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[33] **Japan**
[31] **43/27900**

[56]

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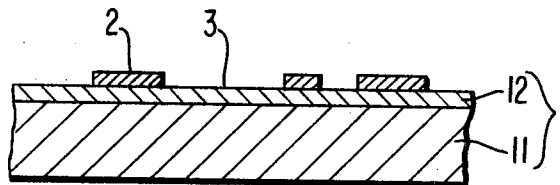
[54] **ELECTROPHOTOGRAPHIC LIQUID DEVELOPER**
HAVING A PROTEOLYTIC ENZYME
5 Claims, 3 Drawing Figs.

[52] U.S. Cl. **252/62.1,**
96/1

[51] Int. Cl. **G03g 9/04**

[50] Field of Search **252/62.1;**
195/3

ABSTRACT: An electrophotographic liquid developer useful in converting an electrostatic latent image formed on an insulating surface into a visible or material image, comprising a nonpolar, highly insulating carrier liquid and a toner powder which contains therein or absorbs a finely divided proteolytic enzyme, or consists of a finely divided proteolytic enzyme, having a suitable polarity of charge dispersed in said carrier liquid.



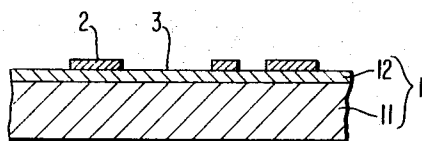


FIG. 1

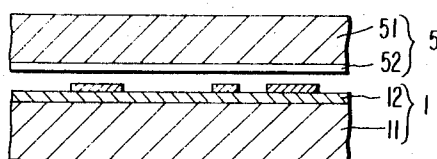


FIG. 2

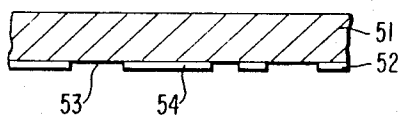


FIG. 3

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ELECTROPHOTOGRAPHIC LIQUID DEVELOPER HAVING A PROTEOLYTIC ENZYME

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a novel composition for an electrophotographic liquid developer.

2. Description of the Prior Art

A liquid developer for use in electrophotography generally comprises a highly insulating, nonpolar organic liquid and electrostatically charged, finely divided particles dispersed therein, the former being sometimes referred to as the carrier liquid and the latter as the toner.

Among a variety of developing methods used in electrophotography, the liquid development method, or electrophoretic development, is known to be capable of producing a developed image of the highest resolution and satisfactory tone reproduction mainly because the toner particles are stably dispersed in the carrier liquid as a far finer unit than in other developing materials, and because they deposit on a latent electrostatic image in the form of dispersed unit particles and not in agglomerated form.

Many modified image-recording processes have been devised in which specific functionalities are imparted to the electrophotographic toner material. A typical example is given by a formation of an etch-resist pattern by electrophotography utilizing a photoconductive pigment/resin coating containing a curable resinous material and a catalytic developer which can promote or initiate the curing reaction of the resin.

SUMMARY OF THE INVENTION

The present invention relates to electrophotography wherein a toner is employed having a specific functionality. A liquid developer of the present invention is characterized in that it contains a toner which comprises a proteolytic enzyme.

Once a toner image is obtained on a photoconductive coating of an electrophotographic light-sensitive member employing such a liquid developer, a master or matrix for printing or image duplication can be prepared by a quite simple operation.

Therefore, the present invention provides an electrophotographic liquid developer useful in converting an electrostatic latent image formed on an insulating surface into a visible or material image, comprising a nonpolar, highly insulating carrier liquid and a toner powder which contains therein or absorbs a finely divided proteolytic enzyme, or consists of a finely divided proteolytic enzyme, having a suitable polarity of charge dispersed in said carrier liquid. The above-mentioned carrier liquid has an electric resistance or more than 10^9 ohm-cm. and a specific dielectric constant of less than 3.5.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 to 3 illustrate schematic cross-sectional views of electrophotographic and matrix materials, showing procedures to produce a gelatin matrix employing a developer of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

A typical procedure will be described in detail hereafter referring to the accompanying drawings.

FIG. 1 is a cross-sectional view of an electrophotographic recording member carrying on its light-sensitive surface a coating having a toner image containing a proteolytic enzyme (which will be hereinafter abbreviated as protease). In this figure, 1 designates an electrophotographic recording member which comprises an electrically conductive support 11, and a photoconductive insulating layer 12. The support is generally made of a material having a specific resistance lower than about 10^9 ohm-cm., suitable material including paper, metal plate, metallized paper or plastic films, etc. The photoconductive insulating layer 12 may be of any type known in the art of electrophotography.

Typical examples of the photoconductive insulating coating are an amorphous selenium layer, zinc oxide/resin mixture layers, organic photoconductive layers, etc. A toner image 2 contains therein a protease. The area 3 is not covered with the toner. The toner image may be provided by means of a typical xerographic process, which comprises charging in darkness of the photoconductive layer, image exposure of the charged surface, and development of the thus-produced latent electrostatic image by depositing the toner in sequence. Other processes may also be employed to produce a toner image in the present invention, such as a Kallman process utilizing photoconductive aftereffect, or a thermoxerographic one in which an imagewise thermal radiation is used in place of visible light radiation.

FIG. 2 illustrates a procedure of matrix formation whereby the toner image-bearing recording member 1 is kept in an intimate contact with a matrix material 5 in the presence of sufficient moisture. The matrix material 5 comprises a water-resistant backing 51 and a gelatin layer 52 coated thereon and having a thickness of several microns. Suitable materials for backing 51 include films made of cellulose triacetate, polycarbonate, polyethyleneterephthalate, etc. or water-resistant paper. The gelatin layer 52 may be colorless, but, for convenience of operation, it may also be intentionally dyed or made opaque by suitable materials.

Since the activity of the enzyme in the toner upon the gelatin is very weak when the gelatin is substantially dried, and since the activity is also dependent on the pH value of the moisture, the gelatin layer 52 may preferably be moistened, prior to contact with the enzyme image, and, at the same time, treated to have a desirable pH value. The decomposition of gelatin is enhanced by heating the assembly to a temperature of from about 40° to 50° C.

FIG. 3 illustrates the matrix material after having been subjected to imagewise decomposition by the enzyme pattern followed by washing with cold water. The enzyme containing toner has decomposed the corresponding area 53 of the gelatin layer during the intimate contact, while the other area 54 remains unchanged, thus leaving a relief image. The relief image thus produced may be used for a conventional dye transfer process or other photographic processes. An optically positive toner image will produce an optically negative dye image through a dye transfer process. Accordingly, in general cases, one may provide electrophotographically an optically positive image from which a positive dye image will be produced. As for special arrangements of the toner image, a toner image of the proper arrangement will give the final print of the same arrangement, since the gelatin relief is the mirror image relative to the toner image.

Advantages of the present method will be summarized as follows:

1. Since the protease can work well on hardened gelatin, the relief preparation is accompanied with less difficulty as well as markedly decreased loss compared with those encountered in the relief preparation through tanning development.
2. Electrophotographic procedures requiring a toner image are simple, time saving, and economical.
3. Enzymes retain their catalytic activities when maintained in a dried condition, and likewise when they are dispersed in a nonpolar, carrier liquid which contains extremely little moisture.
4. A very short processing period is required for relief preparation.

The enzymes which are employed in the present invention include those which originate in animals, such as pepsin, cathepsin, rennin, trypsin, chymotrypsin; plant protease such as bromelain, papain, chymopapain, ficin, asclepain; and bacteriolytic protease such as *Bacillus subtilis* protease, etc.

Some of these enzymes, such as papain, and ficin, require activators such as cystine, glutathione, or ascorbic acid for exertion of enzymatic activity. Such activators may be added to the liquid developer of the present invention.

Since enzymes have polypeptide chains in their molecular structure, they acquire an electrostatic charge of positive polarity when dispersed in an insulating carrier liquid. Therefore, fine particles of enzymes will be attracted to the charged area when applied on an electrostatic latent image of positive polarity, accomplishing attraction development, while, on the other hand, a repulsive or reversal development will occur with a latent image of negative polarity.

In a preferred embodiment of the present invention, a liquid developer will be formulated so that the toner particles will mainly comprise a water-insoluble charge controlling resinous material and an enzyme as a minor ingredient in order to minimize lateral diffusion of the enzyme during the intimate contact with a moistened gelatin coating. Since examples of charge controlling resinous material for use in electrophotographic liquid developers are described in many patent specifications (for example, U.S. Pat. No. 2,907,675; U.S. Pat. No. 3,078,231 and U.S. Pat. No. 3,198,649) or literature references already published, they will not be illustrated here. When an enzyme is incorporated in a charge controlling resinous material, the time required for decomposition of gelatin will be somewhat lengthened. This is because the enzyme dissolution is retarded because it is encapsulated in the water-insoluble material. This problem can be solved by modifying the preparation method of the developers. An improved method for developer preparation is recommended in which a proteolytic enzyme is incorporated into a carrier liquid. Since, in general, the amount of the former is far less than that of the latter, the electrophoretic characteristic of the resulting dispersion will be primarily determined by the property of the latter, i.e., the resinous material. For example, in the case where a small amount of protease powder which will acquire a positive charge in a carrier liquid, is dispersed together with a large amount of polyvinylchloride powder having a negative polarity, a liquid developer will result containing a toner of negative polarity, since the protease particles are absorbed on the surface of the polyvinylchloride powder by coulomb interaction between charges of opposite polarities. The size of the resinous toner particles containing or absorbing a protease is from 0.05 to 10 microns. The amount of the protease in the resinous toner is more than 0.05 percent by weight of the resinous toner, and more particularly from 0.2 to 5 percent by weight. The amount of the protease in the developer ranges from 0.000005 to 0.25 percent by weight based on the carrier liquid.

The toners contained in the liquid developer of the present invention may consist of only finely divided protease particles, the size of the protease particles being from 0.01 microns to 5 microns.

In general, suitable concentration of resinous toner in the liquid developer of the present invention is from 0.01 to 5 percent by weight of the carrier liquid. However, when the liquid developer having a large amount of protease particles contained therein is employed, a lack of image, namely a spot, is formed in the obtained gelatin relief.

Other ingredients such as unsaturated vegetable oils which impart a self-fixing property to the developed image may also be incorporated in the developers. Stabilizers for enzymes may also be added. Further, it is suitable to stabilize the liquid developer by dissolving in the liquid developer a carrier liquid soluble resin such as long oil varnish, an alkyl resin, or a resin-modified phenol formaldehyde resin.

The above-mentioned carrier liquid soluble component may be added to the liquid developer of the present invention in an amount of from 0.2 to 30 percent by weight of the carrier liquid.

Suitable materials for the carrier liquid of the developers include aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, polymethyl siloxane, etc.

The present invention will be further illustrated by the following examples which are intended to be nonlimiting in nature.

EXAMPLE 1

One hundred mg. of a proteolytic enzyme purchased from Kaken Chemical Co., (located at Komagome, Bunkyo-ku, Tokyo) under the trade name "Pronase P" was added into 150 ml. of purified kerosene, and subjected to supersonic agitation for several minutes. A homogeneous dispersion resulted. The dispersion was applied onto a zinc oxide electrophotographic paper, which had been charged and image-exposed, bearing an electrostatic latent image of negative polarity. Since the Pronase particles are positively charged, attraction development was accomplished.

EXAMPLE 2

Into a mixture comprising 100 ml. of cyclohexane and 50 ml. of kerosene was dispersed 100 mg. of the same enzyme as was described in example 1. Then, 1 g. of resin-modified phenol-formaldehyde resin was dissolved in the liquid. In the dispersion the enzyme particles proved to assume a charge of positive polarity.

EXAMPLE 3

A liquid developer containing fine particles of polyvinyl chloride having a diameter of from 0.1 to 0.5 micron was prepared by supersonic agitation. This developer contained 0.2 percent of the toner by weight. To 1000 ml. of this developer was added 100 mg. of Pronase under supersonic agitation. A zinc oxide electrophotographic paper, bearing thereon an electrostatic latent image, was immersed in the resulting dispersion, whereby a repulsive development was accomplished due to the negatively charged dispersed particles. It was shown by the preparation of a gelatin relief employing this developed image that Pronase particles had deposited together with polyvinyl chloride particles on the sheet.

EXAMPLE 4

This example differs from example 3 only by the fact that 300 mg. of concentrated pepsin powder (dilution ratio 1:100) was substituted for the Pronase. Again it was proved that pepsin had been associated with polyvinyl chloride during electrophoretic behavior. Preparation of a gelatin relief was carried out in a low pH condition so as to raise the activity of the pepsin.

What is claimed is:

1. An electrophotographic liquid developer useful in converting an electrostatic latent image formed on an insulating surface into a visible or material image, comprising a non-polar, highly insulating, carrier liquid having an electric resistance of greater than 10^9 ohm-cm. and a specified dielectric constant of less than 3.5, and a resinous toner powder ranging in size from 0.05 to 10 microns, said toner powder containing therein a finely divided proteolytic enzyme at a level of from 0.000005 percent to 0.25 percent by weight based on the carrier liquid, having a suitable polarity of charge dispersed in said carrier liquid.

2. An electrophotographic liquid developer as in claim 1, wherein said toner powder has absorbed therein a finely divided proteolytic enzyme.

3. An electrophotographic liquid developer as in claim 1, wherein said toner consists of a finely divided, charge-controlling resinous material containing a finely divided proteolytic enzyme.

4. An electrophotographic liquid developer as in claim 1, wherein said proteolytic enzyme is a member selected from the group consisting of pepsin, cathepsin, rennin, trypsin, hymotrypsin, bromelin, papin, chmspapin, ficin, asclepain, and *Bacillus subtilis* protease.

5. An electrophotographic liquid developer useful in converting an electrostatic latent image formed on an insulating surface into a visible or material image, comprising a non-polar, highly insulating, carrier liquid having an electric resistance of greater than 10^9 ohm-cm. and a specified dielectric constant of less than 3.5, and a resinous toner powder, said

toner powder ranging in size from 0.01 to 5 microns and being a finely divided proteolytic enzyme at a level of from 0.000005 percent to 0.25 percent by weight based on the carrier liquid, having a suitable polarity of charge dispersed in said carrier liquid.

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