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METHOD OF FORMING VESICULAR IMAGES WITH PEROXIDASE ACTIVE, IODIDE IONS GENERATING COMPOUNDS

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ABSTRACT OF THE DISCLOSURE

Catalase-active and/or peroxydase-active compounds are produced imagewise in a layer by exposing a layer which contains compounds capable of splitting off iodine or iodine ions upon exposure to actinic light, the visible image being formed by decomposition of peroxide compounds by the said catalase-active or peroxylase-active compounds.

This invention relates to a process for the production of photographic images by imagewise formation of catalase-active and/or peroxydase-active compounds by exposing a light-sensitive layer and decomposing peroxide compounds imagewise on these compounds, a visible image being formed either physically through the imagewise production of vesicles or chemically by a dye-forming imagewise reaction of the peroxid compounds with a suitable reaction component.

In addition to the conventional photographic processes in which light-sensitive silver halide emulsion layers are used, there are several other processes by which photographic images can be obtained. For example, vesicle images can be produced by using a photographic material containing a layer with a photodecomposable compound, for example diazo salts, dispersed in a binder. Upon imagewise exposure, the compound decomposes to liberate a gas at the light-struck areas. Upon subsequently heating the exposed material, the gas bubbles are allowed to expand and a vesicle image is formed. Since the vesicles scatter the light imagewise, these areas appear dark in transmitted light and light in reflected light. At the unexposed areas the processed layer is transparent.

Belgian Pat. No. 725,903 relates to the production of photographic images consisting of a silver image and a vesicular image superimposed upon the silver image. In this process, a silver image is initially produced in the usual way in the hydrophilic layer, which has a much lower silver density than conventional black-and-white images. The layer is then brought into contact with hydrogen peroxide which is decomposed at the finely distributed image silver to form vesicles of oxygen gas. It is thus possible to intensify the silver image to a very considerable extent, deep black images of extremely high contrast being obtained even in cases where layers of very low silver content are used. Although the quality of the photographic images obtained by this process is satisfactory, the process has its disadvantages insofar as initially a silver image has to be produced by conventional photographic development and then reacted with hydrogen peroxide in a second stage in order to produce the vesicle image in accordance with the silver image.

The other known photographic processes which do not use silver halide layers are quite generally of only limited

utility on account of their low light-sensitivity. In contrast to conventional silver halide photography, the quantum yield is relatively low in photographic systems of this kind because only one color-producing photochemical conversion of 1 molecule per absorbed quantum of light is possible. There is no evidence here of the intensifying effect obtained in the development of conventional exposed silver halide emulsion layers.

It is the object of the invention to provide photographic recording processes free from silver halide which yield black and white or colored images having excellent contrast by simple processing methods.

We now have found a process for the production of photographic images by exposure of a layer containing substances which form catalase active or peroxidase active compounds on exposure to light, followed by treatment with a peroxide compound to form a visible image, whereby the light-sensitive layer contains compounds which split off iodide or iodine ions on exposure to light.

Iodoform or derivatives thereof, i.e. compounds which contain a triiodomethyl group, are suitable, e.g. those of the following formula:

$$R—CI_3$$

wherein R represents (I) hydrogen, (II) a saturated or an olefinically unsaturated aliphatic group containing preferably up to 5 carbon atoms, such as methyl or ethyl, these radicals optionally containing substituents, e.g. a halogen atom or a phenyl group, (III) an aryl group, especially a radical of the phenyl series, (IV) carboxyl or esterified carboxyl, (V) carbamoyl, (VI) nitrile, (VII) aldehydo or (VIII) a heterocyclic radical.

The only condition which the compounds have to be met is that they must split off iodine or iodine ions on exposure to light. Although presumably iodine ions are the active component with respect to the catalase or peroxydase activity compounds which split off iodine are also effective since according to the redox equation iodine/iodine ions the ions are formed from iodine in the layer.

In particular suitable are iodine-substituted acetic acids such as di- or triiodo acetic acid or dervatives thereof such as salt esters or the like.

The images obtained are practically invisible when exposed to light in the usual manner. To render them visible, they are brought into contact with peroxide compounds, for example hydrogen peroxide. The peroxide compound is activated imagewise at the area where decomposition catalysts have formed.

Rendering the image visible by means of the activated peroxide may be effected by physical or by chemical means. Thus, the oxygen evolved can be rendered visible as a bubble image, e.g. by the process described in the abovementioned Belgian Pat. No. 725,903 which corresponds to U.S. patent application Ser. No. 783,420, now U.S. Pat. No. 3,615,491. Alternatively, the peroxide compound may be decomposed in the presence of reactants for a color-forming oxidation reaction. Processes of this type are described in U.S. Pat. application Ser. No. 881,610.

The layers according to the invention contain the light-sensitive triiodomethyl compounds preferably dispersed in a binding agent. Suitable binders are e.g. silica, polyvinyl acetate, partly saponified polyvinyl acetate, polyvinyl alcohol, cellulose esters such as cellulose acetate or cellulose butyrate, carboxymethyl cellulose or natural binders, especially proteins such as gelatin.

If desired, the triiodomethyl compounds may be added directly to the layer support by treating the support with a solution or dispersion of triiodomethyl compound.

The concentration of the triiodomethyl compounds in the light-sensitive material may vary within wide limits.

Concentrations of between 0.3 and 5 g./m.² of light-sensitive material have been found suitable. The optimum quantity for a given reproduction process can be determined by a few simple laboratory tests.

Suitable peroxide compounds for the process according to the invention are inorganic peroxide compounds, e.g. perborates, percarbonates or persulfates, but especially hydrogen peroxide. Organic peroxide compounds, e.g. benzoyl peroxide, may also be used. Hydrogen peroxide is used for preference owing to its effectiveness and ease with which it can be handled in the form of aqueous solutions.

The peroxide compound is preferably applied in the form of a solution. Hydrogen peroxide e.g. may also be applied in vapour form.

For the production of a vesicular image, the exposed layer is heated before or during the treatment with hydrogen peroxide. A vesicular image then forms at the areas where decomposition catalysts have been produced imagewise.

The strength of the vesicular image depends on the quantity of hydrogen peroxide used and on the quantity of decomposition nuclei formed. The heat treatment of the material for producing the visible vesicles should be as brief as possible. The temperature to be observed during this treatment depends on the properties of the binder. Satisfactory results can already be achieved at relatively low temperatures of about 60° C. to 70° C. but higher temperatures may also be employed if the softening point of the binder necessitates this. If the binder used is gelatin, which is the most suitable binder, it is advisable to carry out the operation in the presence of small quantities of water because this promotes swelling of the gelatin and hence bubble formation. The same also applies to other binders which swell in water.

According to a preferred embodiment, the exposed layer is subjected to a water vapour atmosphere at about 50° C. to 90° C. for a few seconds, e.g. 1.5 seconds, after the treatment with the hydrogen peroxide vapour. Vesicle formation, which sets in only slowly when hydrogen peroxide is used alone, then starts very rapidly. It has been found even more advantageous to expose the layer which has been treated with hydrogen peroxide to an alkaline water vapour atmosphere, pH values of between 8 and 12 being suitable. This can easily be achieved by adding small quantities of ammonia or vapours of volatile amines to the water vapour. The concentration of the alkaline additive is not critical. Quantities of between 0.1 to 5 volumes percent, preferably about 0.3 to 1 volume percent, have generally been found sufficient.

The visible image can be produced chemically by carrying out the treatment of the exposed layer with the peroxide compound in the presence of reagents for a color-forming oxidation reaction. Suitable processes have been described in U.S. patent application Ser. No. 881,610.

The formation of dye by peroxide also proceeds more rapidly if the layer has been subjected to a brief treatment with water vapor after the exposure to light.

Especially suitable for the oxidative dye formation are, of course, those reactants which produce very deeply colored compounds on oxidation with the catalytically activated peroxide compound.

The reactants may be organic compounds which themselves yield image dyes on oxidation, e.g. amino, hydroxy, or aminohydroxysubstituted isocyclic or heterocyclic aromatic compounds.

The following are mentioned as examples:

Phenol, aniline, pyrocatechol, resorcinol, hydroquinone, o-, m- and p-phenylenediamine, N,N-dimethyl-phenylenediamine, N,N-diethyl-phenylenediamine, N,N-ethyl-methyl-phenylenediamine, o-, m- and p-aminophenol, p-methylaminophenol, 2,4-diaminophenol-(1), 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 1,6,7-trihydroxynaphthalene, 1,2-diaminonaphthalene, 1,8-diaminonaphthalene, benzidine, 2,2'-diaminonaphthalene, 4,4'-diaminodiphenyl, 8-hydroxyquinoline, 5-hydroxyquinoline, 2-hydroxycarbazole, 1-phenylpyrazolone-(3), etc.

The amino, hydroxy or aminohydroxy compounds may also be substituted, e.g. with halogen atoms or alkyl, aryl, alkoxy, sulphonic acid, nitro, keto, carboxylic acid or carbonamide groups. The following are mentioned as examples:

2,5-dichloro-p-phenylene diamine, guaiacol, 4-methoxy-napthol-(1), 1-hydroxy-2-aminobenzene-4-sulphonic acid, 1-amino-2-hydroxybenzene-4-sulphonic acid, 3-amino-5-sulpho-salicyclic acid, 1,6,7-trihydroxy-naphthalene-3-sulphonic acid, benzidine-2,2'-disulphonic acid, benzidine-3,3'-disulphonic acid, 1,8-dihydroxy-naphthalene-disulphonic acid-(3,6) and 4-nitropyrocatechol.

In some cases, mixtures of several such compounds result in much stronger dye formation on oxidation than the individual components. Thus, for example a mixture of o-phenylene diamine and pyrocatechol results in stronger dye formation. Even compounds which on their own do not yield dyes on oxidation, e.g. tetrabromohydroquinone or tetrabromopyrocatechol, may reinforce dye formation when added to other hydroxy, amino or aminohydroxy compounds.

In the oxidation of the aromatic amino, hydroxy and/or aminohydroxy compounds, monomeric or polymeric dyes which are related to the quinone imines and azines are formed. Some examples of this oxidative dye formation are described by H. R. Schweizer, "Künstliche organische Farbenstoffe und ihre Zwischenprodukte," Springer—Verlag, Berlin—Gottingen—Heidelberg (1964), pp. 222, 275, 281 and 293; N. I. Woroshow, "Grundlagen der Synthese von Zwischenprodukten und Farbstoffen," Akademie—Verlag, Berlin (1966), pp. 703 to 789; A. Schaeffer, "Chemie der Farbestoffe und deren Anwendung," (Technische Fortschrittsberichte, vol. 60)., Theodor Steinkopff—Verlag, Dresden—Leipzig (1963), pp. 59 et seq.

Apart from the dye precursors there may, of course, also be used leuco dye compounds and vat dyes which can be oxidized to dyes. For examples of these see H. R. Schweizer, "Künstliche organische Farbstoffe und Zwischenprodukte," Springer—Verlag, Berlin—Gottingen—Heidelberg (1964), pp. 250 and 320.

Oxidisable organic compounds of the type which yield the image dye only in a secondary reaction with other compounds are also suitable for the process according to the invention. In principle, any reaction systems which yield dyes by oxidative coupling may be used. Reference may be made especially to the so-called color-forming photographic developers of the phenylenediamine or aminopyrazolone series (see e.g. C. E. K. Mees and T. H. James, "The Theory of the Photographic Process," 3rd edition, Macmillan Co., New York (1966), p. 382; J. R. Schweizer, "Künstliche organische Farbstoffe und ihre Zwischenprodukte," Springer—Verlag, Berlin—Gottingen—Heidelberg (1964), p. 295). Isocyclic and heterocyclic hydrazines may also be coupled oxidatively with suitable compounds to yield dyes (see e.g. H. Hünig et al., Angew. Chem. 70 (1958), 215; S. Hünig, Chimia 15 (1961) 133, and Angew. Chem. 74 (1962), 818). The dye-forming photographic developer substances are catalytically oxidized by the peroxide compounds at the imagewise distributed catalyst. Their oxidation products may then react with known photographic color couplers present at the same time to yield dyes. Any color couplers are suitable for this purpose, e.g. those of the phenol or naphthol series as cyan couplers, those of the indazole or pyrrazole series as magenta couplers and those of the benzoyl acetanilide series as yellow couplers.

EXAMPLE 1

Preparation of the light-sensitive material

A layer of the following casting solution is applied to a support of cellulose acetate:

50 ml. of a 2% solution of iodoform in ethanol
100 ml. of a 6% aqueous gelatin solution and
5 ml. of a 30% aqueous solution of formaldehyde.

Processing

The dry layer is exposed in a conventional sensitometer behind a grey step wedge (exposure time 10 seconds with a 100 watt lamp). The layer is then exposed for about one minute to a water vapour atmosphere at about 70° C. It is then washed for 10 minutes and exposed to daylight. A barely visible blue image of the original is obtained from this treatment.

The image is intensified by bathing the layer for 15 minutes in a bath of the following composition:

20 g. of N,N-diethyl-p-phenylenediaminosulfate
1 g. of pyrocatechol made up to 1 l. with water adjusted to pH 6 with Na_2CO_3
50 cc. of a 30% aqueous solution of hydrogen peroxide is added to this solution just before use.

A deep negative image of the original is obtained. The optical density of the image has been increased by a factor of about 100 by the intensifying bath. The layer is then washed for 15 minutes.

For formation of the vesicles, the exposed layer is treated for about 30 seconds with saturated hydrogen peroxide vapour at 70° C. and then exposed for ½ second to a water vapour atmosphere at 75° C. A very marked insensifying effect is immediately obtained by bubble formation, the density of one area, for example, which is 0.05 in the original image, being increased to 1.8 in focussed white light.

EXAMPLE 2

Preparation of the light-sensitive material

A layer of the following casting solution is applied onto a support of a polyester on the basis of polyethylene terephthalate:

50 ml. of a 2% solution of diiodoacetic acid in ethanol
100 ml. of a 6% aqueous solution of gelatin and
5 ml. of a 30% aqueous solution of formaldehyde.

Processing

The dried layer is exposed in a sensitometer through a test wedge customarily employed in the art (exposure time 10 seconds with a 500 watt lamp—type Osram HQA). The layer is then treated for 20 seconds with a saturated hydrogen peroxid atmosphere at a temperature of 70° C. and thereafter shortly heated to 90° C. A negative vesicle image is immediately formed, having a maximum density of 1.5 measured with focussed white light.

I claim:

1. A process for the production of photographic images by imagewise exposure to light of a layer containing a compound capable of forming upon exposure catalase-active or peroxidase-active compounds, followed by treatment with a peroxide wherein the said compound which splits off iodide or iodine ions on exposure to light has the following formula

$$R—CI_3$$

wherein

R represents (1) hydrogen, (2) a saturated or olefinically unsaturated alkyl group having one to five carbon atoms, (3) a radical of the phenyl series, (4) carboxyl or esterified carboxyl, (5) carbamoyl (6) nitrile or (7) aldehydo.

2. The process of claim **1**, wherein the light-sensitive layer contains iodoform.

3. The process of claim **1**, wherein the exposed image is treated with a peroxide compound which is decomposed at the imagewise produced catalase-active compounds with formation of oxygen, and the resulting gas is then expanded by heating of the layer to form a vesicle image.

4. The process of claim **1**, wherein mixtures of peroxides and hydrazines are used for producing the vesicle image.

5. The process of claim **1**, wherein the exposed layer is treated with hydrogen peroxide.

6. The process of claim **1**, wherein the treatment with peroxy compounds is carried out in the presence of color-forming photographic developers of the p-phenylenediamine series and photographic color couplers.

7. The process of claim **1**, wherein the components for the color-forming reaction are amino and/or hydroxy substituted compounds of the benzene or naphthalene series.

8. The process of claim **7**, wherein the components for the color-forming reaction are a hydroxy and/or amino substituted naphthalene and in addition a hydroxy substituted benzene.

9. The process of claim **7**, wherein the components for the color-forming reaction is a diamine from the benzene series and in addition to hydroxy substituted benzene or naphthalene.

10. The process of claim **7**, wherein the components for the color-forming reaction is a hydroxy substituted benzene or naphthalene, and in addition an aromatic hydrazine.

11. The process of claim **10**, wherein the aromatic hydrazine is a sulfo substituted phenyl hydrazine.

References Cited

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