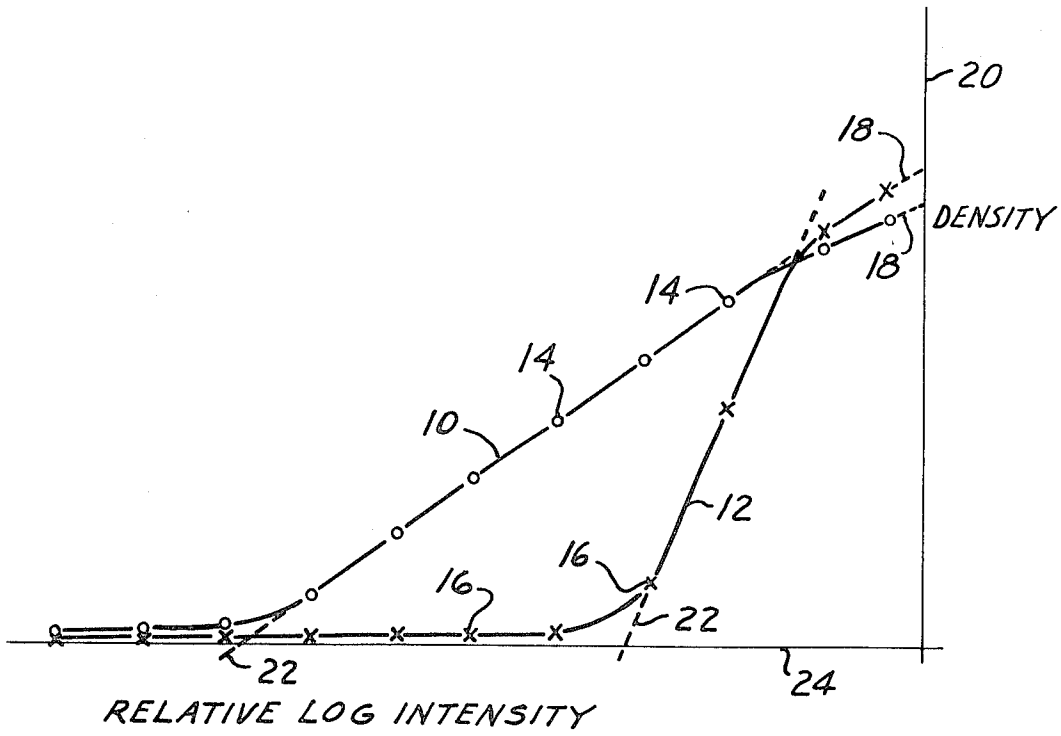
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ORGANIC PHOTO-MATERIAL OF INCREASED CONTRAST

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ORGANIC PHOTO-MATERIAL OF INCREASED CONTRAST

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ABSTRACT OF THE DISCLOSURE

A photosensitive composition is disclosed yielding a color in light-struck areas and comprising an N-vinyl compound and a polymerization inhibitor. The inhibitor increases gamma, or contrast, by reducing photosensitivity to low levels of light without significantly decreasing photosensitivity to levels of light exposure used to make the image exposure.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The field of art to which the invention pertains includes the field of photographic chemistry, particularly light-sensitive compositions.

(2) Description of the prior art

A variety of organic photosensitive systems are known in the art and generally involve two or more organic materials which react under the influence of actinic light to produce a color. As early as 1921, Murray C. Beebe and his co-workers described numerous organic photographic systems utilizing halogen compounds in combination with a second ingredient (e.g. U.S. Pat. Nos. 1,574,357; 1,574,358; 1,574,359; 1,575,143; 1,583,519; 1,587,269; 1,587,270; 1,587,271; 1,587,272; 1,587,273; 1,587,274; 1,587,274; 1.604,674; 1,618,505; 1,655,127; 1,658,510; and 1,820,593). It has been theorized that light effects the release of a radical from the halogen compound which carries out a color-forming reaction with the second compound. Subsequent workers such as Eugene Wainer (e.g., U.S. Pat. Nos. 3,042,515; 3,042,516; 3,042,517; 3,042,518; 3,046,125; and 3,056,673) as well as a number of other workers, have continued the development of various photographic systems involving a photo-energized reaction of a combination of a halogen containing compound and one or more other compounds. Other recent disclosures include British Pat. No. 917,919 and Belgian Pat. No. 516,094.

More recently, it has been discovered that some of the above combinations can be advantageously dispersed in a continuous phase in which the combinations are substantially insoluble (e.g. gelatin or other, similar aqueous support). When an N-vinyl compound is used as the color former, particularly in combination with a photo-initiator, markedly superior speeds result. This discovery has been described in British Pat. No. 1,065,548.

With the foregoing N-vinyl compounds and photo-initiator, particularly in the form of a dispersion, an image-wise exposure can cause both colorless polymerization and color formation. The two reactions apparently compete so that substantial gray scale is obtained under negative-mode conditions, that is, under conditions yielding a color in light-struck areas. It is desirable to reduce such gray scale when using the photosensitive material to reproduce line copies. In this utility it is preferred to use a material having a high gamma characteristic curve, i.e., high contrast, so that the background areas are less sensitive to light and therefore remain cleaner.

SUMMARY OF THE INVENTION

The present invention provides photosensitive material which utilizes a color forming N-vinyl compound but which has increased gamma or contrast. Gamma is increased by incorporating a polymerization inhibitor, particularly in a concentration sufficient to decrease the photosensitivity of the material but insufficient to significantly decrease image color density. In a particular embodiment, the polymerization inhibitor is an aromatic amine.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the drawing, illustrative characteristic curves **10** and **12** are shown which are H & D curves, as known in the art, in which the density is plotted against logarithm of exposure, in this case the relative logarithm of intensity of exposure. Data points are obtained by exposing the photosensitive material through a step wedge having **11** steps, the first step being nearly transparent. A densitometer is used to read the developed image and to read the developed image and to obtain the points which are plotted in the figure.

Utilizing a photosensitive material containing an N-vinyl compound, but without a polymerization inhibitor, data points are obtained and plotted as small circles **14** to form the characteristic curve **10** of the material. Utilizing the same material but with a polymerization inhibitor in accordance with this invention, data points are obtained and plotted as small x's **16** to form the characteristic curve **12** of the improved material.

Comparing the curves **10** and **12**, we see that by incorporating a polymerization inhibitor the toe of the curve shifts significantly representing a significant decrease in photosensitivity to low levels of exposure or light intensity. On the other hand, the maximum density does not decrease. The result is an increase in the slope of the characteristic curve.

Gamma represents the degree of contrast of a developed photographic image and is determined by measuring the slope of the straight-line portions of the characteristic curve of a photographic material. In the drawing, straight dashed lines **22** are drawn through the characteristic curves **10** and **12** to intercept the abscissa **24**. Gamma for the curves can then be obtained by determining the tangents of the angles of such interception. By extending the upper portion of the curves, e.g. at **18**, to intercept the ordinate **20**, one can approximate the maximum density obtainable under the conditions of exposure.

The N-vinyl compound utilized in our invention can be any of a variety of N-vinyl compounds known to the art to yield a color when in combination with a photo-initiating compound or when otherwise formulated to be photosensitive. Such aromatic N-vinyl compounds as are found in the aforenoted British Pat. 1,065,548 can be utilized here, for example, N-vinyl phthalimide, N-vinylcarbazole or N-vinylindole. N-vinylcarbazole is particularly efficacious.

As polymerization inhibitor, one can use any of the wide variety of different types of inhibitors for vinyl polymerization known to the art. Such inhibitors include phenolic compounds, quinones, nitroaromatics, aromatic amines, and the like, and miscellaneous other materials. For the purpose of this specification and the appended claims, the term "aromatic amine" is meant to include N-heterocycles, such as phenothiazine. The aromatic amines are particularly effective.

When a photo-initiator is used, it is generally a compound which produces free radicals or ions upon exposure to light of a suitable wavelength, such as the haloalkanes, halomethylnaphthalenes, haloketones, halogenated acids,

sulfonyl chlorides and aroyl peroxides. Such of these materials as are discussed by McCloskey and Bond in Industrial Engineering Chemistry, volume 47, page 2125 et seq. (1955), are of interest here, and such disclosure is incorporated herein by reference. Other materials include aromatic hydrocarbon photo-initiators such as found in U.S. 2,902,421; substituted benzoins described in U.S. 2,722,512; metal mercaptides as described in U.S. 2,738,-319; benzene thiols as described in U.S. 2,861,934; ethylenic compounds as described in U.S. 2,716,633; and thiruam monosulfides as described in U.S. 2,861,933, the disclosures of the above patents being incorporated herein by reference.

In general, the organic halogen compounds are particularly effective photo-initiators and such compounds are described in detail in the aforementioned British Pat. 1,065,548. Of these, a particularly effective group of compounds are those in which there is present at least one active halogen, selected from the group consisting of chlorine, bromine and iodine, atached to a carbon atom having not more than one hydrogen atom attached thereto. Examples of such compounds include carbon tetrabromide, bromotrichloromethane and 1,1,1 - tribromo-2-methyl-2-propanol. Other compounds can be found in the noted patents issued to Eugene Wainer and Robert Sprague such as U.S. Pats. Nos. 3,042,515; 3,042,516; 3,042,517; 3,042,518; 3,042,519; 3,046,125; 3,056,673; and 3,082,086, the disclosures of such patents being incorporated herein by reference.

In a further embodiment of this invention, the photosensitive material is in particulate form. Preferably, the material is dispersed in a substantially non-solubilizing continuous phase which is generally water-penetrable. Such dispersions are particularly well-suited for contrast control in accordance with this invention. The solid film-forming component used to achieve the continuous phase may be any of a number of generally photographically inert materials, which are, in most cases, soluble in water or so finely dispersible therein in the concentrations of use that for practical purposes there is no distinction between solution and dispersion for these materials in the continuous phase. Such materials include the starch and starch derivatives, proteins, (i.e. casein, zein, gelatin, thiolated gelatin, etc.) alginates, gums, and the like materials which are generally considered to be natural derivatives of natural film-forming materials, any one of which in its conventional "water soluble" form is usable in films of the instant invention. In addition synthetic water-soluble film-formers are particularly suitable binders for photosystems of this invention and such materials include polyvinyl alcohol, commercially available water-soluble polyacrylics or acrylates (i.e. water-soluble polyacrylic acid salts having substantially the molecular weight and water compatibility of the polyvinyl alcohol), various commercially available amine or amine-aldehyde resins, etc. Also, a number of cellulose derivative film-formers may be used, and these include the various water-soluble cellulose ethers, carboxymethyl-cellulose, hydroxypropyl-methylcellulose, etc. Essentially these materials are photo-insensitive and their principal function is that of forming the desired film to retain the dispersed phase in discreate particle form. Of the above materials, gelatin, casein, polyvinyl alcohol, gum arabic, starch, alkali metal carboxymethylcellulose (e.g. sodium carboxymethylcellulose) and hydroxyethylcellulose are particularly useful in this invention.

In addition to the foregoing components, a sensitizer can also be added in small sensitizing amounts either to create a variety of color responses or to impart panchromatic response to the film. For a suitable sensitizer reference can be made to a 1957 publication of Brooker and Vittun entitled, "A Century of Progress in the Synthesis of Dyes for Photography" in the Journal of Photographic Science, volume 5, 1957, pages 71–78, the disclosure of such publication being incorporated herein by reference. All of these materials tend to absorb actinic energy and all have exhibited their ability to transmit the absorbed energy by a physical molecular contact or by engagement to other molecules receptive of actinic enery for purposes of photo-response. Illustrative materials are: compounds having a characteristic rhodamine ring structure and nominal substitution as an amino group, such as the rhodamines (i.e. aminophthaleins); materials having simple (unsubstituted) carbon chains interconnecting fused heterocyclic and benzenoid ring structures, such as pinacyanole and related carbocyanine or cyanine type dye bases; light absorbers containing heterocyclic rings fused with benzenoid rings, such as eosin dye bases; and light absorbers having a triphenylmethane structure particularly leuco forms thereof and compounds having thiazine, alizarine, acridine and anthraquinoid groups of structures. In general, light absorbers having a styryl substituent such as the styryl azastyryl dye bases are particularly useful in our invention.

The concentrations of the foregoing components depends on the particular photosensitive composition utilized. Generally, a weight ratio of N-vinyl compound to photo-initiator of from about 1:5 to about 50:1 is satisfactory. A concentration of N-vinyl compound in the binder can vary from as low as 5% of the binder, or lower, to where no binder is used in some embodiments. When a sensitizer is used, generally from about 0.001 to about 100 mg. of sensitizer per gram of N-vinyl compounds is satisfactory.

The polymerization inhibitor is present in a concentration sufficient to decrease photosensitivity of the material but insufficient to significantly decrease the density of developed color. The amount varies in accordance with the nature of the photosensitive material as well as the nature of the polymerization inhibitor. Generally, for more effective inhibitors such as the aromatic amines, as little as 0.001 mg. and as high as 100 mg. can be used. Other, less effective, inhibitors may require as high as 500 mg. or even higher to be effective.

The following examples illustrate the variety of polymerization inhibitors effective utilized in this invention.

EXAMPLES 1–4

Baryta paper was coated to about 1.5 mil wet thickness with emulsions of the following formulations:

TABLE I

Examples	Component	Amount
All	Gelatin	10 grams.
All	Water	36 ml.
All	N-vinylcarbazole	4 grams.
All	Carbon tetrabromide	3.2 grams.
All	4-(p-dimethylaminostyryl)-quinoline	4 mg.
All	1.5% aqueous Tergitol 4 (Union Carbide)	10 drops.
1	Phenothiazine	0.10 mg.
2	Tetramethylbenzidine	1.0 mg.
3	Hydroquinone	10 mg.
4	1,4-benzoquinone	10 mg.

In preparation, the N-vinylcarbazole was dissolved in 2 ml. of acetone and the 4-(p-dimethylaminostyryl)-quinoline was added thereto, the solution being maintained at about 43–45° C. The carbon tetrabromide was added to the acetone solution under a red safe-light and stirred to dissolve. This solution was then added to a solution made up of the water, gelatin and Tergitol 4, the combination being mechanically stirred with a high-shear mixer for about 5 minutes to yield an emulsion with an average particle size of about 8 microns. After coating with a standard vacuum plate and coating bar, the sheets were dried for about 10 minutes in an oven with forced air circulation at about 30° C. The dry coating weight was about 1.8 grams per square foot.

Each sheet was exposed behind a step wedge, as in the previously described procedure, to a 650-watt Sylvania Sun Gun at 14 inches for 5 seconds. The step wedge has 11 steps ranging in density from near zero to just over 3, in steps of approximately 0.3. The sheets were then warmed for about 15 seconds on a rotating drum

heater at about 70° C. to form an image varying in color intensity in correspondence to the variation of density of the step wedge spaces.

The sheets were stored in the dark and densitometry readings were obtained soon thereafter. The images can be stabilized against light deterioration, e.g. by bathing with an aqueous solution of sodium sulfite, but such procedure somewhat affects the image color. Accordingly, densitometry readings were obtained without stabilizing the image and because the image was lacking in stability to light, a red Corning 2–59 filter was placed over the reading light in the reflectance unit of the densitometer. This reduced the sensitivity of the instrument, but there was still sufficient range available to read reflection densities to 1.5. The densitometer was a standard Welch Densichron 1, with reflectance unit Catalog No. 3832A.

By placing a negative sign in front of the step wedge densities, a "relative logarithm of intensity" number is obtained that is analogous to variations in exposing light and which is useful in plotting and evaluating data. The data were plotted under standard H & D procedures in which the density of the example is plotted against the logarithm of exposure; in the present case "intensity" is used rather than "exposure" because the figures are available from the densities of the step wedge.

Curves were obtained which are generally similar to the curves described with reference to the drawing and having generally the same maximum density for the control sample as for each of the examples. The slope of each curve was measured to determine gamma. The following Table II lists the results of such data analyses.

TABLE II

Example	Inhibitor	Amount, mg.	Gamma
Control	None		1.23
1	Phenothiazine	0.10	1.66
2	Tetramethylbenzidine	1.0	1.64
3	Hydroquinone	10	1.43
4	1,4-benzoquinone	10	1.31

Referring to Table II, we see that each of the polymerization inhibitors caused an increase in gamma or contrast. One may also note that a wide range of concentrations are utilized, depending on the material. In each case, the concentration represents a range of concentration that has been found to be effective for that material.

In general, the aromatic amines, as exemplified herein by phenothiazine and tetramethylbenzidine, are generally more effective than other types of inhibitors.

It will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of this invention.

What is claimed is:

1. A photosensitive formulation, comprising:
a composition responsive to light yield a color in light-struck areas and comprising a polymerizable aromatic N-vinyl compound, an organic halogen compound, which produces free radicals or ions upon exposure to light of a suitable wavelength, as a photo-initiator for said N-vinyl compound, and a polymerization inhibiting compound, selected from the group consisting of phenolic compounds, quinones, nitroaromatics and aromatic amines, in a concentration sufficient to increase contrast of said material but insufficient to significantly decrease the density of said color, said N-vinyl compound, organic halogen compound and polymerization inhibiting compound being dispersed in a hydrophilic binder.

2. The material of claim 1 wherein said polymerization inhibitor is an aromatic amine.

3. The material of claim 1 wherein said N-vinyl compound is N-vinylcarbazole.

4. The material of claim 1 wherein said polymerization inhibitor is phenothiazine.

5. The material of claim 1 wherein said polymerization inhibitor is an N-heterocycle.

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