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PHOTOSENSITIVE DISPERSION IN A HYDROPHILIC BINDER INCORPORATING A STABILIZER

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ABSTRACT OF THE DISCLOSURE

A recording medium including a dispersion in a solid film-forming hydrophilic binder of a photosensitive combination of organic halogen compound and aromatic nitrogen-containing compound, and incorporating a stabilizer for background and image areas.

This invention relates to photosensitive compositions, films or articles and to improved stabilization methods relating thereto. In particular, this invention relates to a method of stabilizing or fixing images obtained with organic photosensitive compositions.

In general, it is old and well known in the photographic arts to provide photographic systems involving 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 coworkers described numerous organic photographic systems (e.g., U.S. Pats. 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; 1,604,674; 1,618,505; 1,655,127; 1,658,510; and 1,820,593). Generally, these systems relate to the use of various halogen compounds (e.g., iodoform and others) in combination with a second ingredient, in which Beebe and subsequent workers have 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. Pats. Nos. 3,042,515; 3,042,516; 3,042,517; 3,042,518; 3,042,519; 3,046,125; and 3,056,673) and Robert Sprague (U.S. Pat. No. 3,082,086), as well as a number of other workers since the time of Beebe, 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. 596,094.

More recently, it has been discovered that incorporation of certain of the above combinations as dispersions in a continuous phase, e.g., gelatin, in which such combinations are substantially insoluble, results in a photographic composition of superior speed, sensitivity and other properties. This discovery has been described in an application of Yoshikazu Yamada and Thomas H. Garland, Ser. No. 481,759, filed Aug. 23, 1965, entitled "Production and Use of Photosensitive Compositions and Films." In that application, it is explained that the selection of an aromatic N-containing compound as there described merely for its ability to form some sort of color with a halogen-containing compound under the influence of actinic light is a practical minimum for purposes of demonstrating the invention.

A drawback of exposed films incorporating the above compositions is their tendency to darken upon prolonged exposure to light. Among the objects of this invention is to provide a photographic composition utilizing organic photosensitive combinations which can be readily stabilized, and to provide stabilizing methods. It is a further object to provide such compositions and methods wherein the photosensitive combinations comprise dispersions of an organic halogen compound and a second ingredient in a non-solubilizing continuous phase. It is a still further object to provide compositions and methods wherein a photographic image is effectively stabilized against darkening of background areas and can be used repeatedly as a master in diazo and other reproduction process involving repetitious exposure to light of any wavelength. Other and further objects, features and advantages of this invention will become apparent from the following description thereof.

The above and other objects are accomplished by providing a photographic recording medium comprising a support having thereon a dispersion of organic photosensitive material in a continuous phase in which the photosensitive material is substantially insoluble, and a desensitizer for the photosensitive material in the continuouos phase, the continuous phase being penetrable by solvent in which the desensitizer has significant solubility. In operation the recording medium is exposed to actinic light to form an image thereon, e.g., by exposure through a transparency. The photosensitive material undergoes some form of reaction in response to the exposure to form a color in exposed areas or a color-forming material, i.e., a "latent" image; or the photosensitive material is "desensitized" in response to the light, and unexposed portions form a color by some subsequent treatment. After exposure, a solvent in which the desensitizer has significant solubility, and which can penetrate the continuous phase or binder, is applied to cause the desensitizer to intimately contact the photosensitive material rendering it photo-insensitive.

In one form of the invention the solvent is supplied by immersion of the recording medium therein. In another form of the invention, where the solvent contemplated is water, it can be supplied either as above or by incorporation into the binder of a water-releasing agent which releases water on the application of heat. Heating the recording medium, after the desired exposure, releases the water which carries the desensitizer into intimate contact with the photosensitive material.

The use of any desensitizer having significant solubility in a solvent that can penetrate the continuous phase is contemplated in this invention. The following desensitizers are, for the most part, readily available materials whose solubility in various solvents is known or can be readily determined. One type of desensitizer that can be used is a compound having the formula

$$M_{3-v-w}(H)_wS_{1+x}O_{3+2x}$$

wherein x is selected from 0 and 1, M is a cation selected from ammonium, alkali metals and alkaline earth metals, v is the valence of the selected cation, and w is 0 when v is 2 and is selected from 0 and 1 when v is 1. The cation chosen should be such that the compound is soluble in the particular solvent or solution used. Examples of such compounds include ammonium sulfite, lithium sulfite, sodium sulfite, potassium sulfite, magnesium sulfite, potassium metabisulfite, sodium metabisulfite, ammonium bisulfite, potassium bisulfite and sodium bisulfite. Further descriptions and examples of such compounds are given in an application by Yoshikazu Yamada and Thomas H. Garland, entitled "Photographic Method," filed concurrently herewith.

Another type of desensitizer that can be used is a carbonyl-bisulfite complex, particularly a carbonyl complex of a bisulfite of alkali metal or ammonium. Carbonyl compounds that can be used to form such complexes include

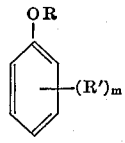
the aliphatic methyl ketones, cycloaliphatic ketones and aliphatic, cycloaliphatic and aralkyl aldehydes. In structural terms, the carbonyl compounds generally have the formula



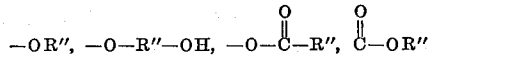
wherein is selected from hydrogen, methyl and methylene, R_1 is an aliphatic or aralkyl group when R is hydrogen, is an aliphatic group when R is methyl, and, together with R, forms a cycloaliphatic group when R is methylene. In general, "aliphatic" refers to alkyl or olefinic groups having from 1 to about 8 carbon atoms, "aralkyl" refers to benzene substituted alkyl groups having from 7 to about 12 carbon atoms and "cycloaliphatic" from about 5 to about 12 carbon atoms. Ketones are generally preferred. Examples of suitable complexes include: acetaldehyde-sodium bisulfite, acetone-cesium bisulfite, acetone-ammonium bisulfite, methyl ethyl ketone-rubidium bisulfite, methyl propyl ketone-sodium bisulfite, isobutyl ketone-potassium bisulfite, benzaldehyde-sodium bisulfite, o-methylbenzaldehyde-potassium bisulfite, cyclohexanone-lithium bisulfite, 4-ethylcyclohexanone-sodium bisulfite, and the like. Carbonyl complexes of alkali metal bisulfites are preferred, such as those of sodium and potassium. Acetone, 2-octanone, methyl ethyl ketone, and cyclohexanone are preferred carbonyl compounds as they are generally more effective than other members of the above classes. The acetone bisulfites are most particularly effective. Further descriptions and examples of such compounds are given in an application by Peter Bruck, entitled "Photographic Method," filed concurrently herewith.

Another type of desensitizer that can be used is a compound having a reactive oxygen atom, preferably selected from (1) organic peroxides and hydroperoxides and (2) inorganic peroxides, perchlorates and perborates. Examples of suitable inorganic peroxides include hydrogen peroxide (as such, or in combined form with a carrier material, e.g., urea peroxide), sodium peroxide, cesium peroxide and rhenium peroxide. Examples of suitable inorganic perchlorates include perchloric acid, sodium perchlorate, aluminum perchlorate, ammonium perchlorate, barium perchlorate, cadmium perchlorate, cesium perchlorate, cobalt perchlorate, copper perchlorate, gallium perchlorate, indium perchlorate, iron perchlorate, lead perchlorate, lithium perchlorate, magnesium perchlorate, nickel perchlorate, strontium perchlorate, thallium perchlorate and zinc perchlorate. Sodium perborate, potassium perborate, and the like, are examples of suitable inorganic perborates. Suitable organic hydroperoxides, which are meant to encompass peroxy acids and dibasic acid peroxides, include succinic acid peroxide, tert-butylhydroperoxide, 2,5 - dimethylhexane-2,5-dihydroperoxide, cumene hydroperoxide, acetyl hydroperoxide, cyclohexyl hydroperoxide, ethyl hydroperoxide, methyl hydroperoxide and perbenzoic acid. Suitable organic peroxides include: the aromatic and aliphatic diacyl peroxides such as dibenzoyl peroxide, di(p-chlorobenzoyl) peroxide, di(2,4-dichlorobenzoyl) peroxide, di(1-naphthyl) peroxide, di(3-nitrobenzoyl) peroxide, di(4-nitrobenzoyl) peroxide, dilauroyl peroxide, didecanoyl peroxide, didodecanoyl peroxide, diacetyl peroxide, dipropionyl peroxide and acetyl benzoyl peroxide; the ketone peroxides such as bis(1-hydroxycyclohexyl) peroxide, cyclohexanone peroxide and bis(2,2 - dihydroperoxybutane); peroxyesters, including carbonate ester peroxides, such as tert-butyl peroxy, tert-butyl peroxyacetate, tert-butyl peroxyisobutyrate, tert-butyl peroxypivalate, tert-butyl peroxybenzoate, tert-butyl peroxymaleic acid, di-tert-butyl-di(peroxyphthalate), 2,5-dimethylhexane - 2,5 - (peroxybenzoate) and diisopropyl peroxydicarbonate; and dialkyl peroxides such as di-tert-butyl peroxide, 2,5-dimethyl-2,5-di(tert-butyl peroxy) hexane, 2,5-dimethyl-2,5-di(tert-butyl peroxy)hexyne-3, n-butyl-4,4-bis-(tert-butyl peroxy)valerate, dicumyl peroxide, diacetyl peroxide, diethyl peroxide and hexafluorodimethyl peroxide. Further descriptions and examples of such compounds are given in an application by Yoshikazu Yamada and Lester F. M. Storm, entitled "Photographic Method," filed concurrently herewith.

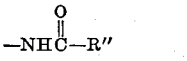
Still another type of desensitizer is a compound containing a substituted phenoxy group. It is preferred that the compound have the formula:



wherein m is an integer of from 1 to 3, R is a substituent selected from the group consisting of hydrogen, aliphatic groups, and aromatic groups and each R' is independently selected from aliphatic groups, aromatic groups, primary amines, secondary amines, tertiary amines, hydroxy and groups having the formula:



and



wherein each R'' is independently selected from aromatic and aliphatic groups. Examples of suitable substituents include :—CH_3, —C_2H_5, —C_3H_7, —C_4H_9, —C_5H_{11},



—C_6H_5, —OH, —OCH_3, —$OCH_2C_6H_5$, —OCH_2CH_2OH, —$NHC(O)CH_3$, —NH_2, —$C(O)OCH_3$, —$C(O)OC_6H_5$, and the like. Examples of useful compounds include p-cresol, m-cresol, o-amino-p-cresol, di-o-amino-p-cresol, hydroquinone, p-aminophenol, di-o-aminophenol, 2,4,6-triaminophenol, p-methylanisole, m-ethylanisole, hydroquinone monomethyl ether, hydroquinone dimethyl ether,

p-(benzyloxy)phenol,
1-tert-butyloxy-4-cyclopentyloxybenzene,
1-cyclopentyloxy-4-(5'-dodecyl)benzene,
3-isopropyl methyl salicylate,
1-benzyloxy-4-ethoxybenzene,
1-p-tert-amylbenzyloxy-3-sec-butylbenzene,
1,3-diamino-4-(3'-dodecoxy)benzene,
1-n-butoxy-4-(di-o-n-propyl-cyclohexoxy)benzene,
1-ethyl-2-hydroxymethyl-5-(p-n-hexylphenoxy)benzene,
1-tert-octoxy-4-phenoxybenzene,
2,5-di-tert-butylhydroquinone,
1-n-propoxy-3-p-tert-octyl-phenoxybenzene,
1-amino-4-n-butyl-2-methoxy-5-p-methylphenylbenzene,
p-dibenzyloxybenzene,
hydroquinone di-beta hydroxyethyl ether,
4-hydroxyacetanilide,

resorcinol monobenzoate, and the like. Further descriptions and examples of such compounds are given in an application by Yoshikazu Yamada and Lester F. M. Storm, entitled "Photographic Treatment," filed concurrently herewith.

Mixtures of the above desensitizers or with other desensitizers can also be used. Additionally, it is desirous to maintain the formulation in a somewhat basic condition, which can be accomplished by adding a small amount of base, e.g., sodium orthophosphate (Na_2HPO_4), sodium carbonate ($NaHCO_3$) or the like. Generally, from about 0.01 to about 1 part of base per hundred parts of continuous phase is sufficient for this purpose.

The desensitizer reacts with the photosensitive material to destroy its photosensitivity or by some means prevent the photo-reaction. It is, therefore, surprising that such compounds could be incorporated into the binder without seriously affecting the photosensitivity of the product.

especially when they are incorporated at the dispersion stage of preparation. The dispersion can be obtained by adding the photosensitive materials to the continuous phase followed by violent agitation. After substantial dispersion the desensitizer can be added. It is found that particularly good results are obtained if the photosensitive material or one of the components thereof is first dissolved in a solvent therefor, which may be only a small amount, and then dispersed in the continuous phase with consequent volatilization of solvent. In general, little agitation is needed when a solvent is so used. For example, when a combination of N-vinylcarbazole and carbon tetrabromide is used as the photosensitive material, the N-vinylcarbazole, the carbon tetrabromide, or both, can be dissolved in a small amount of acetone, added to a continuous phase of aqueous gelatin and stirred to form discrete globules of photosensitive material upon volatilization of acetone. The desensitizer can then be added. Products formed in such manner have substantially full photosensitivity until treated to be desensitized as will be described. The preparation of dispersions by the foregoing methods is described in detail in the Yoshikazu Yamada and Thomas H. Garland application Ser. No. 481,759, referred to above, the disclosure of which is hereby incorporated by reference.

The term "significant solubility" refers to a solubility that is adequate to provide a desensitizing amount of the compound in accordance with the method used. In general, the presence of any amount of desensitizing compound will diminish background darkening. A practical upper limit is about 15 weight percent of the continuous phase and generally about 0.1 weight percent will noticeably prevent such darkening. A preferred range is from about 0.5 to about 10 weight percent of the continuous phase.

As noted, one method of "activating" the desensitizer is to immerse the recording medium in a solvent in which the desensitizer has significant solubility and which can penetrate the continuous phase sufficiently to cause the desensitizer to intimately contact the photosensitive material. The choice of solvent depends on the particular desensitizer and continuous phase used. Solvents useful in this invention include water, ethanol, methanol, isopropanol, ether, acetone, benzene, octane, glycerol, m-dioxane, p-dioxane, chloroform, acetic acid, ethyl acetate, carbon tetrachloride, carbon disulfide, dimethylsulfide, mixtures thereof, and the like. In those cases where a particular desensitizer and a particular solvent is desired, but the solubility of the desensitizer in that solvent is not sufficient for purposes of this invention, then a second or even third solvent can be added; e.g., most of the desensitizers would have sufficient solubility in a mixture of acetone, ethanol or benzene; or methanol, ether and octane. The solvent ratios can be adjusted to afford proper solubility of the desensitizer. Where the continuous phase is water-penetrable, water may be used with a desensitizer having significant solubility therein. Immersion of the exposed film for from about a few seconds to about 5 minutes is generally satisfactory.

In a preferred embodiment, the continuous phase is water penetrable and, in this embodiment, a particularly suitable, and preferred, solvent comprises substantial amounts of (1) water and (2) an organic solvent having significant miscibility in water. The solubility of the various desensitizers in the common solvents are, for the most part, known or can be readily determined by simple methods known to the art. Here also, where the solubility of the desensitizer in a particularly desired solvent is not sufficient then a second or even third organic solvent can be added. The solvent ratios can be adjusted to afford proper solubility of the desensitizer in the aqueous solutions. The solvents enumerated above are useful in this preferred embodiment; acetone, the dioxanes and methanol are particularly suitable. For example, the desensitizers are generally significantly soluble in a miscible water-acetone solution. In general, from about 5 to about 90 volume percent of water, preferably at least 10 volume percent, is added to the organic solvent to form the miscible solution.

In another form of the invention, where the solvent contemplated is water, it can be supplied by incorporation into the binder of a water-releasing agent which releases water on the application of heat. Suitable water-releasing agents include: sodium sulfate decahydrate (Glauber's salt, which loses 10 molecules of water at 100° C.); sodium tetraborate decahydrate (borax, which loses 8 molecules of water at 60° C.); potassium aluminum sulfate (kalinite, which loses 9 molecules of water at 64.5° C.); sodium orthophosphate monohydrogen, both dodecahydrate and heptahydrate (each of which loses 5 molecules of water at 35° C. and 48° C., respectively); lithium nitrate trihydrate (which loses 2.5 molecules of water at 29.9° C.); and the like. Other materials that can be used include sodium triphosphate, sodium metasilicate, sodium alginate, sugar, and the like. It is preferable to use a more unstable hydrate, even containing less available water rather than hydrate which loses more water but at a higher temperature, so as to avoid prolonged heating of the photographic medium. Generally, from about 0.5 to about 15 weight percent of water as water-releasing agent can be added, based on the weight of the continuous phase.

In order to "activate" the desensitizer the recording medium containing the water-releasing agent can be heated to an appropriate temperature, e.g., by placing over a heated platen, or by exposure to infrared, or in any convenient manner, whereupon water is released which carries the desensitizer into intimate contact with the photosensitive material, rendering it photo-insensitive. If desired, a flexible transparent layer, resistant to penetration by water vapor, can be coated, or temporarily placed, over the recording medium to retain the water. Alternatively, the record can be heated with a moisture-impermeable sheet or flexible belt in contact with the exposed surface thereof.

Both negative-working and positive-working systems can be desensitized by the methods of this invention. In a negative-working system the photosensitive film is subjected to actinic light in an image-wise projection (or exposure) wherein light is projected through the transparent or translucent areas of the original image to corresponding areas which are "light-struck" on the photosensitive film; and these light-struck areas ultimately appear as the darker colored areas either as a result of direct print-out by the projected actinic light or as a result of subsequent heating or other treatment. The areas that are not "light-struck" during the image-wise initial exposure retain their photosensitivity (as in the case of non-light-struck silver halide areas in silver photography). The instant invention provides a method of desensitizing these areas so that they will not later develop or otherwise impair the desired image on the film during storage or subsequent use.

A particularly important use involved in the practice of the instant invention is in the diazo reproduction system. In such a system, a so-called diazo master or intermediate is prepared, by a negative-working mode, and this diazo intermediate is employed in conjunction with actinic near ultraviolet light to produce a succession of prints on diazo paper. In this use the diazo intermediate is subjected to repeated exposures of actinic near ultraviolet light and the instant invention provides a method for desensitizing previously unexposed areas of the diazo intermediate such that they will not develop or darken during such repeated exposure.

In a preferred embodiment of the invention, the photosensitive combination comprises at least two starting agents, (a) and (b), one of which, (b), is an organic halogen compound. In other preferred embodiments, the other starting agent, (a), is a nitrogen atom-containing compound having certain structural characteristics. Thus,

the process is particularly suitable when the nitrogen atom-containing compound used in the photosensitive combination has a nitrogen atom attached directly to at least one benzene ring, said benzene ring being free from carbon atom substitution in the position para to said nitrogen atom attachment. The process is also particularly suitable with nitrogen atom-containing compounds in which the nitrogen atom is a member of a heterocyclic ring. Still another type of nitrogen atom-containing compound with which the process is particularly useful is an N-vinyl compound.

It will be appreciated that there is substantial overlap between the above types of nitrogen-containing compounds and that the process is useful with photosensitive combinations that are formulated with nitrogen atom-containing compounds falling within one, two or even all three of the above terms; e.g., N-vinylcarbazole. It will also be appreciated that there is no generic term available in accepted chemical terminology that will effectively embrace all of the above types of nitrogen atom-containing compounds. It is merely important to note that photosensitive combinations containing a compound which has at least one of the above characteristics can be readily desensitized by the process of this invention. Photosensitive combinations containing compounds having more than one of the above characteristics lend themselves even better to the process. Examples of particularly effective nitrogen atom-containing compounds include N-vinylcarbazole, N-ethylcarbazole, indole and diphenylamine.

In another embodiment of this invention, the continuous phase, in which the photosensitive combination is dispersed, is water-penetrable. Such dispersions are discussed in detail in the above-mentioned Yamada and Garland application. Generally, the solid-film-forming component used to achieve a 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 derivatives of natural film-forming materials, any one of which in its conventional "water-soluble" form is used in the practice of the instant invention. In addition, synthetic water-soluble film-formers may also be used to particular advantage in the practice of the 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 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, carboxymethylcellulose, hydroxypropylmethylcellulose, etc. Essentially these materials are photo-insensitive and their principal function is that of forming the desired film which will retain the dispersed phase in discrete 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.

The use of nitrogen-containing compounds, particularly N-vinyl compounds, as part of the photosensitive combination is also described in detail in the above-mentioned Yamada and Garland application, as well as in several of the above-cited patents. When an N-vinyl compound is used in a non-solubilizing continuous phase, a complication arises which is solved by the present invention. In the environment of such a continuous phase the combination of organic halogen and N-vinyl compound is capable of undergoing two separate and distinct reactions on exposure to actinic light. In one reaction, in a negative-working mode, a colored material is formed in light-struck areas. In another reaction, in a positive-working mode, "colorless" polymer is thought to be first formed and subsequent blanket exposure to "'stronger" light, forming a color in the initially non-light-struck areas, yields a positive-working image. These two reactions are competitive, the kinetics of which say that one or the other will predominate depending on the wavelength-intensity-exposure of light, with the "colorless" polymer-forming reaction occurring with "weaker" light. The result is that in the negative-working mode in fringe areas of exposure, especially where the exposure is by projection or in contact exposure where the contact is not exact and uniform, some polymeric reaction takes place; not enough reaction to form a line of demarcation between the image and non-image areas, but enough to form a protective polymeric coating around globules of material that are still photosensitive and capable of forming colored material. This same effect is also found when reproducing tonal images in both the positive and negative-working modes; those areas of the image which receive only a slight exposure to light tend to form polymeric coatings around globules of still photosensitive materials. Even in those areas which are not exposed to imaging light, if a heat-treatment is used to bring out the image, some polymer may form as a result of previous slight light exposure during preparation of the coating and handling of the coated paper. Thus, if extreme measures are not taken to exclude all traces of actinic light during preparation of the coated paper, exposure to such traces of light may be sufficient, on subsequent heat-treatment, to form a polymeric coating around still photosensitive material. These fringe, tonal and partially "exposed" areas are particularly difficult to desensitize as the polymeric coating is impenetrable by most desensitizing materials. The desensitizing material must be capable of some penetration into the thin polymeric encapsulating coating without adversely reacting with the colored portions of the image. This invention provides methods for bringing desensitizing material into sufficiently intimate contact with such polymeric coating to allow it to penetrate therethrough and desensitize the film.

The processes of this invention are particularly suitable to desensitizing photosensitive combinations in which the organic halogen compound is selected from the group of compounds which produce free radicals or ions upon exposure to light of a suitable wavelength and in which there is present at least one active halogen selected from the group consisting of chlorine, bromine and iodine, attached to a carbon atom having not more than one hydrogen atom attached thereto. Compounds of this preferred group are described in U.S. Pats. 3,042,515, 3,042,516 and 3,042,517 and the descriptions and disclosures of these patents are hereby incorporated by reference. Examples of suitable organic halogen compounds include bromotrichloromethane, bromoform, iodoform, 1,2,3,4-tetrabromobutane, tribromacetic acid, 2,2,2 - tribromoethanol, tetrachlorotetrahydronaphthalene, 1,1,1 - tribromo-2 - methyl - 2 - propanol, carbon tetrachloride, p-dichlorobenzene, 4 - bromobiphenyl, 1 - chloro - 4 - nitrobenzene, p - bromoacetanilide, 2,4 - dichlorophenol, 1,2,3,4 - tetrachloroenzene, 1,2,3,5 - tetrachlorobenzene, brominated polystyrene, n - chlorosuccinimide, n - bromosuccinimide, 2 - chloroanthraquinone, tetrabromophenophthalein, tetrabromo - o - cresol, and the like. Particularly effective compounds include carbon tetrabromide, tribromochloromethane, dibromodichloromethane, pentabromoethane, hexachloroethane and hexabromoethane. In general, bromides are preferred.

Organic halogen compounds that are most particularby suitable with this invention have the formula

$$Br—C—(X)(X')(X'')_n(CY_3)_{1-n}$$

wherein X, X' and X'' are halogens, each Y is independently selected from the group consisting of halogen, hy-

drogen, hydroxy, methyl and methylol and n is selected from 0 and 1, such that when n is 0, X and X' are Br. Such componuds are more readily obtainable than others and yield better results.

In general, the weight ratios of the nitrogen-containing and halogen compound starting agents, (a) and (b) respectively, may vary widely, from a minimum practical weight ratio of (a):(b) of about 1:5 to a maximum ratio of about 50:1. If the proportion of halogen compound used is greater than that specificed in the foregoing range, it is ordinarily found that no practical advantage is obtained, and, in general, the weight ratio of (a):(b) used is not below about 1:2, except in special situations wherein losses of a halogen compound (e.g., carbon tetrabromide) are contemplated prior to the actual use. Also, if the amount of halogen compound used is less than the minimum just specified, the combination may be inadequately photosensitive. When a combination of two or more organic halogen compounds are used in the practice of the instant invention in a continuous water penetrable phase, it has been found that advantages are obtained ofttten in the use of weight ratios of 5:1 to about 20:1.

With regard to the relative weights of the solid compounds (a) and (b) in the dispersed phase compared to the solids (2) in the continuous phase, it is found that the solids weight ratio of (1):(2) is preferably about 1:2, but may range from a maximum practical ratio of about 5:1 to a practical minimum ratio of about 1:50. The continuous phase may be 100% "solids" in the sense that the entire system solidifies without any loss of water, but generally the solids-to-liquid ratio in the continuous phase is within the range of about 1:1 to about 1:30.

Preferably, also the dispersed phase particles are in the range of about 0.1 to about 20 microns, but the preferred range is about 0.3 to 10 microns, with an average particle size preferably of about 3 to 4 microns.

Further descriptions and examples of nitrogen atom-containing compounds, organic halogen compounds, dispersing mediums and other facets of compositions that can be desensitized by our process are given in the Yamada and Garland application referred to above, the disclosure of which is herein incorporated by reference.

The following examples illustrate various embodiments of this invention:

EXAMPLE 1

The following formulation was prepared and coated on baryta paper, 1.5 mil wet thickness:

Aqueous gelatin, 20%—50 ml.
N-vinylcarbazole—4 g.
Carbon tetrabromide—3.2 g.
Acetone—2 ml.
4-(p - dimethylaminostyryl)-quinoline (dye sensitizer—2 mg.
1.5% Tergitol 4—10 drops
5% chrome alum—5 drops
37% Formalin—2 drops
Sodium phosphate (Na_2HPO_4)—0.1 g.
Sodium metabisulfite—3 g.
Water—5 ml.

The Formalin and chrome alum act as gelatin hardeners; the Tergitol is a wetting agent. They were added to the gelatin, followed by the acetone solution of the N-vinylcarbazole and dye sensitizer, and then carbon tetrabromide. The mixture was stirred for 5 minutes to effect a dispersion of the N-vinylcarbazole and carbon tetrabromide. The sodium phosphate and sodium metabisulfite, in the 5 millimeters of water, was then added. The sodium phosphate serves to maintain the formulation somewhat basic. A control sheet of baryta paper was also coated with a similar formulation but without the sodium phosphate and sodium metabisulfite.

A 2.5 second contact exposure of both sheets, through a transparency, was made with a 275 watt G.E. sunlamp at 15.5 inches. followed by heating at 64° C. for about 10 seconds. A portion of the test paper received no furtther treatment. Another portion, along with the control, was immersed for 5 minutes in water. After drying, the strips were exposed to light from a fluorescent desk lamp at about 12 inches. After 16 hours of exposure, the background of the immersed test strip was strikingly lighter than the background of either tthe non-immersed test strip or the control strip.

EXAMPLE 2

A baryta sheet was coated with the formulation of Example 1 except that a 25 ml. water solution containing 1 g. of sodium carbonate ($NaHCO_3$) and 3 g. of sodium sulfite was used in place of the 5 ml. water solution of sodium phosphite and sodium metabisulfite.

A 60 second contact exposure, through a transparency was made with a 275 watt G.E. sunlamp at 15.5 inches, followed by heating at 64° C. for about 10 seconds. A portion of the test paper received no further treatment while another portion was immersed for 30 seconds in water. After drying, the strips were exposed to light from a fluorescent desk lamp at about 12 inches. After 16 hours of exposure, the background of the immersed test strip was essentially undarkened whereas the background of the non-immersed test strip darkened appreciably.

EXAMPLE 3

A dispersion was obtained and coated on baryta paper as in Example 1, but using the following formulation:

Aqueous gelatin, 20%—50 ml.
N-vinylcarbazole—4 g.
Carbon tetrabromide—3.2 g.
Acetone—1 ml.
Benezene—1 ml.
4-(p-dimethylaminostyryl)-quinoline (dye sensitizer)—2 mg.
1.5% Tergitol 4—10 drops
5% chrome alum—5 drops
37% Formalin—2 drops
Sodium metabisulfite—4 g.
Water—10 ml.

The N-vinylcarbazole and dye sensitizer were added with the acetone and benzene. A 2.5 second contact exposure, through a transparency, was made with a 275 watt G.E. sunlamp at 15.5 inches, followed by heating at 68° C. One-half of the test paper was wiped with water and then blotted; the other half was used as a control. The test paper was exposed to light from a fluorescent desk lamp at about 12 inches. After 16 hours of exposure, the background of that portion of the test paper that was wiped with water was very substantially lighter than the background of the control portion.

EXAMPLE 4

A formulation can be prepared following the procedure of Example 1, but which additionally contains 4 grams of lithium nitrate trihydrate, sodium orthophosphate dodecahydrate, borax, kalinite, or Glauber's salt. The sheet can be exposed as in Example 1 and then heated for 5 minutes at 35° C., 48° C., 64° C., 70° C. or 100° C., respectively, to yield records with backgrounds that resist darkening.

With each of the above formulations, prior to heating, an overcoating of Scotch tape, or other flexible, transparent, water-impermeable material, can be applied to retain moisture and enhance desensitization.

EXAMPLE 5

Following the procedure of Example 1, N-vinylcarbazole and carbon tetrabromide can be dispersed in continuous phases of casein, polyvinyl alcohol, gum arabic, starch, sodium carboxymethylcellulose or hydroxyethylcellulose

but otherwise formulated, coated, exposed and heated as in Example 1 to form negative mode image records. The sheets can be immersed in water for 30 seconds to desensitize the images thereon.

EXAMPLE 6

Following the procedure of Example 1, separate aqueous gelatin dispersions of N-vinylcarbazole and tribromochloromethane, pentabramoethane, hexachloroethane, bromotrichloromethane, p-dichlorobenzene, or 2,2,2-tribromoethanol can be otherwise formulated, coated, exposed and heated as in Example 1 to form negative mode image records. The papers can be immersed in water for 1 minute to desensitize the images.

EXAMPLE 7

Following the procedure of Example 1, separate aqueous gelatin dispersions of carbon tetrabromide and N-ethylcarbazole, indole, diphenylamine, benzylthiazoline or benzoxyazoline can be otherwise formulated, coated, exposed and heated as in Example 1 to form negative mode image records. The papers can be immersed for 2 minutes in water to desensitize the images.

EXAMPLE 8

Formulations can be prepared and coated on paper following the procedure of Example 1 except that 2 grams of acetone-sodium bisulfite, 4 grams of tert-butyl peroxide or 3 grams of hydroquinone monomethyl ether can be substituted for the sodium metabisulfite. The coated paper can be exposed and heated as in Example 1 to form negative mode images thereon. The papers can be immersed in a 50:50 volume percent solution of acetone:water, in ethanol, or in a 5:55:40 volume percent solution of benzene:methanol:water, respectively, to yield records with background resistant to darkening.

EXAMPLE 9

Following the formulation and procedure of Example 1, an aqueous gelatin dispersion of carbon tetrabromide and N-vinylcarbazole can be prepared and coated on baryta paper. The coated sheet can be exposed to an 8× projected positive Kodachrome image (e.g., with a Bell & Howell slide projector with a 300 watt lamp) at 3 feet, for 10 seconds, left at room temperature for 15 minutes to enable a colorless polymer image to form, exposed for 1 second with a sunlamp at 7.5 inches and then developed for 1 hour at 140° C. to obtain positive mode photographs. The photographs can be immersed for 1 minute in water to yield a record that is resistant to darkening.

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

We claim:

1. A photographic recording medium, comprising a solid film-forming hydrophilic binder on a support, and a photosensitive combination in said binder of:

(a) an organic halogen compound selected from the group of compounds which produce free radicals or ions upon exposure to light of a suitable wavelength and in which there is present at least one active halogen selected from the group consisting of chlorine, bromine, and iodine, attached to a carbon atom having not more than one hydrogen atom attached thereto, and

(b) an aromatic nitrogen atom-containing compound which is able to form a color with said halogen compound under the influence of actinic light, and

a stabilizer for the combination in said binder wherein image and background areas can be stabilized by applying to said medium a solvent for said stabilizer, said stabilizer being selected from the group consisting of:

(1) compounds having the formula

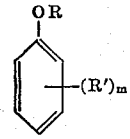
$$M_{3-v-w}(H)_wS_{1+2+x}O_{3+2x}$$

wherein x is selected from 0 and 1, M is selected from alkali metals and alkaline earth metals, v is the valance of the selected metal, and w is 0 when v is 2 and is selected from 0 and 1 when v is 1;

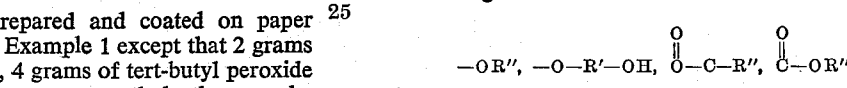
(2) alkali metal bisulfite-carbonyl complexes;

(3) compounds having a reactive oxygen atom and selected from (a) organic peroxides and hydroperoxides and (b) inorganic peroxides, perchlorates and perborates;

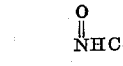
(4) compounds having the formula



wherein m is an integer of from 1 to 3, R is a substituent selected from the group consisting of hydrogen, aliphatic groups, and aromatic groups and each R′ is independently selected from aromatic groups, primary amines, secondary amines, teritary amines, hydroxy, groups having the formula:



and



wherein each R″ is independently selected from aromatic and aliphatic groups, and non-amine aliphatic groups; and

(5) mixtures thereof.

2. The recording medium of claim 1 in which said stabilizer is dispersed to the extent of at least 0.1 weight percent of said binder.

3. The recording medium of claim 1 wherein the nitrogen atom-containing compound is an N-vinyl compound.

4. The recording medium of claim 1 wherein the nitrogen atom-containing compound is selected from the group consisting of N-vinylcarbazole, N-ethylcarbazole, indole and diphenylamine.

5. The improvement of claim 1 wherein the binder is selected from the group consisting of gelatin, casein, polyvinyl alcohol, gum arabic, starch, alkali metal carboxymethylcellulose and hydroxyethylcellulose.

6. The recording medium of claim 1 wherein the binder additionally contains a water-releasing agent which releases water on the application of heat to serve as said solvent.

7. The recording medium of claim 6 wherein the binder is selected from the group consisting of gelatin, casein, polyvinyl alcohol, gum arabic, starch, alkali metal carboxymethylcellulose and hydroxyethylcellulose.

8. A process which comprises exposing to actinic light a photosensitive combination of:

(a) an organic halogen compound selected from the group of compounds which produce free radicals or ions upon exposure to light of a suitable wave length and in which there is present at least one active halogen selected from the group consisting of chlorine, bromine and iodine, attached to a carbon atom having not more than one hydrogen atom attached thereto, and

(b) an aromatic nitrogen atom-containing compound which is able to form a color with said halogen compound under the influence of actinic light,

said compounds being dispersed in a solid film-forming hydrophilic binder, with a stabilizer for image and background areas applying to said binder an aqueous solution of water-miscible organic solvent to thereby penetrate the binder and solubilize the stabilizer.

9. A method for preparing a photographic material which comprises dissolving in a solvent therefor at least one of

(a) an organic halogen compound selected from the group of compounds which produce free radicals or ions upon exposure to light of a suitable wave length and in which there is present at least one active halogen selected from the group consisting of chlorine, bromine and iodine, attached to a carbon atom having not more than one hydrogen atom attached thereto, and

(b) an aromatic nitrogen atom-containing compound which is able to form a color with said halogen compound under the influence of actinic light,

adding the solution and remaining components to a solid film-forming hydrophilic binder, forming a dispersion of photosensitive material in the binder upon volatilization of solvent, and adding to the binder a stabilizer for image and background areas, said stabilizer being selected from the group consisting of:

(1) compounds having the fomula

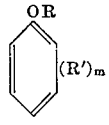
$$M_{3-v-w}(M)_wS_{1+x}0_{3+2x}$$

wherein x is selected from 0 and 1, M is selected from alkali metals and alkaline earth metals, v is the valence of the selected metal, and w is 0 when v is 2 and is selected from 0 and 1 when v is 1;

(2) alkali metal bisulfite-carbonyl complexes;

(3) compounds having a reactive oxygen atom and selected from (a) organic peroxides and hydroperoxides and (b) inorganic peroxides, perchlorates and perborates;

(4) compounds having the formula



wherein m is an integer of from 1 to 3, R is a substituent selected from the group consisting of hydrogen, aliphatic groups, and aromatic groups and each R′ is independently selected from aromatic groups, primary amines, secondary amines, tertiary amines, hydroxy, groups having the formula:

$$-OR'', -O-R'-OH, -\overset{O^-}{\overset{\|}{O}}-C-R'', \overset{O}{\overset{\|}{C}}-OR'' \text{ and } -\overset{O}{\overset{\|}{N}}HC-R''$$

wherein each R″ is independently selected from aromatic and aliphatic groups, and non-amine aliphatic groups; and

(5) mixtures thereof.

10. The recording medium of claim 1 in which said stabilizer is dispersed to the extent of at least 0.1 weight percent of said binder.

11. The recording medium of claim 4 in which said stabilizer is present in from about 0.1 to about 15 weight percent of said binder.

12. The process of claim 8 in which said stabilizer is dispersed to the extent of at least 0.1 weight percent of said binder.

13. The method of claim 9 in which said stabilizer is dispersed to the extent of at least 0.1 weight percent of said binder.

14. The recording medium of claim 1 wherein the organic halogen compound is selected from the group consisting of carbon tetrabromide, tribromochloromethane, dibromodichloromethane, tribromoacetic acid, pentabromoethane, hexachloroethane and hexabromoethane.

References Cited

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NORMAN G. TORCHIN, Primary Examiner

R. E. FICHTER, Assistant Examiner

U.S. Cl. X.R.

96—67, 90, 88

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,544,322 Dated December 1, 1970

Inventor(s) Yoshikazu Yamada et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 9, after "wherein" insert -- R --. Column line 62, "chloroenzene" should read -- chlorobenzene --. Colu 9, line 22, "oftten" should read -- often --. Column 11, line 75, the formula should appear as shown below"

$$M_{3-v-w}(H)_w S_{1+x} O_{3+2x}$$

Column 12, lines 26 and 27, the formula should appear as show below:

$$-OR'', \quad -O-R''-OH, \quad -O-\overset{\overset{O}{\|}}{C}-R'', \quad -\overset{\overset{O}{\|}}{C}-OR''$$

lines 30 and 31, the formula should appear as shown below:

$$\overset{\overset{O}{\|}}{NHC}-R''$$

Column 13, line 22, the formula should appear as shown below:

$$M_{3-v-w}(H)_w S_{1+x} O_{3+2x}$$

Column 14, lines 6 to 8, the formula should appear as shown b

$$-OR'', \quad -O-R''-OH, \quad -O-\overset{\overset{O}{\|}}{C}-R'', \quad -\overset{\overset{O}{\|}}{C}-OR'' \text{ and } \quad -\overset{\overset{O}{\|}}{NHC}-R''$$

Signed and sealed this 7th day of December 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Pat

USCOMM-DC 60376