and is volatile on warming to form said radiation scattering discontinuities,

and (2) a coating composition comprising said layer (*b*) and, superimposed on it, said layer (*a*),

the other side of said film base being coated with a coating composition comprising a second leuconitrile color former which is sensitive only to light having a wave length below 3500 Angstrom units and upon irradiation with said light having a wave length below 3500 Angstrom units produces an image having a different color, and said base being opaque to light having a wave length below 3500 Angstrom units.

2. A color photographic material as set forth in claim **1** in which said film base is polyethylene terephthalate, said light decomposable agent is a diazonium compound, and said leuconitrile color formers are sensitized with a hydrocolloid.

3. A color photographic material as set forth in claim **2** in which said hydrocolloid is gelatin.

4. A color photographic material comprising a polyethylene terephthalate base, a first photosensitive coating consisting essentially of a leuconitrile color former and gelatin on one side of said base, said leuconitrile color former being sensitive only to ultraviolet light irradiation at wave lengths below 3500 A. and forming a colored image upon such irradiation; a further photosensitive coating superimposed on said first coating, said further coating consisting essentially of a dispersion of light sensitive diazonium compound in a vinylidene chloride-acrylonitrile polymer, said diazonium compound being sensitive to near ultraviolet light having a wave length above 3500 A.; and a third photosensitive coating on the opposite side of said base, said third coating consisting essentially of a different leuconitrile color former in gelatin, said different color former being sensitive only to ultraviolet light irradiation at wave lengths below 3500 A. to form a different colored image upon such irradiation.

5. The material of claim **4** covered with a filter which prevents substantially the passage of ultraviolet light having a wave length below 3500 A.

6. A dry process for preparing a multi-color photographic record which comprises providing a color photographic material according to claim **1**; exposing the side of said film carrying said first color former and said photosensitive composition (*b*) to an image pattern using ultraviolet light while filtering out ultraviolet having a wave length below 3500 A.; then dry heating the thus exposed material to develop light-scattering centers from said photosensitive composition *b* according to said image pattern; thereafter withdrawing the image pattern and exposing said side overall to ultraviolet while continuing to filter out the ultraviolet having a wave length below 3500 A.; then exposing the same side of said film to an image pattern using ultraviolet light without filtering whereupon a color image is formed from said first color former and then exposing the opposite side of said film to an image pattern using ultraviolet light without filtering whereupon a different color image is formed.

7. The process of claim **6** wherein said material, after exposing said second color former, is protected from

fogging by covering same with a filter for ultraviolet light having a wave length below 3500 A.

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