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POLYVINYL CARBAZOLE PHOTOGRAPHIC SYSTEMS

James M. Lewis, Aurora, and John E. Shirey, Bedford, Ohio, assignors to Horizons Incorporated, a division of Horizons Research Incorporated

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ABSTRACT OF THE DISCLOSURE

Compositions suitable for photographic duplication and reproduction either by projection or contact printing, the compositions comprising at least one N-vinyl monomer, such as N-vinylcarbazole, dispersed in polyvinylcarbazole along with a free radical source, such as iodoform, and the procedures whereby such compositions are utilized.

This application is a continuation-in-part of forfeited United States patent application Ser. No. 20,052 filed Mar. 16, 1970; United States patent application Ser. No. 28,548 filed Apr. 14, 1970; and United States patent application Ser. No. 28,558 filed Apr. 14, 1970.

This invention relates to photosensitive compositions and to their use in duplication and reproduction processes.

More particularly, it relates to photosensitive compositions similar in many respects to those described in Wainer U.S. Pat. No. 3,042,517, except that in the compositions of the present invention the binder in which the other active ingredients are dissolved or dispersed is a polyvinylcarbazole with which the dispersed or dissolved constituents appear to react during the procedures described below.

One aspect of the invention is the provision of means for varying the gamma and contrast by manipulation of the temperature at which the development steps are carried out.

Another aspect of the invention is that it provides a photosensitive composition which is either negative working or positive working depending on the sequence of exposures to visible and to ultraviolet radiation.

The compositions of this invention include a variety of constituents, the essential constituents being herein-after identified as activator, color former ad binder, and optional constituents include fog inhibitors, stabilizers and other additives now known in this art.

THE ACTIVATOR

The most suitable activators for the purpose of this invention are compounds which contain a carbon atom to which at least three halogen atoms are attached. These are trihalomethanes, trihaloethanes, trihalo derivatives of the methane or ethane substituent on an aryl ring, and derivatives thereof.

Compounds suitable for the purpose of this invention are given in Table 1 and are identified in U.S. Pat. 3,042,515, the disclosure of which is incorporated herein by reference.

THE COLOR FORMERS

The color formers are generally designated as N-vinyl monomers and when the parent compound is a heterocyclic compound, these are sometimes called 9-vinyl monomers. The N-vinyl monomers contain a nitrogen moiety to which is attached a terminal vinyl group. Color formers of the type suitable for the purpose of this invention are listed in Table 2. Each of these may be utilized as the single color former, if desired. However, better results

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are normally obtained if they are used in admixture with N-vinylcarbazole.

THE POLYMERIC BINDER

The preferred polymeric binder is polyvinylcarbazole. However, the polymeric forms of the monomers given in Table 2 are also effective and other than polyvinylcarbazole, Nos. 2 through 13 represent such a group. This general group of N-vinyl polymers appears to be unique in their behavior for the purpose of this system in that similar effects are not obtained with binders such as polymethylmethacrylate, polystyrene or polyvinylchloride or mixtures thereof. The nitrogen containing vinyl polymer utilized should have a molecular number of at least 500 and a molecular number of 1,000 or higher is preferred. For example, molecular weights (not molecular number) of the polymer of the order of 100,000 have been found to be quite satisfactory. With molecular numbers much below 500 some difficulty in drying is obtained. While all of the polymeric forms of the N-vinyl compounds based on Nos. 1 through 13 in Table 2 are effective and as such are similar in their action, polyvinylcarbazole is preferred because of its low cost and ready availability.

TABLE 1

The activators

- (1) Iodoform
- (2) Carbon tetrabromide
- (3) Monobrom-trichloro-methane
- (4) Hexachlorethane
- (5) $\alpha, \alpha', \alpha''$ -trichlorotoluene
- (6) $\alpha, \alpha', \alpha''$ -tribromotoluene
- (7) Carbon tetraiodide
- (8) Pentabromomethane

TABLE 2

The N-vinyl monomer color formers

- (1) N-vinylcarbazole
- (2) N-vinyl phenyl-alpha-naphthylamine
- (3) N-vinyl diphenylamine (stabilized with 0.1% NaOH)
- (4) N-vinyl indole
- (5) N-vinyl pyrrole
- (6) N-vinyl pyrrolidone
- (7) N-vinyl succinimide
- (8) N-vinyl phthalimide
- (9) N-vinyl acetanilide
- (10) N-vinyl phenylacetamide
- (11) N-vinyl methylacetamide
- (12) N-vinyl diglycolylimide
- (13) 9-(beta-chlorethyl)-3-(p-hydroxyanilino)-carbazole
- (14) 3-(2-hydroxy-1-naphthylazo)-9-vinylcarbazole
- (15) 3-(9'-xanthyl)-9-vinylcarbazole
- (16) 9-vinyl-(2',3':3,4)-naphthacarbazole
- (17) 9-vinyl-3-(p-hydroxyanilino)-carbazole
- (18) 3-indole-phenol-9-vinylcarbazole
- (19) 3-indole-phenol-azo-9-vinylcarbazole

THE PREFERRED COMPOSITION RANGES

The preferred composition ranges are given in Table 3. In making up the photosensitive material, the preparation is carried out under red safelight conditions, as further described in Photographic Science and Engineering, Volume 5, Number 2, March-April 1961, pages 98-103 and Volume 8, March-April 1964, pages 91-103. Items 1, 2 and 3 are first mixed together completely and then the various items are added consecutively in the order given in the table. Each solid reagent is dissolved completely before adding the next and a clear solution results. It should be noted that this composition is not an emulsion nor a dispersion of hydrophilic reagents in a hydrophobic

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matrix or the reverse. Item 4, the cresol, is added for purposes of enhancement of shelf stability. The combination of items 5 and 6 are the primary color formers. Rubrene sensitizes the composition to the visible up to approximately 6000 Å. In the absence of rubrene, the primary sensitivity of the composition is in the range of 3800 to 4500 Å. Triphenylstibine stabilizes the composition against premature decomposition in the heating step which is described in the preferred methods of operation. While the composition in the absence of rubrene shows a sensitivity range for latent image formation between 3800 and 4500 Å, the peak of sensitivity is 4100 to 4200 Å., whereas in the presence of rubrene the peak of sensitivity is in the range of 4800 to 5500 Å.

TABLE 3

Preferred composition ranges of ingredients

Regent:	Range in parts by weight
(1) 10% solution of polymer in benzene	grams-- 2 to 10
(2) Toluene -----do-----	0.3 to 2.0
(3) Methyleneiodide or methylenechloride	grams-- 0.5 to 2.0
(4) 2,6-di-tert-butyl-p-cresol -----grams--	10 to 100
(5) N-vinyl monomer -----mg--	10 to 200
(6) Halomethane or equivalent -----mg--	50 to 200
(7) Rubrene -----mg--	0 to 50
(8) Triphenylstibene or equivalent -----mg--	0 to 10

The invention will be more fully understood from the examples which follow in which the novel compositions of this invention and their uses are illustrated.

Example 1

A formulation was prepared by putting the following ingredients in the order indicated into a container and stirring to effect complete mixing and dissolution of the added material.

2.5 ccs. of 10 percent polyvinylcarbazole in benzene
0.5 ccs. of toluene
1 cc. of methylene chloride
50 mg. of 2,6-di-tert-butyl-p-cresol
100 mg. of N-vinylcarbazole
125 mg. of iodoform

This formulation was coated 0.0015 inch (wet thickness) on a transparent polyester film (tradename "Mylar") in which the Mylar had been subbed with a ketone soluble polyester at a thickness not exceeding 0.05 micron, after which the coated film was dried for 30 seconds at 90 degrees C. in a forced air oven. Preparation of the formulation, the coating of the formulation on the film base and the drying were carried out under dark room conditions utilizing red light. A square root of two stepwedge exhibiting a maximum density of 3.0 in the highest density step was used as a negative and the coated film was exposed through the stepwedge, to radiation from a tungsten iodine lamp for a sufficient period of time to yield a total energy at the image plane of 80 millijoules. After exposure, the film was then heated in a forced air oven for time periods depending on the temperature used, these time periods being 20 to 30 seconds to 150 degrees C. and 3 to 5 seconds at 170 degrees C. After such heat treatment, the film was given a blanket exposure to a G.E. 250-watt sunlamp of the RS type at a distance of 4 inches for 1 minute. A negative image reproducing 16 steps of the original stepwedge was produced in which the image color was greenish-brown.

The primary sensitivity of the formulation of Example 1 is in the 4000 Å. to 4500 Å. and lower wavelengths. The range of optimum wavelength of fixing is 2800 Å. to 3300 Å. with optimum results at 3130 Å.

Example 2

The procedure of Example 1 was repeated, except that

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the initial exposure was carried out through an interference type filter of a 100 Å. bandwidth with the peak transmission of the filter at 4100 Å. Under these conditions, an exposure of 16 millijoules at the image plane was required to yield a 16 step rendition from the square root of two stepwedge, indicating that at this wavelength the system was approximately 5 times more sensitive than to an equal energy exposure covering the full range of the output of the tungsten iodine lamp.

Example 3

The procedure of Example 1 was repeated, except that during the heat treatment step described in Example 1, the specimen was given a blanket exposure to red light totalling 500 millijoules at the image plane. This blanket exposure is made using a 1.5 kilowatt tungsten iodine lamp, fitted with a Corning glass No. 2030 filter which has a short wavelength cutoff of 630 nanometers. After ultraviolet development and fixing, as defined in Example 1, it was found that again 16 steps of the original square root of two stepwedge could be reproduced with an initial visible light exposure of approximately 25 millijoules of a factor of 3 faster when proceeding as described in Example 1.

Example 4

In a further variation of this procedure, a sodium arc lamp of the Lucalox (trade name G.E.) type was utilized without the intervention of a filter and a speed of between 4 to 5 times greater than that shown in Example 1 was obtained after ultraviolet development and fixing, with, however, a slight degree of fogging yielding a product, however, of a still useable nature.

This example defines that increase in speed can be obtained with blanket long wavelength irradiation after imagewise exposure without interfering substantially with the desired end results in the ultraviolet photo development and photo fixing step.

Example 5

A formulation was prepared as in Example 1 consisting of:

3.0 ccs. of 10 percent polyvinylcarbazole in benzene
0.5 cc. of toluene
1.0 cc. of methylene chloride
50 mg. of 2,6-di-tert-butyl-p-cresol
75 mg. of N-vinylcarbazole
125 mg. of iodoform

The formulation was coated and exposed as described in Example 1, except that the substrate in this case was baryta paper, a gelatin coated paper. An exposure between 75 and 85 millijoules was required to yield the same maximum density as exhibited in Example 1, this maximum density being approximately 1.5 on film with an equivalent reflection density on paper, this level of reflection density being more than adequate for complete legibility on a glossy white paper background.

Example 6

Example 1 was repeated, except that 15 milligrams of the polyacene, rubrene, was added to the formulation. Following the exposure and heat treatment procedure, as defined for Example 1, it was found that approximately 15 millijoules was required to yield the 16 steps equivalent to that obtained in Example 1, indicating that the photographic speed of the formulation had been increased by a factor of 5. When 30 milligrams of rubrene was utilized in the formulation, 8 millijoules of initial light exposure was required to produce the 16 visible steps thus indicating that the speed had been increased by a factor of 10 over that described in Example 1.

The spectral sensitivity of the formulation containing rubrene under equal energy conditions, was found to have been extended to approximately 5800 Å., which may ac-

count for at least a part of the increased speed through the broadening of the spectral response of the system.

When this system was red light treated in the heating step, as described previously, it was found that filters having a short wavelength cutoff of 710 nanometers were required and an approximate tripling of the speed was obtained with the rubrene containing formulation through the addition of this simultaneous step of red lighting during the heating step. Such red light is provided through the medium of a No. 2600 Corning glass filter.

The rubrene leaves a residual red color after the completion of the heating step with or without the red light treatment. This red color bleaches out completely in the ultraviolet development and fixing step, leaving clean white backgrounds. Again, the color of the final image was green to green-brown, as in previous examples.

Example 7

Positive working systems of utility are available at the same photographic speed defined for Example 1 by the use of bleach-out dyes. An example of such a bleach-out dye is 4[1-cyano-7(3)-ethyl-2(3H)-benzothiazolylidene]-1,3,5-heptatrienyl]quinoline. Addition of 1 milligram of this bleach-out dye to the formulation given in Example 1 and exposed and heat treated only as defined in Example 1, yields a positive image in which the image portions appear yellow and the background is cyan to cyan-violet. The contrast is surprisingly good and the image is easily legible. The image is reversed and reinduced negative yielding a dark green-brown image color of high density (transmission density of 2.3) on the post-exposure treatment to the ultraviolet. However, treatment time of 3 to 5 minutes under the conditions given in Example 1 are required for the complete reversal. If 2 milligrams of this bleach-out dye is utilized, a post exposure time treatment of 5 to 10 minutes is required for complete reversal which is, as indicated, negative in which the image color is greenish-black and the background is white. The positive image is stable under roomlight conditions using tungsten illumination for a period of several days without notable reversal, whereas under fluorescent light, which emits a significant portion of ultraviolet, reversal starts to become noticeable within about two days. Nevertheless, for temporary proofing purposes where the photographic result is normally thrown away after being viewed briefly, the positive working system has good utility.

Example 8

In a further variation of this procedure utilizing 5 milligrams of the bleach-out dye 3-ethyl-5[(1-methyl-2, (1H)-pyridylidene)-ethylidene]-rhodanine, a positive image was again obtained in which the image color was deep magenta and the background a very pale yellow, after visible light exposure, as described in Example 1, followed by the heat treatment. If the heat treated sample was then given a post-exposure to the ultraviolet lamp, a period of 5 to 10 minutes was required to yield a reversal producing a negative image in which the image color was again green and the background essentially colorless. The stability in roomlight was approximately double that defined for the quinoline derivatives bleach-out of Example 7 and again the initial photographic speed was approximately equivalent to that defined in Example 1.

Example 9

The image color obtained after complete processing in accordance with Example 1 may be modified through the addition of dye bases. For example, the addition of 5 to 10 milligrams (10 milligrams being preferred) of Rhodamine B base added to the formulation given in Example 1 produces a negative image after ultraviolet light development and fixing a deep violet color with a pale yellow to colorless background. No change in this color is noted on post-exposure to the ultraviolet lamp described in Example 1 for a period of at least 10 minutes.

Example 10

Similarly, the addition of 5 milligrams of auramine base to the formulation given in Example 1 processed under the conditions described in that example, produces a negative image in which the image color is a deep yellow, with a colorless background and this deep yellow color has a density in excess of 4.0 when read with a pale blue filter on the densitometer. No change in color or density takes place on post-exposure for a period of 10 minutes with the ultraviolet lamp in accordance with the instructions given in Example 1.

The congeners of N-vinylcarbazole, more properly called 9-vinylcarbazole, are useful not only for the purposes of this invention, but add certain improvements of considerable value. Typical congeners of the type which have been found useful are listed in Table 2 above, particularly useful congeners of 9-vinylcarbazole being compounds 13 through 19 in Table 2.

Substantial all of the congeners extend the range of spectral sensitivity over the formulation given in Example 1, some slightly and others very broadly to the point where the system will respond to the full panchromatic spectrum. When the addition of the specific substituted N-vinylcarbazole extends the spectral response range up towards or into the panchromatic region, i.e., the red (as far as 7000 Å.), the photographic speed is found to be increased significantly over that of Example 1 formulations. When the addition of the congener increases the range of spectral response only slightly, the photographic speed is equal to or slightly greater than that of the base response system.

The polyvinylcarbazole utilized in the compositions of this invention should have a molecular number of at least 500 and a molecular number of 1,000 or higher is preferred. For example, molecular weights (not molecular number) of the polymer in excess of 100,000 have been found to be quite satisfactory and somewhat superior, but not greatly so, than samples of polymer exhibiting a molecular number of 500. With molecular numbers below 500, some difficulty in drying is obtained and the specimen tends to exhibit a mottled appearance.

The congeners of N-vinylcarbazole, as listed in Table 2, may be substituted in whole or in part for the N-vinylcarbazole in the formulation in Example 1. A preferred formulation is a substitution of equal parts of N-vinylcarbazole for that particular formulation. In such formulation, a preferred amount for optimum use of the congener is 50 milligrams of N-vinylcarbazole plus 50 milligrams of the congener.

Photographically useful results are obtained using formulations similar to those in the preceding examples with amounts of N-vinylcarbazole in the range of 50 milligrams of N-vinylcarbazole to 200 milligrams of N-vinylcarbazole. When the congener is utilized, the total amount of the combination of N-vinylcarbazole and the congener should also be within this range.

When a combination of N-vinylcarbazole and a congener is utilized in the optimum ranges noted above, and the film is processed in accordance with the previous examples, the system is negative working, the color obtained is very deep green-black, the maximum density achieved for equivalent exposures is normally in excess of 2.5 and in the specialized cases described below, significant increases in speed are achieved.

With regard to spectral sensitivity, the addition of the congeners 13 thru 17 inclusive to the base formulation given in Example 1 and in the optimum ranges defined in the preceding sentences will shift the maximum spectral sensitivity the region of 4500 Å. to 4800 Å. and approximately 50 to 60 millijoules are required to yield the 16 steps which have been defined as the result of Example 1, this being a small but significant increase in speed over that defined in Example 1, possibly due to the broader

range of spectral response and the greater completeness of response to the tungsten iodine illumination.

Compounds 18 and 19 in Table 2 above are, however, unusual. Not only do these extend the range of spectral sensitivity up to about 700 nanometers and yield the high density green-black color typical of the other congener additives when used in the optimum amounts as defined in this example, but as a consequence of this improved spectral response, photographic speed is multiplied by a factor of between 5 and 10 since the full density of approximately 2.5 of the green-black image can be achieved with an exposure of 8 to 10 millijoules to the tungsten iodine lamp source. Even greater speed has been achieved through addition of rubrene, a photographic speed of at least 20 times that listed in Example 1, using an energy level at the image plane of the order of 2 to 4 millijoules, has been obtained.

Red light enhancement of the speed in the heating step can also be utilized with congeners 13 through 17 inclusive by utilizing a 2030 Corning glass filter, a filter exhibiting a short wavelength cutoff of 6300 nanometers. A blanket exposure of the order of 500 millijoules is required for obtaining this increase in speed. The panchromatic systems available through the use of either of the congeners 18 or 19 in Table 2, without or with the addition of rubrene, can also be red light intensified providing the short wavelength cutoff of the red filter utilized is 830 nanometers.

In the case of the congeners, red light intensification in the heat step increases the photographic speed by a factor in the range of 10 to 100.

In the formulations given above by way of illustration, various substitutions may be made without departing from the invention, in addition to the use of one or more of the compounds 13 through 19 in Table 2, for some or all of the N-vinylcarbazole.

Instead of methylene chloride, benzene and toluene, other solvents or mixtures of solvents may be used provided they are compatible with the remaining constituents, and provided that they evaporate from the formulation so that it can dry.

Instead of the 2,6-di-tert-butyl-cresol; 2,6-di-tert-butyl-phenol; 2,2-methylene-bis(4-methyl-tert-butyl-phenol), or similar compounds may be used. Between about 10 and 100 mg. of such an ingredient should be present in the formulation.

It is also possible to obtain a positive rendition with the compositions described above, and this may be accomplished at very much higher photographic speeds than those required to yield the negative image. To achieve this result, the route of exposures is altered and instead of an imagewise exposure to visible light in the wavelength range of 4000 to 6000 Å. followed by a brief heating step and then a blanket exposure to ultraviolet radiation in a specific wavelength range, the preferred exposure sequence for obtaining a positive rendition is imagewise exposure to ultraviolet radiation, followed by blanket exposure to visible light in the range of 4000 to 6000 Å., followed by a very brief heating at approximately 140 to 170° F. to complete fixing.

Under these conditions, the variety of halomethanes which can be utilized for the purpose is also increased.

As with the previously described compositions, the role of polyvinylcarbazole as a part of the photoactive binder produces an effect not obtainable with other binders such as polymethylmethacrylate, polystyrene, polyvinylchloride or mixtures of such binders.

The method of processing.—The composition without the presence of rubrene is first given a visible light exposure to light of wavelengths in the range of 4000 to 4500 Å., a wavelength of 4100 to 4200 Å. being preferred. The specimen is then heated for 1 or 2 seconds at 170° C., after which it is immediately given an exposure to ultraviolet light whose optimum wavelength is in the

range of 2800 to 3300 Å. with optimum results being obtained at 3130 Å. This ultraviolet light develops out the latent image (the ultraviolet light exposure being a blanket exposure) and at the same time fixes the system. As noted before, the end result is negative working and the initial dosage of visible light for forming the full density latent image is generally in the range of 5 to 80 millijoules.

To yield the positive working mode with the various types of reagents described in this specification (all of which will operate negatively if utilized in accordance with the procedures given in the preceding examples), an extremely short exposure of imagewise nature is first made in the ultraviolet in the wavelength range of 2800 to 3300 Å., a wavelength of approximately 3100 Å. being preferred. This exposure is made most appropriately to a pulsed xenon arc lamp or a high pressure mercury lamp in which the light has been filtered through an interference filter whose peak of transmission is at 3100 Å. and having a band transmission width of approximately 400 Å. The time of exposure is usually not more than 1 to 2 milliseconds under conditions where the light source is roughly 10 inches away from the image plane of the copying system and exposure times down to 0.1 millisecond have been found to be effective. Measurements of the energy required to yield the desired exposure indicate that the optimum energy range for obtaining full density falls in a range of 0.001 to 1.0 millijoules indicating the extraordinary photographic speed of the system. The result of this first ultraviolet exposure is non-visible so that the image may be properly designated as latent. Thereafter, the specimen is then heated in the darkroom to 170° C. for a period of 1 to 2 seconds, and after cooling to room temperature, it is then given a blanket exposure to visible light and a suitable source of such blanket exposure is tungsten iodine lamp fitted with a quartz envelope. To ensure that no ultraviolet light is striking the film, this exposure is normally made through a Wratten and Wainright 2B filter which filters out the ultraviolet light below the 4000 Å. In the absence of rubrene, the amount of energy in this visible light range required to develop out the image and yield permanent fixing is of the order of 50 to 100 millijoules, whereas in the presence of rubrene the amount of energy required to yield full developing out and fixing is of the order of 10 to 20 millijoules. Since rubrene sensitizes the system to the visible, most of the energy from the lamp in its absence is wasted, whereas in the presence of rubrene, a large percentage of the energy from the lamp is utilized.

In the presence of rubrene, the heating step may be eliminated entirely if desired to yield a fully fixed, fully developed image. In this case the ultraviolet exposure is made as before and the visible light exposure to the tungsten iodine lamp is made through a Wratten and Wainright 4 filter which cuts out all of the radiation below 4500 Å. In this case, a blanket exposure to visible light of this wavelength of 100 millijoules is normally required to achieve fully developed out and fully fixed systems.

The following examples are indicative of the method of practice:

Example 11

2.5 ccs. of 10% polyvinylcarbazole in benzene
0.5 cc. of toluene
1.0 cc. of methylene iodide
50 mg. of 2,6-di-tert-butyl-p-cresol
100 mg. of N-vinylcarbazole
125 mg. of iodoform

This formulation is coated with 0.0015 inch of wet thickness on a transparent polyester film base taken from the polyethyleneterephthalate family in which such polyester has been subbed with a ketone soluble polyester at a thickness not exceeding 0.05 micron on the dry basis, after which the specimen is dried for 30 seconds at 90° C. in a forced air oven. Preparation of the formulation on the film base and the drying is carried out under dark-

room conditions utilizing dim red light. A square root of two stepwedge exhibiting a maximum density of 3.0 in the highest density step is used as the negative. Exposure is made through this stepwedge with a high pressure mercury lamp with an interference filter and for the time of exposure used indicated that the total energy at the image plane was 1.0 millijoule at the step exhibiting a density of 0.1 unit, 0.1 millijoule at the density step equivalent to 1.0, 0.01 millijoule at the density of step equivalent to 2.0 units of density and 0.001 millijoule at the density of step equivalent to 3. Thus, the energy per unit area of exposure through this stepwedge covered a range of 0.001 to 1.0 millijoules. After exposure to the ultraviolet, the specimen was heated in a forced air convection oven for 2 seconds at 170° C., after which it was given a blanket exposure to a tungsten iodine lamp through a Wratten and Wainright 2B filter. This 2B filter transmits radiation above 4000 Å. and cuts out all radiation below 4000 Å. The total exposure of the energy at the image plane with a combination of light source and distance amount to 80 millijoules at the image plane.

A positive image of the original stepwedge was obtained and all 21 steps were visible indicating that an exposure as short as 0.01 millijoule was sufficient to give a positive indication on the film in this positive working mode.

Example 12

2.5 ccs. of 10% polyvinylcarbazole in benzene
1.0 cc. of toluene
1.0 cc. of methylene chloride
50 mg. of 2,6-di-tert-butyl-p-cresol
125 mg. of N-vinylcarbazole
30 mg. of rubrene
125 mg. of iodoform.

Preparation and original light exposure was made in the same manner as in Example 11. After heating for 2 seconds at 170° C. exposures with the tungsten iodine lamp were made through a Wratten and Wainright 4 filter and it was found that 16 millijoules of energy was required to show the 21st step, thus indicating that even with this smaller total amount of energy, that significant image formation took place in the ultraviolet exposure at an energy level of 0.001 millijoule.

Example 13

3.0 ccs. of 10% polyvinylcarbazole in benzene
1.0 cc. of toluene
1.0 cc. of methylene iodide
50 mg. of 2,6-di-tert-butyl-p-cresol
125 mg. of N-vinylcarbazole
30 mg. of rubrene
5 mg. of triphenylstibine
125 mg. of iodoform

Exposure and development was carried out in the manner described in Example 12 with the exception that the exposure to a tungsten lamp was carried out for a sufficient duration of time to yield an energy at the image plane in this visible light exposure of 25 millijoules. Again, the 3 density step in the original stepwedge was duplicated indicating that a useful photographic result could be achieved at an imagewise exposure of 0.001 millijoule.

The colors of the images obtained in each of the first three examples produced in the manner described were greenish-brown. These colors remained greenish-brown if heated at 150° C. for 30 seconds and some evidence of fogging was obtained in Examples 11 and 12 in uncolored areas though not sufficient to eliminate the utility of these samples for most commercial purposes. However, in the case of Example 13, heating under the same conditions showed no fog development and in addition the color of the non-image portions became greenish-black and much darker in color than shown in Examples 11 and 12.

EXAMPLES 14 THROUGH 18

The compositions of Examples 14 through 18 are given in Table 4. These are made up as before and imagewise exposed as described in Example 11. The visible light development with the tungsten iodine lamp through the No. 4 Wratten and Wainright filter was adjusted until the step equivalent to the density of 3 on the original stepwedge was made visible and the energy required to yield this degree of visibility is given in column 3 of Table 4 and the colors obtained as a consequence of this treatment are given in column 4. If heat treated for 15 seconds at 150° C. after the visible light exposure, which is usually sufficient to yield complete fixing for practical purposes, all of the colors become deeper and blacker, generally showing a black rendition with a faint overtone of either green or brown and the longer the heating was extended, the more dense the black color achieved.

EXAMPLES 14-18

TABLE 4

Replace halomethane of Example 13 as follows:

Ex. No.	Halomethane substitute	Energy of visible light exposure thru No. 4 filter (millijoules)	Color of non-image portions
14	75 mg. of carbon tetrabromide	8	Brown, black.
15	125 mg. of hexachlorethane	60	Green.
16	120 mg. of carbon tetratride	10	Grey-black.
17	125 mg. of alphas tribromotoluene	30	Brown-black.
18	80 mg. of pentabromethane	12	Do.

EXAMPLES 19-35

The compositions in accordance with Table 5 were made up and exposed, heat treated and re-exposed as in Example 13. The amount of energy required to yield full density rendition as a consequence of this visible light exposure through the No. 4 Wratten and Wainright filter is given in the table and the colors obtained thereby listed in the final column of the table. On heat treatment for 30 seconds at 150° C. after the colors listed in the table were obtained, again, as before, the colors shifted towards considerable darker hues and in the cases of Examples 19, 20, 26, 27 and 29 through 35, these colors were a deep lustrous black. Example 21 was a black with a slight reddish tone visible, whereas Examples 22, 23, 24, 25 and 28 were brownish-black.

EXAMPLES 19-35

TABLE 5

Variations on Example 13. Each example following contains 40 mg. of N-vinylcarbazole. Added thereto is the amount of different N-vinyl compound listed following.

Ex. No.	Reagent	Energy of visible light exposure thru #4 filter (millijoules)	Color of non-image area
19	50 mg. N-vinylphenyl-alpha-naphthylamine	30	Green-brown.
20	75 mg. N-vinyldiphenylamine	25	Blue-brown.
21	75 mg. N-vinyl indole	25	Red-brown.
22	100 mg. N-vinyl pyrrole	60	Pale brown.
23	100 mg. N-vinyl pyrrolidone	60	Do.
24	40 mg. N-vinyl succinimide	60	Do.
25	100 mg. N-vinyl phthalimide	60	Do.
26	40 mg. N-vinylphenylacetanilide	20	Black.
27	40 mg. N-vinylmethylacetanilide	20	Do.
28	100 mg. N-vinyldiglycolimide	60	Pale brown.
29	50 mg. 9-(beta-chlorethyl)-3-(p-hydroxyanilino)carbazole.	18	Green-black.
30	50 mg. 3-(2-hydroxy-1-naphthyl-azo)-9-vinylcarbazole.	18	Do.
31	50 mg. 3-(9'-xanthyl)-9-vinylcarbazole.	18	Do.
32	50 mg. 9-vinyl-(2',3',3',4)-naphtho-carbazole.	18	Do.
33	50 mg. 9-vinyl-3-(p-hydroxyanilino)-carbazole.	18	Do.
34	50 mg. 3-indole-phenol-9-vinylcarbazole.	14	Do.
35	50 mg. 3-indole-phenoleazo-9-vinylcarbazole.	14	Do.

THE PRIOR ART

U.S. Pat. No. 3,042,517 describes compositions somewhat similar in make-up to those in the instant specification. However 3,042,517 differs in two important particulars. In the first case, the unique characteristic of the polymers derived from the monomers listed in Table 2 is not recognized, it being evident that polymers of this type and particularly polyvinylcarbazole show markedly enhanced speed characteristics over the type of binders utilized in 3,042,517. While negative to positive and positive to positive renditions are described, the routings and techniques utilized are radically different. To yield a negative working image, for example, the specimen is exposed to visible or ultraviolet light and subsequently developed and fixed by heat. To yield a positive to positive type of image, the specimen is first given a brief blanket exposure to light of ultraviolet or visible nature and then exposed thermographically in order to yield a positive image. In a third variation, the first exposure is made to an infrared source on an imagewise basis, then finally exposed to light of shorter wavelength to print-out the non-infrared exposed areas. The highly specific differences in exposure for positive and negative routing over the procedures described in this specification should be noted.

U.S. Pat. No. 3,042,518 again describes a variety of systems containing mixtures of color forming agents similar to those in the instant description. Again in this specification, the unusual characteristic of polyvinylcarbazole and its congeners with regard to marked improvement in photographic speed and processing speed was not recognized. The negative working mode in 3,042,518 is accomplished by an initial relatively short exposure to visible or ultraviolet light, followed by subsequent development with heat or infrared light. The positive to positive working mode in 3,042,518 is the same as described in 3,042,517. For both 3,042,517 and 3,042,518 examination of the conditions of exposure indicate that the energy required to yield an image in the negative working mode is at least 10 millijoules and may range as high as 50 millijoules, whereas the energy required to yield the positive working mode is several times greater than the amount quoted for the negative working mode, this being in contrast to the energy levels listed in the present application.

U.S. Pat. No. 3,042,519 utilizes a combination of hydrocarbon waxes as the plastic binder, these again being totally different than the types of binders described in this specification. Again, the unusual characteristics of polyvinylcarbazole and its congener polymers were not recognized. The wax binder suffers from relatively low melting points, poor structural characteristics and the surface is easily scratched or abraded. The negative-positive and positive-positive working characteristics of the materials described in 3,042,519 was recognized, however, with significant differences in procedure than available in the present specification. Negative working materials were produced first by short exposures to a sunlamp in which a large portion of the light is in the near ultraviolet range and the image is developed out in the negative working mode by exposure to an infrared lamp. The positive working mode was achieved by a short initial exposure in the range of 2200 to 2500 Å. and this is followed by a fairly lengthy exposure to a sunlamp which has most of its emission in the near-ultraviolet of the order of 3600 to 4000 Å. Fixing was accomplished by heating. In view of the nature of the substrate or binder used for 3,042,519, the desired increase in processing speed made available in this description which involves heating for a short period of time to 170° C. is not possible.

U.S. Pat. No. 3,275,443 describes the effect of the use of the certain triaryl compounds as a means for eliminating the fog from the heating step where N-vinyl compounds of the type described in Table 2 of the present specification are used as a principal color former. These compounds may be used in place of the triphenylstibine utilized by preference in the examples above.

In examining these first four references of the prior art, it should be noted that even though the initial exposure in the majority of the cases is in the ultraviolet region, exposures in the region given in these references of the prior art which are somewhat comparable to those described in the instant specification yield a negative working image rather than a positive working image and the one case where positive working images are obtained the initial exposure is in the extreme far ultraviolet at wavelengths very much shorter than those preferred in the instant specification and developing out is given through use of near ultraviolet rather than through the use of the visible as indicated in the instant description.

U.S. Pat. No. 3,374,094 describes color forming systems based on mixtures of N-vinyl compounds and halo-methanes in which such color forming systems are dispersed as hydrophobic droplets in a hydrophilic base, exposures are made through a negative for lengthy periods and then fixed with an infrared lamp. This system is negative working and slow photographically and the positive working mode is not described. Again, the unique advantages of the polyvinylcarbazole type of binder and its congeners were not recognized.

U.S. Pat. No. 3,476,562 uses emulsion technology based on gelatin or other water soluble or water dispersable binders as the matrix and again the unusual characteristics of polyvinylcarbazole binders and its congeners for the development of high speed in these systems was not recognized. The exposure routings and wavelengths to obtain the various positive to positive and negative to positive effects as described in this specification are radically different than those described in the instant application. For example, in column 8 of 3,476,562, the inventor indicates that he obtains a positive result by first exposing to the visible, followed by a second exposure to the ultraviolet, followed by heating to 70° C. for about 10 seconds. In a variation of the procedure he first exposed to the ultraviolet, followed by heating and then again exposes to the same ultraviolet, followed by a second heating to yield a positive working mode. In his Example 3, he attempts to establish that the same light source can be used both for imaging and blanketing exposures in making a positive picture. The work described in the instant specification indicates much better results are obtained by placing close attention to the relative wavelengths of exposure with regard to the presumed chemistry that is effective as a function of various ingredients which are present, this chemistry obviously being different in using a polyvinylcarbazole type of binder rather than the water dispersable type of binder described in 3,476,562. In Example 43, column 49 of 3,476,562, exposures are first made to the visible, followed by blanket exposure to the red in order to obtain a positive picture. In no case is the same routing of exposure and development steps or the same range of wavelengths utilized in 3,476,562 used as is defined in this specification. It has been established that the photographic speeds available from the teachings of this specification are much greater than any of those which have been described in the prior art.

We claim:

1. Photosensitive material comprising at least one color-forming N-vinyl monomer and at least one organic halogen compound in which at least three halogen atoms selected from the group consisting of Cl, Br and I are attached to a single carbon atom, said monomer and said halogen compound being dispersed in a polyvinylcarbazole binder, which has a molecular number greater than about 500.

2. The photosensitive material of claim 1 in which the N-vinyl monomer is N-vinylcarbazole and the halogen compound is iodoform.

3. The photosensitive material of claim 1 in which the organic halogen compound is represented by the general formula $A-C-X_3$ wherein A is a monovalent member selected from the group consisting of H, Cl, Br,

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I, alkyl, substituted alkyl, aryl and aroyl and each X represents a halogen atom selected from the group consisting of Cl, Br and I, and not all of the X's are required to be the same halogen.

4. The photosensitive material of claim 1 in which the composition additionally includes a substituted phenol selected from the group consisting of 2,6-di-tert-butyl-p-cresol; 2,6-di-tert-butyl-p-phenol; and 2,2-methylene-bis (4-methyl-tert-butyl-phenol) in an amount sufficient to improve the shelf stability of said material.

5. The photosensitive material of claim 1 coated as a thin film on a transparent support.

6. The photosensitive material of claim 1 including, in addition, a polyacene compound in an optically sensitizing amount.

7. The photosensitive material of claim 1 including, in addition, a bleach-out dye, in an amount sufficient to render the material positive working.

8. The photosensitive material of claim 1 including, in addition, a dye base, in an amount sufficient to change the nature of the image color.

9. The composition of claim 1 in which the N-vinyl monomer portion of the composition comprises 9-vinylcarbazole and at least one congener of 9-vinylcarbazole.

10. The photosensitive material of claim 9 in which the congener is selected from 9-(beta-chlorethyl)-3-(p-hydroxyanilino)-carbazole; 3-(2-hydroxy-1-naphthylazo)-9-vinylcarbazole; 3-(9'-xanthyl)-9-vinylcarbazole; 9-vinyl-(2',3':3,4) - naphthocarbazole; 9-vinyl-3-(p-hydroxyanilino)-carbazole; 3-indole-phenol-9-vinylcarbazole; and 3-indole-phenol-azo-9-vinylcarbazole.

11. The photosensitive material of claim 9 in which the amounts of N-vinylcarbazole and congener of 9-vinylcarbazole are approximately equal.

12. A process of producing a visible image which comprises:

preparing the photosensitive material of claim 1 as a thin film;

exposing the material to a pattern of ultraviolet radiation thereby producing a latent image in said photosensitive material;

and thereafter heating said material to a temperature between about 140 and 170° C., while said latent image bearing photosensitive material is maintained in the dark.

13. The process of claim 12 wherein, after the photosensitive material has cooled to room temperature after the heating step, it is given a blanket exposure to visible light in the range of 3800 to 4500 A.

14. The process of claim 13 wherein after the photosensitive material has been given a blanket exposure to visible light, it is heated again to about 150° C. to darken the colors in the non-image portions of said material.

15. The process of claim 12 in which the first exposure is a brief exposure to ultraviolet in the range of 2800 to

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3300 R., and the heating is at about 170° C. for a short interval of time.

16. The process of claim 12 wherein after the exposure to the ultraviolet and before the preheating step, the photosensitive material is given a blanket exposure to visible light in the range of 4000 to 6000 A. after which it is heated briefly to a temperature between about 140° C. and 170° C. to complete the fixing of the photosensitive material.

17. A process of producing a visible image which comprises:

preparing the photosensitive material of claim 6 as a thin film;

exposing the material to a pattern of ultraviolet radiation, thereby producing a latent image in said photosensitive material;

and thereafter giving said photosensitive material a blanket exposure to visible light in the range of 3800 to 4500 A.

18. The process of claim 12 wherein the pattern of the ultraviolet is determined by an original subject from which a positive copy is to be made and the result is a positive to positive copy of the original subject.

19. The process of producing a visible image which comprises preparing the photosensitive material of claim 1; exposing the material to a pattern of visible radiation; thereafter heating the photosensitive material for a short interval to develop an image and then post exposing the photosensitive material to a suitable dose of U.V. radiation to fix the image.

20. The process of producing a visible image which comprises preparing the photosensitive material of claim 1; exposing the material to a pattern of visible radiation; thereafter blanket exposing the photosensitive material successively to infrared to develop an image and then U.V. radiation to fix the image.

21. The process of producing a visible image which comprises preparing the photosensitive material of claim 1; exposing the material to a pattern of visible radiation; thereafter blanket exposing the photosensitive material to red light radiation to develop the image and then to U.V. radiation to fix the image.

References Cited

UNITED STATES PATENTS

3,476,562	11/1969	Yamada et al.	96—90
3,351,467	11/1967	Sprague et al.	96—90
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50 NORMAN G. TORCHIN, Primary Examiner

R. FICHTER, Assistant Examiner

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