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TREATMENT OF IMAGEWISE EXPOSED CATALASE ACTIVE OR PEROXIDASE ACTIVE ENZYME CONTAINING LAYER WITH PEROXIDE

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ABSTRACT OF THE DISCLOSURE

For the production of positive photographic images are used layers containing catalase active and/or peroxidase active enzymes, which are inactivated on exposure to light, thus becoming incapable of decomposing peroxide compounds. The peroxide compounds are used either to form an image of gas bubbles in the layer or to produce a dye image by a color-forming oxidation reaction. The sensitivity can largely be increased by substances which on exposure to light liberate halogen or cyanide, which latter products act as poisons for the enzymes.

The invention relates to a process for the production of photographic images by the imagewise inactivation of catalase active and/or peroxidase active enzymes by the exposure of a light-senstitvie layer and the imagewise decomposition of peroxide compounds by these enzymes, a visible image being formed by the imagewise production of gas bubbles either by physical means or by an imagewise color-forming reaction of the resulting oxygen with a suitable reactant.

Apart from the conventional photographic processes which make use of light-sensitive silver halide emulsion layers, numerous other processes have already become known for the production of photographic images. Thus, for example, bubble images can be produced by means of a photographic material comprising a layer which contains, dispersed in a binder, a compound which can be decomposed by light, e.g. a diazo salt. When such a material is exposed to form an image, the compound decomposes in areas corresponding to the image, a gas being liberated in the process. The gas bubbles expand as a result of the subsequent heating of the exposed material, and a bubble image is formed. Since the bubbles formed scatter the light imagewise, these areas appear dark in transmitted light and bright in reflected light. Most of the incident light in the unexposed areas of the layer is transmitted.

Belgian Pat. No. 725,903 also discloses the production of photographic images which consist of a silver image and a bubble image superimposed on the silver image. According to the process described there, a silver image is first produced in the conventional way in a hydrophilic layer, but this image has substantially less covering power than the conventionally produced black and white images. The layer is then brought into contact with hydrogen peroxide which decomposes imagewise in the areas containing the silver in a finely divided form to yield oxygen bubbles. The silver image is thus greatly intensified and deep black images with high contrast are obtained even when layers which have a very low silver content are used. Although the quality of the photographic images obtained by this process is satisfactory, the process is disadvantageous in that a silver image must first be produced by the usual conventional development, and this silver image is then reacted in a second stage with hydrogen peroxide so as to produce the bubble image which is superimposed on the silver image. The process is, therefore, rather complicated. Moreover, only negative images of the original can be obtained directly by this process.

The other known photographic processes which do not use silver halide layers are, generally speaking, of only slight practical importance owing to their low sensitivity to light. The reason for this is that in contrast to conventional silver halide photography, the quantum yield is low in these light sensitive systems since per absorbed light quantum only one molecule can be converted photochemically with color-forming. No multiplying effect occurs as in the development of conventionally exposed silver halide emulsion layers.

It is an object of the invention to evolve photographic direct positive production processes as far as possible free from silver which result in black and white or colored images with sufficient contrast by a simple processing technique.

A process for the production of positive photographic images by imagewise exposure of a layer followed by treatment with a peroxide compound with formation of a visible image has now been found in which a light-sensitive layer is used which contains uniformly distributed catalase active or peroxidase active enzymes which are inactivated imagewise by exposure with actinic light.

Practically any light-sensitive enzymes are suitable for the process according to the invention, i.e. enzymes which are inactivated by the action of light and which are capable of catalytic decomposition of peroxide compounds. Examples of such enzymes are catalase, peroxidase, haemoglobin and haemin.

The sensitivity of the layers to light can be substantially increased by the addition of compounds which, when exposed to light, split off products in areas corresponding to the image which act as poisons for the enzymes used according to the invention, i.e. such added compounds have an additional inactivation effect on these enzymes in the exposed areas. Since the catalase active or peroxidase active enzymes used according to the invention generally contain iron, bound in the form of a complex, the substances most suitable for this purpose are inorganic or organic substances liberating halogen or cyanide on exposure to light, which products are capable of inactivating these enzymes.

Suitable inorganic halides which split off halogen on exposure to light are, for example, silver halides such as silver chloride, silver bromide or silver iodide. Suitable organic halides include aliphatic halides containng a tribromo or triiodo group, e.g. iodoform, tribromoethanol or tribromoacetic acid or highly halogenated aromatic compounds, e.g. benzenes which are substituted in at least three positions on the nucleus with bromide or iodine, e.g. pentabromophenol. Compounds of this type have been described e.g. in British Pat. No. 957,192.

Inorganic and organic cyanide compounds which split off cyanide on exposure to light include in particular iron-(II) cyanides or iron-(III) cyanides or complex cyanides or complex cyanides or nitro-prussides described e.g. in the book by M. H. Ford-Smith "The Chemistry of Complex Cyanides," London, 1964. Suitable organic compounds include cyanides of triphenylmethane and its derivatives, e.g. those described by A. H. Spore, Trans. Faraday Soc. 57 (1961), 983.

The sensitivity can also be increased by the addition of compounds which generally act as electron acceptors. Chloranil or tetracyano-p-quinodimethane, for example, are suitable.

The light used for exposure is preferably blue or ultraviolet light.

The images obtained on exposure are practically invisible. They are brought into contact with peroxide compounds, such as hydrogen peroxide, to render them visible. The peroxide compound is decomposed imagewise in the areas where the enzymes have remained active. The process of rendering the image visible by decomposition of the peroxide may be either physical or chemical. For example, the oxygen evolved can be rendered visible as a bubble image, e.g. by the process described in the above-mentioned Belgian Pat. No. 725,903 which corresponds to U.S. Ser. No. 783,420. It is also possible to decompose the peroxide compounds in the presence of reactants for a color-forming oxidation reaction. Such processes are described in U.S. application Ser. No. 881,610.

The layers according to the invention preferably contain the light-sensitive enzymes, e.g. catalase or peroxidase, dispersed in a binder. Suitable binders are e.g. silica gel, 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.

On the other hand, the enzymes may be added directly to the layer support by treating the support with a solution or dispersion of the enzyme.

The concentration of the enzymes 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 to be suitable. The optimum quantity for any given reproduction process can be determined by a few simple laboratory tests.

Nearly the same applies to the quantity of additives used for increasing the sensitivity of the layers. Their concentration may also vary within wide limits. Quantities of between 0.2 and 5 g./m.^{2} have been found sufficient in this case, depending on the nature of the light-sensitive compounds. The optimum concentrations and optimum pair of compounds consisting of the enzyme and the substance which increases the sensitivity can easily be determined by the usual 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, are also suitable. Hydrogen peroxide is used for preference owing to its efficiency and the 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, for example, may also be applied in vapor form.

For the production of a bubble image, the exposed layer is heated with hydrogen peroxide during or after the treatment. A bubble image then forms imagewise in the areas where the enzymes have remained active.

The strength of the bubble 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 bubbles should be as short as possible. The temperature to be maintained during this treatment depends on the properties of the binder. Satisfactory results can already be obtained 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 requires this. If the binder used is gelatin, which is the substance preferably used, it is advisable to work in the presence of small quantities of water because this promotes swelling of the gelatin and hence the formation of bubbles. The same applies to other binders which swell in water.

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

The use of peroxides mixed with hydrazines has also been found very advantageous for the catalytic production of the bubble image; not only O_2 but a mixture of O_2 and N_2 is then formed.

The bubble images obtained can be stabilized against moisture by the processes described in U.S. application Ser. No. 885,984 and Ser. No. 887,392 as required.

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

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

These reactants may be organic compounds which themselves yield the image dye on oxidation, e.g. amino, hydroxy or aminohydroxy compounds of 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-diethylphenylenediamine,
N-ethyl-N-methyl-phenylene diamine,
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'-diaminodiphenyl,
4,4'-diaminodiphenyl,
8-hydroxyquinoline,
5-hydroxyquinoline,
2-hydroxycarbazole and 1-phenylpyrazolone-(3)

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

2,5-dichloro-p-phenylene diamine,
guaiacol,
4-methoxynaphthol-(1)
1-hydroxy-2-aminobenzene-4-sulfonic acid,
1-amino-2-hydroxybenzene-4-sulfonic acid,
3-amino-5-sulfo-salicyclic acid,
1,6,7-trihydroxynaphthalene-3-sulfonic acid,
benzidine-2,2'-disulfonic acid,
benzidine-3,3'-disulfonic acid,
1,8-dihydroxy-naphthalene-disulfonic acid-(3,6) and
4-nitro-pyrocatechol.

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

Oxidation of the aromatic amino, hydroxy and/or amino hydroxy compounds yields monomeric or polymeric dyes which are related to quinone imines and azines. Some examples of these oxidative dye formations are described in "Künstliche organiche Farbstoffe und ihre Zwischenproduket" by H. R. Schweizer, Springer-Verlag, Berlin-Göttingen-Heidelberg (1964), pages 222, 275, 281 and 293; in "Grundlagen der Synthese von Zwischenprodukten und Farbstoffen," by N. I. Woroshow; Akademie-Verlag, Berlin (1966) pages 703 to 789; in "Chemie der Farbstoffe und deren Anwendung" by A. Schaeffer, (Technische Fortschrittsberichte, volume 60), Theodor-Steinkopff-Verlag, Dresden-Leipzig (1963), pages 59 et seq.

In addition to dye precursor compounds there may, of course, also be used leuco dye compounds and vat dyes which are capable of being oxidized to dyes. For example of these see "Künstliche organische Farbstoffe und Zwischenprodukte," by H. R. Schweizer, Springer-Verlag, Berlin-Göttingen-Heidelberg (1964), pages 250 and 320.

Also suitable for the process according to the invention are those organic compounds capable of oxidation which yield the image dye only in a secondary reaction with other compounds. In principle, any reaction systems which yield dyes by oxidative coupling may be used, in particular 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), page 382; H. R. Schweizer; Künstliche organische Farbstoffe und ihre Zwischenprodukte," Springer-Verlag, Berlin-Göttinger-Heidelberg (1964), page 295). Isocyclic and heterocyclic hydrazines may also be coupled with suitable components to yield dyes by oxidation (see e.g. H. Hünig et al., Angewandte Chemie 70 (1958); S. Hünig, Chimia 15 (1961) 133 and Angewandte Chemie 74 (1962) 818). The color-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-forming couplers present at the same time to form dyes. Suitable color-forming couplers for this purpose are, for example, those of the phenol or naphthol series as cyan-forming couplers, those of the indazolone and pyrazolone series as magenta-forming couplers and those of the benzoyl acetanilide series as yellow-forming couplers.

The following examples illustrate the invention:

EXAMPLE 1

100 ml. of an aqueous 10% solution of a ferri-tribromoacetate complex compound (to split off halogen; prepared by suspending excess $Fe(OH)_3$ in 10% soduim tribromoacetate solution CBr_3-COONa and filtering from the excess $Fe(OH)_3$) are added in the dark to 1 l. of a 5% aqueous carboxymethyl cellulose solution. 100 ml. of a 0.1% aqueous peroxidase solution are then added.

The mixture is then poured in a thin layer onto a layer support of paper. It is then hardened by bathing it for one minute in 1% $Ba(NO_3)_2$ solution and dried.

The layer is exposed to blue light behind a grey step wedge (exposure time with a 200 watt lamp 10 seconds). It is then treated with the following solution:

20 g. of 1,7-dihydroxynaphthalene [1]
40 g. of phenylhydrazine sulfonic acid-(2) [1]
Water up to 1 l.; adjusted to pH 11 with Na_2CO_3
5 ml. of 30% aqueous H_2O_2 added just before use

[1] As dye forming reactants.

A black and white positive dye image of the original is obtained within 5 minutes.

Finally, the layer is washed for 15 minutes and dried.

EXAMPLE 2

20 ml. of a dispersion which contains 100 g. of silver bromide and 20 g. of carboxymethylcellulose per liter are added as light-sensitive halogen donor to 1 l. of an aqueous 2% carboxymethylcellulose solution in the dark. 100 ml. of an alkaline 1% aqueous haemoglobin solution are then added as peroxidase active catalyst. The mixture is poured out in a thin layer on a cellulose acetate support. It is then hardened as described in Example 1 and dried.

The layer is exposed to white light behind a grey step wedge (exposure time with a 200 watt lamp 1 second) and then treated with the following solution:

25 g. of 1-aminonaphthol-8-sulfonic acid-(4) [1]
10 g. of 2-ethoxyphenol [1]
Made up to 1 l. with water, adjusted to pH 8 with Na_2CO_3
100 ml. of 30% aqueous H_2O_2 added just before use.

[1] As dye forming reactants.

A black and white positive dye image of the original is obtained within 5 minutes at 20° C. Lastly, the layer is washed for 15 minutes and dried.

EXAMPLE 3

50 g. of tribromoethanol as halogen donor are dissolved in 2 l. of an aqueous 6% gelatin solution in the dark. 25 ml. of a 0.1% catalase solution are then added to the above solution. The mixture is then poured out as a thin layer on a layer support of polyethylene terephthalate (layer thickness approximately 15μ).

It is exposed in a sensitometer behind a grey step wedge as described in Example 1. The exposed material is then subjected to a water vapor atmosphere at about 50° C. for about ½ second.

For bubble formation, the layer is treated for about 30 seconds with saturated hydrogen peroxide vapor at 70° C. and then exposed for ½ second to a water vapor atmosphere at 75° C.

An image which has a density of 1.8 in collimated white light is obtained.

EXAMPLE 4

25 ml. of a 1% catalase solution are added to 1 l. of a 6% gelatin solution. 50 ml. of a saturated solution of Malachite green leucocyanide (nitrile of Malachite green; substance which splits off cyanide) are then emulsified in ethyl acetate in the dark with vigorous mixing. The solution is then cast and the material is processed to produce a bubble image, as described in Example 3.

We claim:

1. In a process for the production of positive photographic images by imagewise exposure of a light-sensitive layer, the steps of imagewise exposure of a light-sensitive layer containing uniformly distributed in a binding agent a catalase active or peroxidase active enzyme, which enzymes are capable of decomposing peroxide compounds and capable of being inactivated by exposure to actinic light, and treating the exposed layer with a peroxide compound.

2. In the process of claim 2 the light-sensitive layer contains compounds which split off halogen or cyanide on exposure to light.

3. In the process according to claim 1, the enzyme and peroxide is contained in a binder selected from the group consisting of gelatin, silica gel, polyvinyl acetate, partly saponified polyvinyl acetate, polyvinyl alcohol, and cellulose esters in which binder the peroxide is decomposed.

4. In the steps of the process according to claim **1** mixtures of peroxide compounds are used.

5. In the steps of the process according to claim **1**, producing a color-forming oxidation reaction by treating the exposed layer with peroxide compounds in the presence of a reagent selected from the group consisting of amino-, hydroxy-, and amino-hydroxy isocyclic aromatic compounds and amino-, hydroxy- and amino-hydroxy heterocyclic aromatic compounds.

6. In the process according to claim **1** the active enzyme selected from the group consisting of catalase, peroxidase, haemoglobin, and haenium.

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