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PHOTOGRAPHIC PROCESSES AND ELEMENTS

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ABSTRACT OF THE DISCLOSURE

The ability of an enzyme to hydrolyze protein can be altered upon exposure to light in the presence of a photosensitive material, thus permitting the production of photographic images. The enzyme can be converted from an active state to an inactive state, or vice versa. After exposure, development with water hydrolyzes and removes the protein from those areas where the enzyme is present in the active state.

This invention relates to novel photographic processes and to photosensitive compositions and elements for use in such processes. In a particular aspect it relates to a photographic process in which the ability of an enzyme to hydrolyze gelatin is employed in the production of an image.

Methods for the preparation of photographic images using silver compounds are well known. However, because of the cost and relative scarcity of silver, there is a constant search for photosensitive systems which will reduce the dependence of the photographic industry on this metal. Thus over a period of time, photographic methods based on compounds other than silver have been developed. Examples of such other methods include xerographic processes, electrophotographic processes, diazo processes, processes employing photopolymerization and photocrosslinking, etc. None of these systems, however, have been applied in as broad a range of uses as have the various silver systems. Furthermore, many of them have various processing or handling limitations which restrict or complicate their use. Such limitations include, sensitivity to only specific types of radiation, impermanence of the image produced, complicated equipment necessary to produce an image, numerous and complicated processing steps, etc. Thus the search for new photographic systems continues in order to avoid the limitations of prior art systems and to further reduce dependence upon silver systems.

It is an object of the present invention to provide novel photographic processes.

It is a further object of this invention to provide novel photographic processes which require a minimum of processing steps.

It is still a further object of this invention to provide novel photographic processes in which an image can be developed by simple processing steps.

It is another object of this invention to provide novel photosensitive compositions and elements for use in these processes.

These and other objects will be apparent to those skilled in the art upon studying the more detailed description of this invention which follows.

The compositions and processes of the present invention provide a useful method for the production of photographic images which is different from previously known processes. This process makes use of the ability of enzymes to attack and hydrolyze proteins, thereby breaking down the protein into smaller molecules which are readily soluble in water. It has now been found that this

ability of enzymes to hydrolyze protein can be used in photographic systems by employing light sensitive materials which are capable of altering the activity with which enzymes hydrolyze protein. Thus, according to the present invention there is provided a composition comprising a protein, an enzyme or enzymes which can exist in an active state in which they hydrolyze protein and in an inactive state in which they do not hydrolyze protein, and a photosensitive material or a group of photosensitive materials which in the presence of light convert the enzyme from one state to the other. On exposing this composition to light, the ability of the enzyme to hydrolyze the protein is altered, thus permitting one to establish a differentiation between exposed areas and non-exposed areas.

In one embodiment of the present invention an enzyme is present in its active state in which it is capable of hydrolyzing protein. In this embodiment, exposure to light converts the photosensitive material to a material which catalyzes the conversion of the enzyme to an inactive state in which it is not capable of hydrolyzing protein. Thus, in this embodiment, the protein in exposed areas is not hydrolyzed and remains intact while in unexposed areas it is hydrolyzed and may be removed easily.

In a second embodiment an enzyme is initially present in an inactive state in which it is not able to hydrolyze and degrade protein. On exposure to light the photosensitive material converts the enzyme to an active form in which it is capable of hydrolyzing protein. Thus, in this embodiment, the protein is hydrolyzed and can be removed from exposed areas, while in unexposed areas the protein remains intact.

A wide variety of proteins can be employed in the practice of the present invention. Such proteins include globulin, glutin, casein, keratin, etc. However, the preferred protein is gelatin, because of its availability, its transparency as well as its hydrophilic and film-forming characteristics.

The enzymes which are particularly useful in the practice of the present invention are the protease enzymes such as trypsin, papain, erepsin, pepsin, chymotrypsin, bromelin, rennin, etc., and various other bacterial proteases and fungus proteases. In their active form these enzymes actively hydrolyze proteins such as those mentioned above in the presence of water. However, these enzymes become inactive and can no longer hydrolyze protein when they are oxidized or when they are blocked, for example, by complexing or chelating them with other compounds.

The photosensitive materials that are used advantageously according to the present invention comprise a great number of compounds known up to now for playing the role of photosensitizers in photooxidation reactions. It seems that in the reactions of the present invention they play a different role, or different roles depending upon the embodiment in which they are used. However, the essential point is that under the action of light and in the presence of these photosensitive materials, the enzyme is converted to the desired form. Included among the photosensitive materials which are useful in the practice of the present invention are dyes such as fluorescein and its derivatives, such as rose bengal, erythrosin, eosin, etc., riboflavin, various thiazinic compounds, such as methylene blue, thionine, etc., derivatives of acridine, such as proflavine, acriflavine, etc. Particularly useful are photoreducible dyes according to the definition given by G. Oster which is described in the article by J. Spikes and B. Glad, in Photochem. and Photobiol. Journal 3, (1964) p. 479.

In a preferred embodiment of this invention in which the enzyme is present in its active state, there is provided a composition comprising gelatin, an enzyme, a photo-

sensitive dye, and optionally an acid chelating agent. When this composition is exposed to light in the presence of oxygen, the excited dye catalyzes the oxidation of the enzyme, causing it to go from its active form to an inactive form. In the exposed areas where the enzyme is in the inactive state, it is no longer capable of hydrolyzing gelatin, and thus the gelatin remains in its normal state, that is, essentially insoluble in water. In the unexposed areas, where the enzyme has not been oxidized, it remains active and readily hydrolyzes the gelatin in the presence of water. The products of this hydrolysis are soluble in water and thus can be easily removed from the non-hydrolyzed gelatin in the exposed areas. Such chelating agent, however, is not essential to the practice of the invention.

In those embodiments where the enzyme is initially present in its inactive form, the enzyme is typically rendered inactive by complexing it with, for example, a heavy metal salt such as mercuric chloride. Thus, in this embodiment a typical composition would comprise gelatin, an enzyme in the form of an inactive complex, and a photosensitive dye. On exposure to light the photosensitive dye is activated and liberates the enzyme from its inactive complex, converting it to an active form in which it is capable of hydrolyzing gelatin in the presence of water. Thus in the exposed areas the enzyme can hydrolyze the gelatin making it readily removable, while in the unexposed areas the enzyme remains as an inactive complex and is not capable of hydrolyzing the gelatin.

The relative amounts of protein, enzyme and photosensitive material present in the compositions of this invention can vary over a wide range, depending upon the particular combination of protein, enzyme and photosensitive material which is being employed. In general the enzyme should be present in an amount sufficient to completely hydrolyze the protein in those areas where the enzyme is present in an active state. Protein to enzyme weight ratios of from 70 to 30 through 99.5 to 0.5 are typical of operable ratios which may be employed in the practice of this invention. The photosensitive material should be present in an amount sufficient to sensitize the desired conversion of the enzyme. The photosensitive material can be present in amounts ranging from 1 to 100 percent by weight of the amount of enzyme present. Amounts in excess of this can be used, but generally are not necessary. A preferred range of amount of photosensitive is from 2 to 30 percent by weight of the amount of enzyme present.

Elements useful according to the present invention usually comprise a support for the photosensitive composition. A flexible support is preferred, but any suitable surface for supporting the photosensitive composition may be used. Examples of suitable flexible supports include: papers, polyethylene-coated papers, polypropylene-coated papers, glassine, vegetable parchments, metal foils, polystyrene films, cellulose nitrate films, cellulose acetate films, cellulose acetate butyrate films, cellulose acetate propionate films, and polyester films such as poly(ethylene terephthalate).

The photosensitive composition is coated on the support in any well-known manner, such as extrusion coating, hopper coating, dip coating, doctor blade coating, etc. The photosensitive composition can be coated on the support in a wide range of thicknesses. For example, coating thicknesses in the range of 0.1 to 100 microns are suitable.

In those embodiments where the enzyme is present initially in its active state it is preferred that the enzyme be the last component added to the composition, and that after coating the element be dried as rapidly as possible. These precautions, plus storage of the element under conditions of low humidity reduces the possibility of a portion of the protein being hydrolyzed prior to exposure and development.

In the practice of this invention, the photosensitive element is typically exposed to actinic light behind a negative for a period sufficient to effect the desired change in the activity of the enzyme. Thus, there is obtained an element in which image areas are differentiated from non-image areas by the ability or inability of enzyme to hydrolyze protein in these respective areas. This in effect is a latent image. The image can be developed by contacting the element with water, such as by washing to hydrolyze the protein. The temperature of the water used for hydrolysis can vary over a wide range depending upon the particular protein being employed. In the case of gelatin, it is preferred that the water be at room temperature or lukewarm, such as 15–40° C.

Agitation during washing aids removal of the hydrolyzed protein from the element, although the degraded protein may be removed by other means such as swabbing or gentle scraping. After removal of the hydroylzed protein a relief image appears on the element. This image will be a positive or a negative of the image copied depending upon whether the enzyme was initially present in the element in its inactive state or its active state. The contrast of this relief image can be enhanced or augmented by dyeing it with a compatible colorant. The protein image can be rendered less fragile by hardening by procedures well known in the photographic art. A suitable hardening procedure consists of tanning the protein image; a formaldehyde solution being useful for tanning gelatin. The dyeing step can be combined with the hardening step by incorporating the colorant in the tanning solution.

The invention is further illustrated by the following examples of preferred embodiments thereof.

EXAMPLE 1

This example illustrates the inactivation of an enzyme by light. A series of compositions are prepared from the following materials in the order indicated:

	Ml.
Papain (1%)	1
Photosensitive colorant (0.05%)	1
Ethylenediamine tetraacetic acid (0.5%)	1
Gelatin (7%)	50

The compositions are then brought to a pH of 5. Three different compositions are used each containing a different photosensitive colorant or dye. The dyes are methylene blue, proflavin, and rose bengal. The compositions are exposed for 2 minutes in the presence of oxygen to actinic radiation with a 250-watt lamp at a distance of 20 centimeters from the composition. In each case it is observed that the papain enzyme is rendered completely inactive and that it is incapable of hydrolyzing the gelatin. Raw papain containing 80% of active material is utilized.

EXAMPLE 2

The following aqueous composition is coated in the absence of actinic radiation on a cellulose triacetate support:

	Ml.
Gelatin (7%)	250
Rose bengal (0.05%)	50
Ethylenediamine tetraacetic acid (0.5%)	50
Papain (1%)	50

In preparing the above composition, the papain is added last and the composition is coated immediately on the support. The element is dried as rapidly as possible so as to prevent the papain from hydrolyzing the gelatin. The photosensitive element is then exposed through a negative for 2 minutes to actinic radiation with a 250-watt lamp at a distance of 20 centimeters. The exposed film is then dipped in water maintained at 28–30° C. and after about five minutes a relief image appears on the film, a gelatin image forming in the exposed areas. The image is hardened with a dilute solution of formaldehyde to which has been added a colorant for the gelatin in order

to augment the contrast in the image. There is obtained a film which has a hard gelatin image.

EXAMPLE 3

On three separate subbed cellulose triacetate supports there is coated the photosensitive compositions prepared as described in Example 1, except that the ethylenediaminetetraacetic acid is omitted. This coating operation is performed rapidly, and followed by quickly setting and drying it in an atmosphere of low humidity at a temperature of 35° C. The films are then exposed for 15 seconds through a negative to actinic radiation with a 100-watt lamp at a distance of 20 centimeters. The exposed films are developed in lukewarm water (e.g. 30° C.), and after a short period of time an image appears. The gelatin is not removed in the exposed areas while in the unexposed areas the gelatin is hydrolyzed and removed in the course of development. The films are then placed in a coloring solution of Diazo-B-Blue (color index No. 24410), and a colored image is obtained.

EXAMPLE 4

100 mg. of papain in powder form with a titer of 80, is dispersed in 10 ml. of a solution of mercuric chloride at 0.25 g. per liter. The mixture is stirred for 30 min., then the solution is filtered. Then, the solution obtained is poured, in darkness, into 14.3 ml. of a 7% aqueous solution of a pigskin gelatin, at 40° C., containing 30 mg. of dissolved erythrosin. 25 ml. of distilled water is then added, and the mixture is coated at a thickness of 50μ on a subbed cellulose triacetate film by means of a squeegee. Then the coating is dried at room temperature and protected from light. The photosensitive film which is obtained is then exposed behind an original at a distance of 21 cm. from a 200-watt tungsten-filament lamp, for 15 min. The exposed product is treated at about 20° C. in the following manner:

	Min.
Washing in distilled water	10
Tanning with a 10% aqueous formaldehyde bath	1
Dyeing with a 0.2% aqueous bath of pure Diazo-B-Blue (C.I. No. 24,410)	3
Final rinsing in a large amount of flowing water	3

A positive image, dyed blue, is thus obtained from the original. The formaldehyde tanning bath is not indispensible for obtaining the image, but makes possible the preparation of tanned gelatin images which are less fragile than images of untanned gelatin.

EXAMPLE 5

Example 4 is repeated, but using a pigskin gelatin which has a viscosity of 6.1 centipoises at 38° C. at a concentration of 6.16%. Similar results are obtained after 30 min. of exposure.

EXAMPLE 6

Example 4 is repeated, but using a pigskin gelatin having a viscosity of 13 centipoises at 38° C. at a concentration of 6.16%. Good images are obtained after 15 minutes of exposure.

EXAMPLE 7

Example 4 is repeated, except that the erythrosin is replaced with 24 mg. of eosin. The results obtained are quite similar to those obtained in Example 4.

EXAMPLE 8

Example 4 is repeated, but the erythrosin is replaced with 34 mg. of rose bengal and exposure is for 30 minutes. A positive image of the original is obtained.

EXAMPLE 9

On a subbed cellulose triacetate support, at a 50μ thickness, the following aqueous composition, prepared in darkness, is coated:

Papain—150 mg.
Mercuric chloride—15 ml. of a 0.25% solution
Gelatin—14.3 ml. of a 7% solution
Erythrosin—30 mg.
Distilled water—20 ml.

It is exposed as in Example 4, but for 60 minutes and, after treatment, as in Example 4, a positive image of the original is obtained.

EXAMPLE 10

Example 9 is repeated, but in using 50 mg. of papain, 5 ml. of the mercuric chloride solution used in Example 9, 30 mg. of erythrosin and 30 ml. of distilled water, a positive image of the original is obtained.

Although the invention has been described in considerable detail with reference to preferred embodiments thereof, modifications and variations can be effected within the spirit and scope of the invention as described above and as defined in the following claims.

We claim:

1. An element comprising a support and a layer of a composition comprising a protein, an enzyme which can exist in an active state in which it hydrolyzes protein, and in an inactive state in which it does not hydrolyze protein, and a photosensitive material which upon exposure to light converts the enzyme from one of said states to the other of said states.

2. An element as defined in claim **1** wherein the protein is gelatin.

3. An element as defined in claim **2** wherein the photosensitive material is a dye selected from the group consisting of fluorescein compounds, thiazinic derivatives and acridine derivatives.

4. An element as defined in claim **3** wherein the dye is rose bengal.

5. An element as defined in claim **2** wherein the enzyme is present in its active state, and is selected from the group consisting of papain, trypsin, erepsin, and pepsin.

6. An element as defined in claim **5** wherein the photosensitive composition includes an acid chelating agent.

7. An element as defined in claim **5** wherein the enzyme is papain and the photosensitive material is rose bengal.

8. An element as defined in claim **2** wherein the enzyme is present in its inactive state as a complex of a heavy metal salt.

9. An element as defined in claim **8** wherein the enzyme is present as a complex with mercuric chloride and is selected from the group consisting of papain, trypsin, erepsin and pepsin.

10. An element as defined in claim **7** wherein the enzyme is a complex of papain with mercuric chloride, and the photosensitive material is rose bengal.

11. An element comprising a support and a layer of a composition comprising gelatin, a protease enzyme which can exist in an active state in which it hydrolyzes gelatin and in an inactive state in which it does not hydrolyze gelatin, and a photosensitive dye which upon exposure to light converts said enzyme from one of said states to the other of said states, said dye being selected from the group consisting of fluorescein compounds, thiazinic derivatives and acridine derivatives.

12. A photosensitive composition comprising a protein, an enzyme which can exist in an active state in which it hydrolyzes protein, and in an inactive state in which it does not hydrolyze protein, and a photosensitive material which upon exposure to light converts the enzyme from one of said states to the other of said states.

13. A composition as defined in claim **12** wherein the enzyme is present in its active state, and the composition includes an acid chelating agent.

14. A composition as defined in claim 12 wherein the enzyme is present in its inactive state as a complex with a metallic salt.

15. A process for producing a photographic image which comprises the steps of (1) exposing to light an element comprising a support having coated thereon a composition comprising a protein, an enzyme capable of existing in an active state in which it can hydrolyze the protein, and in an inactive state in which it cannot hydrolyze the protein, and a photosensitive dye which on exposure to light converts the enzyme from one of said states to the other of said states, and (2) contacting the exposed element with water to hydrolyze and remove the protein from those areas in which the enzyme is present in its active state, thus yielding a relief image.

16. A process as defined in claim 15 wherein the protein is gelatin.

17. A process as defined in claim 16 wherein after washing the gelatin is hardened by tanning.

18. A process as defined in claim 16 wherein after washing the contrast between exposed and unexposed areas is augmented by dyeing one of said areas with a compatible colorant.

19. A process as defined in claim 17 wherein the tanning solution contains a compatible colorant which augments contrast between exposed and unexposed areas of the element.

References Cited

West and Todd, Textbook of Biochemistry, Macmillan, N.Y. (1961), pages 394–395, 410–413, 424 (Table 11.7).

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