

United States Patent [19]

Tamai et al.

[11] 3,839,028

[45] Oct. 1, 1974

[54] IMAGING PROCESS

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[21] Appl. No.: **214,141**

[30] Foreign Application Priority Data

Dec. 30, 1970 Japan..... 45-123038

[52] U.S. Cl....96/1 R, 96/35.1, 101/463, 117/17.5, 117/37 R, 204/18 PC, 250/317, 346/1

[51] Int. Cl. **G03g 13/22, G03c 5/08**

[58] Field of Search 204/2, 18 PC; 96/27, 35, 96/35.1, 1, 1.5; 101/450, 463; 117/201, 8, 34, 17.5, 37; 250/65.1; 161/6

[56] References Cited

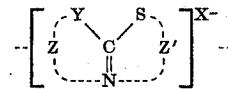
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3,632,484 1/1972 Richards 204/2

Primary Examiner—Charles E. Van Horn
Assistant Examiner—M. B. Wittenberg
Attorney, Agent, or Firm—J. T. Martin; Gerald J. Ferguson, Jr.; Joseph J. Baker

[57] ABSTRACT

An imaging process which comprises selectively eliminating or adding imagewise at least a component of a system consisting of a hydrophilic macromolecular substance, a metal ion, a compound capable of maintaining the pH value of the surrounding medium at not less than 8 when brought into contact with water or a substance which provides such a compound when decomposed and a compound represented by the following general formula:



wherein

Z, Z' : non-metallic atoms constituting heterocyclic structure,
X : anion, and
Y : atom belonging to the group 6B of the periodic table,
from or to the system thereby obtaining an image containing water-insoluble macromolecular substance.

24 Claims, 14 Drawing Figures

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FIG. 1

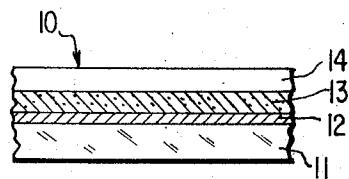


FIG. 2

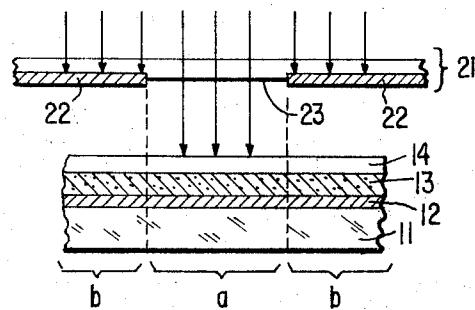
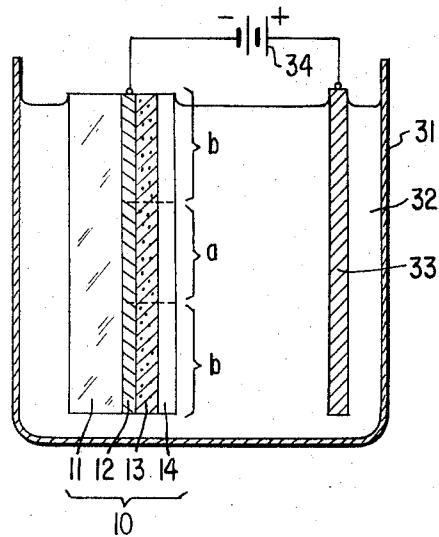


FIG. 3



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FIG. 4

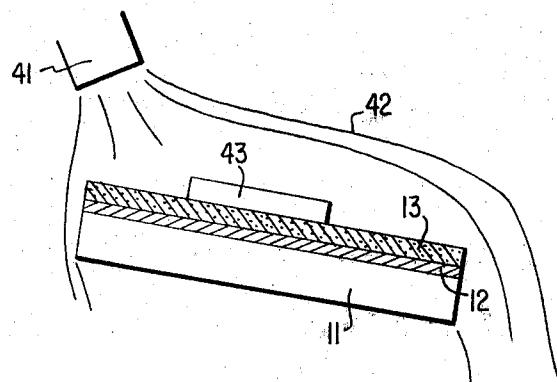


FIG. 5

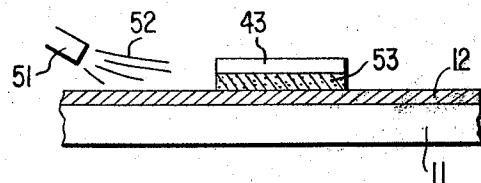


FIG. 6

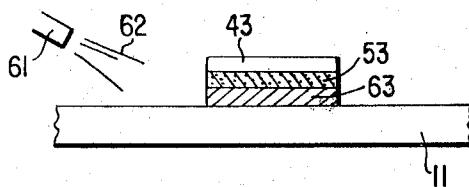
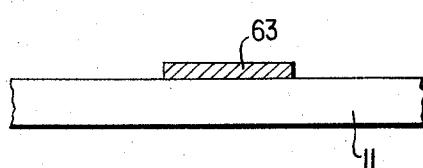


FIG. 7



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FIG. 8

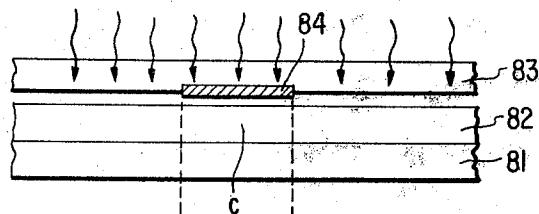


FIG. 9

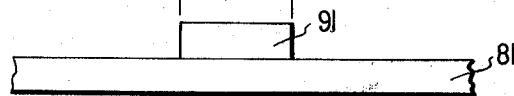


FIG. 10

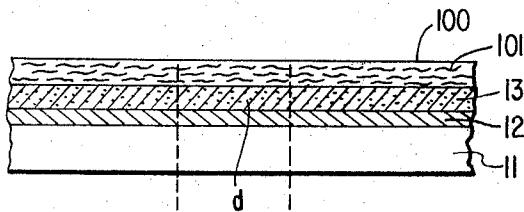


FIG. 11



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FIG. 12

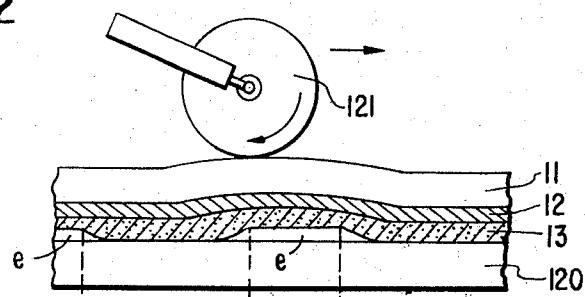


FIG. 13

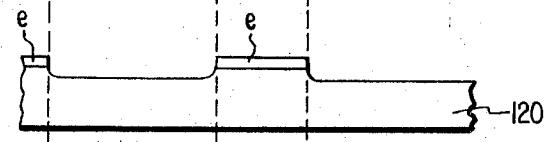
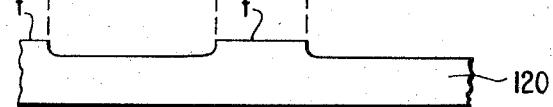


FIG. 14



1
IMAGING PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an imaging process, and particularly to an imaging process utilizing the reaction of compounds capable of effecting a specific reaction with macromolecular substances.

2. Description of the Prior Art

The formation of images consisting of macromolecular substances by tanning development of the matrix film with gelatin and silver halide is known. A process utilizing a silver halide and an addition polymerizable substance is already disclosed for example in U.S. Pat. No. 3,194,661. Also U.S. Pat. No. 2,927,002 disclosed a process not utilizing silver halide, in which addition polymerizable substance and photoactivatable addition polymerization initiator are combinedly used with cellulose derivative. Besides various photosensitive resins are already disclosed in number of patents and made commercially available, such as Dycril from DuPont, Nyloprint from Badisch Anilin und Soda Fabrieken, A.P.R. from Asahi Chemical, T.P.R. from Tokyo Oka Industries, K.P.R. from Eastman Kodak, etc. The earliest composition known in this field is the combination of polyvinyl-alcohol with bichromate. The above-mentioned processes or the materials for obtaining macromolecular image have been associated with drawbacks such as delicate handling, insufficient shelf life, low sensitivity, etc.

Furthermore, the process of obtaining macromolecular image on the surface of electrolytic photosensitive layer is already disclosed in U.S. Pat. No. 3,106,516 according to the process, a hardener or softener pattern obtained by an electrolytic photographic method is pressed against a sheet having a macromolecular substrate for an after-treatment to obtain a macromolecular image. The process, however, involves a transfer step, so that the obtained image lacks in sharpness. Also U.S. Pat. No. 3,172,827 discloses a process in which polyamide resin contained in the electrolytic bath is insolubilized imagewise on the photosensitive layer by means of pH increase at the cathode during electrolysis.

It has been found, however, that by the process it is difficult to obtain an image having sufficient mechanical strength and solvent proof property.

Furthermore, the processes for forming polymer image by the passage of electric current are already disclosed for example in U.S. Pat. No. 3,409,431, U.S. Pat. No. 3,436,215, British Pat. No. 1,178,552 and British Pat. No. 1,136,209. These processes employ polymerizable monomer and therefore pose frequent difficulty in shelf life.

Furthermore, a process of controlling the enzymatic activity by the passage of electric current is disclosed in Japanese Pat. No. 549,870, but this process requires considerable caution to obtain stable gelatin image.

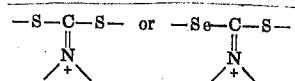
Also the use of polymer as toner in electrophotographic process is already known. Finely powdered polymer obtained by crushing polymer material for example by jet mill is mixed with carrier particles to obtain electrophotographic cascade developer. Also electrophotographic liquid developer can be prepared by dispersing powdered polymer in an insulative liquid incapable of dissolving said polymer. Thus polymer

image can be obtained by developing electrostatic latent image with such developers. In general liquid developer gives better image quality than with dry developer. It has been considerably difficult, however, to obtain stable dispersion when the polymer is hydrophilic. For example, the processes disclosed in German Pat. OLS Nos. 2,004,817 and 2,005,180 show the drawback of requiring complicated procedure to prepare the developer. On the other hand dry developer containing 10 toner consisting of finely powdered hydrophilic polymer has been associated with the drawback of easily absorbing moisture to aggregate.

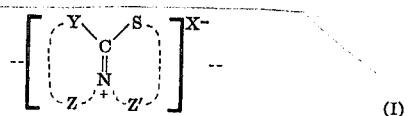
Furthermore, it is well known that protein is insolubilized against water by means of various organic compounds, for example, aldehydes such as formalin, chlorotriazine, mucochromic acid, etc. It is known as well that protein is insolubilized by certain metal ion such as chromium ion. These compounds have been important in photographic industry, but the insolubilizing effect thereof is excessively slow or the stability of compounds themselves is not sufficient.

SUMMARY OF THE INVENTION

As the result of extensive investigations on reaction 25 conditions between hydrophilic macromolecular substances and various organic compounds, the present inventors have found that cyclic compounds containing the following bonding:



35 are capable of extremely rapidly solidifying hydrophilic macromolecular substances such as gelatin, at a pH value not lower than 8 and in the presence of metal ions. On the basis of this finding, the present inventors have reached a novel and useful imaging process which 40 comprises selectively eliminating or adding imagewise at least a compound of a system consisting of (A) hydrophilic macromolecular substance, (B) a metal ion belonging to groups 6A, 7A, 8, 1B or 2B of the periodic table (periodic table of IUPAC Comptes Rendus XXIII 45 Conference, p. 183, 1965), including chromium, manganese, iron, cobalt, nickel, copper, zinc, palladium, silver, cadmium, mercury, gold, molybdenum, tungsten, rhodium, ruthenium, rhodium, osmium, iridium, and platinum. (C) a compound capable of maintaining the pH value of water or a water-containing solvent at not less than 8 when brought into contact therewith or 50 a substance which provides such a compound when decomposed, and (D) a compound represented by the following general formula:



60 wherein Z and Z' represent a group of non-metallic atoms necessary to complete a heterocyclic structure; X represents an anion; and Y represents an atom belonging to group 6B of the periodic table, from or to 65 said system thereby obtaining an image containing water-insoluble macromolecular substance.

In this invention, the imagewise elimination or addition of component(s) of said system can be realized by various methods such as electrolytic electroconductive graphic process, electrophotographic processes, electroconductive recording processes, thermal recording processes, etc., or naturally by direct manual addition.

According to our invention, all four components must be present to form an image. Thus, it is clear that the image can be formed only at those portions where all components are present. For example, by contacting imagewise a gelatin layer (A) containing metal ion (B) and compound (D) with alkali solution (C), an image is formed by an addition process. On the other hand, in the system wherein all four components are present, one (or more) component may be eliminated imagewise. The latter is an eliminating process. Thus, the present invention may be carried out by eliminating at least one component from a system containing all of four components, (A), (B), (C), and (D). For example, the alkali (C) may be removed by adding an acid.

One preferable embodiment according to this purpose comprises (1) introducing into a system containing all of four components a substance which can release a compound acting as an acid by action of electromagnetic radiation, (2) imagewise exposing the system to an electromagnetic radiation to form an acid which neutralizes an alkali (that is removes alkali (C)) whereby an image is formed.

As the substance releasing the acid, organic halogen compounds may be used such as carbon tetrabromide, iodoform, hexachlorethan, polyvinylchloride and polyvinylidene-chloride. These compounds release a halogen radical upon exposure to electromagnetic radiation. The halogen radical catches a hydrogen atom from the system to form hydrogen halide which is a strong acid.

The image obtainable according to this invention is composed of a macromolecular substance and therefore can be utilized not only for ordinary recording and copying but also for preparing printing plate for spirit printing, offset printing, intaglio printing, letterpress printing, and mimeographic printing and preparing gelatin reliefs for dye transfer prints. Also the image obtainable according to this invention can be applied to the preparation of printed circuits, braille printing and transparencies for overhead projection. Also, according to the invention it is possible to produce electron beam recording materials.

In summary, the main object of this invention is to provide a macromolecular image and processes for forming the image.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a magnified cross sectional view of an embodiment of a photosensitive element adapted for use in this invention.

FIG. 2 shows a method of imagewise exposure of a photosensitive element.

FIG. 3 shows a method of electrolytic treatment applied to the photosensitive element after said imagewise exposure.

FIG. 4 shows the method of treatment with warm water on the photosensitive element after said electrolytic treatment.

FIG. 5 shows the method of removing the photoconductive layer from the photosensitive element after said treatment with warm water.

FIG. 6 shows the method of removing electroconductive layer.

FIG. 7 shows the metallic image obtained according to this invention.

FIG. 8 shows the method of thermographic copying according to this invention.

10 FIG. 9 shows the polymer image obtained by thermographic copying according to this invention.

FIG. 10 shows the mimeographic plate material according to this invention.

15 FIG. 11 shows the mimeographic plate prepared according to this invention.

FIG. 12 shows the method of transferring the polymer image obtained according to this invention onto a metallic plate.

20 FIG. 13 shows the method of etching the surface of metallic plate after said transfer.

FIG. 14 shows the printing plate obtained by removing the polymer image after said etching.

DETAILED DESCRIPTION OF THE INVENTION

25 The hydrophilic macromolecular substance (A) employed in this invention preferably contains a primary amino radical. Such macromolecular substance can be, for example, a natural protein containing lysine or arginine as amino acid units such as gelatin, glue, casein, 30 aloumin, protamin, globrin, etc. Also, various synthetic macromolecular substances containing primary amino radicals can be used for this purpose.

35 As examples of such synthetic macromolecular substances there are polymers obtained from amine-containing monomers, i.e. aminoethylvinylether (Liebigs Annalen der Chemie, 601, 81 (1956)); aminostyrene (Chemical Abstract 34, 389 (1940)); p-aminophenylvinyl-ether (Chemical Abstract 56, 12,781 (1962) or vinylbenzylamine (Berichte der Deutschen 40 Chemischen Gesellschaft 56, 2,154 (1923)). Copolymers containing the above-mentioned monomers can be utilized for this purpose.

45 Also employable are polymers obtained from macromolecular reactions such as between polymethyl acrylate and diamines (Die Macromolecular Chemie, 22, 31 (1957)) or the reduction of polyacrylamide by lithium aluminum hydride (The Journal of Organic Chemistry, 26, 1274 (1961)). Polymerized primary amines such as polyvinylamines, polylysine, etc. fall within this category.

The following table shows examples of synthetic polymers containing primary amino radical:

	1	2	3	4	5	6	7
Polymer, mol. percent:							
$-\text{CH}_2-\text{CH}-$ CONH ₂	70	90	80	95	90	80	98
$-\text{CH}_2-\text{CH}-$ COOCH ₃	27	8	18	4	9	19
$-\text{CH}_2-\text{CH}-$ CONH(CH ₂) _n NH ₂	3	2	2	1	1	1
$-\text{CH}_2-\text{CH}-$ CH ₂ NH ₂	2	2	2	2	2	2
n	3	3	3	3	2	2
$[\eta]$, * 30°, 1% NaCl.....	2.60	1.85	1.88	1.88	1.54	1.62	3.07

*Intrinsic viscosity at 30° C. in 1% aqueous solution sodium chloride.

These polymers can be prepared by conventional processes, as shown by the following examples.

Synthesis of polymer 1

76 g of a copolymer of methyl acrylate (30 mol. percent) and acrylamide (70 mol. percent) was dissolved in 2 l. of water, and 25 g of 1,3-propane diamine added under agitation. The system was kept at 40° - 50°C for 4 hours. The aqueous solution of polymer containing primary amine thus obtained was subjected to dialysis with distilled water for one night and then freeze-dried. The polymer obtained was found, by titration with 0.05 N hydrochloric acid, to contain amino radicals in an amount of 3 mol. percent. The polymer showed an intrinsic viscosity $[\eta]_{1\% NaCl}^{30^\circ} = 260$.

The copolymers 2 to 6 are prepared repeating the method of synthesis of Polymer 1 except the starting copolymers and the reaction conditions shown in the following table.

Polymer	2	3	4	5	6
Starting copolymer composition					
acrylamide	90	80	95	90	80
methylacrylate	10	20	5	10	20
Reaction time (hour)	4	4	3	3	3
Reaction temperature (°C)	40-50	40-50	30-40	30-40	30-40

Synthesis of polymer 7

14.2 g (0.2 mol.) of powdered polyacrylamide (molecular weight about 100,000) was dispersed in 1 l. of dioxane, 4 g of lithium aluminum hydride and heated for 6 hours under reflux (ca. 100°C) and agitation.

Gradually there was added to the reaction mixture 5 percent hydrochloric acid to inactivate unreacted lithium aluminum hydride. Then dioxane was removed until the reaction product became solid. The solid was dissolved in 100 ml. of a 5 percent aqueous solution of sodium hydroxide to obtain a homogeneous aqueous solution of the polymer. The solution was placed in a cellophane bag, subjected to dialysis overnight in distilled water and then freeze-dried. Yield: 13.0 g, $[\eta]_{1\% NaCl}^{30^\circ} = 3.07$. Titration with 0.05N hydrochloric acid showed that the content of amino radicals was 2 mol. percent.

The macromolecular substance (A) to be employed in this invention is preferred to be soluble in cold or hot water or in a water-containing mixed solvent where there is 20 percent by volume of water, the solvents typically being the alcohols, ketones, dioxanes, etc. Macromolecular substance (A) can be associated with other macromolecular substances miscible with substance (A), for example, polyacrylic acid, polyvinyl alcohol, polyacrylamide, polyvinylbenzene sulfonic acid, polyamide, etc. or copolymers thereof where the ratio of the macromolecular substance (A) must be to the other macromolecular substances is typically greater than 0.1.

The minimum number of primary amino groups in the polymer is two (2). The preferable amount may be more than 2 per 1,000 of recurring units of the polymers. There is no restriction as to the position of the primary amino group in the polymer. The terminal groups of the polymer are not necessarily a substantial part of the invention.

The metallic ion (B) to be employed in this invention is preferred to be an ion of an element belonging to groups 6A, 7A, 8 1B or 2B of the periodic table, such as chromium, manganese, iron, cobalt, nickel, copper, zinc, palladium, silver, cadmium mercury, gold, etc., and particularly suitable for this purpose are the ions of manganese, cobalt, nickel, copper, zinc, silver and cadmium. These metal ions can be employed in the imaging process as a water-soluble salt, or as a salt sparingly soluble in the case of the above-mentioned particularly preferred metals. A complex salt, of course, naturally meets this purpose. These metal ions can be used in this invention singly or in combination. Furthermore, it is possible to use various compounds capable of generating the above-mentioned ions by decomposition, oxidation, reduction, etc. The ions are particularly preferred to be divalent, but ions of other valence states such as Cr⁺⁺⁺ or Fe⁺⁺⁺ can be employed, depending on the

conditions for forming the image. Some kinds of the aforementioned metal ions can per se render gelatin insoluble, but the effect attained according to the invention is far stronger than due to these ions alone. Also, it is found that the quantity of metal ions necessary to render the gelatin insoluble is considerable less as compared to the case of using only metal ions alone.

Compound (c) to be employed in this invention can be an organic or inorganic compound which becomes alkaline when brought into contact with water or water-containing solvent, for example, illustrative inorganics are oxides, hydroxides, carbonates, etc., of alkali metals and alkali earth metals. Water-soluble organic bases such as piperidine, morpholine, triethanolamine can also be employed for this purpose. Further, preferred is the use of compounds capable of rendering the medium alkaline upon being decomposed by an electric current or by heating. An example of such a compound is water, which renders the area in proximity to a cathode alkaline when electrolyzed. Urea, thiourea, ammonium carbonate, etc., can be employed in this invention since these compounds are easily decomposed by heating to render the atmosphere alkaline due to generated ammonia. It is also possible to use substrates capable of generating a basic material under electron beam radiation, for example, polyacrylamide, poly-N-methylol acrylamide, polyvinylpyridine, polyvinylimidazole or copolymers containing said compounds. In this invention a pH value not lower than 8 is required for the formation of the image.

Compound (D) represented by the foregoing general formula (I) is found to be particularly effective when Y therein stands for sulfur or selenium atom. As X, such an ions as Cl⁻, Br⁻, I⁻, ClO₄⁻, HSO₄⁻ and



may be mentioned.

Reaction between the polymer, the compound and the metal ion is thought to occur as follows: a primary amino group of the polymer reacts with compound (D) and bonds to a carbon atom which is attached to $-S$ and $-Y$ to form a Schiff base and simultaneously ring Z' is opened to form an $-SH$ group. (Ring Z is usually remained). Then two $-SH$ groups thus formed are bonded through the metal ion by forming a complex. Thus a cross-linking reaction is completed as illustrated by the following model:

Polymer—compound—metal ion—compound—polymer

As mentioned above, the compound (D) must react with the primary amino group and form an $-SH$ group which reacts with the metal ion. In this respect the cyclic compound (D) having the linkages represented by the foregoing general formula (I) are suitable. Compound (D) easily reacts with a primary amino group and causes a ring-opening reaction to form an $-SH$ group.

As a subclass of the heterocyclic nucleus, Z and Z' may be non-metallic atoms which form a five or six membered heterocyclic ring which may have further substituents including fusing rings.

Particularly preferred examples of species of compound (D) are listed below.

Compound	Melting point, °C.
1.....	Br— 258
2.....	Br— 288
3.....	Br— 260
4.....	Br— 267
5.....	Br— 275
6.....	Br— 288 55
7.....	Br— 235
8.....	Cl— 201

8
—Continued

Compound	Melting point, °C.
5.....	Cl— 305
10.....	Cl— $\cdot 2H_2O$ 95
11.....	ClO ₄ ⁻ 196
12.....	ClO ₄ ⁻ 220
13.....	ClO ₄ ⁻ 185
14.....	HSO ₄ ⁻ 255

Compounds 11-14 may be prepared as described in Nippon Yakugaku Zasshi (Journal of the Pharmaceutical Society of Japan Vol. 89, pages 469-474 (1969)).

Compound (D) can generally be easily synthesized by heating an azole compound containing a methylmercapto radical and ethylene bromide or 1,3-dibromopropane at ca. 160°C, as shown by the following examples.

Synthesis of Compound 1

20 g of ethylene bromide and 16 g of 2-methylthiobenzothiazole were heated at 160°C for 4 hours. After cooling, the precipitated crystal was collected by filtration and recrystallized from ethanol to obtain 17 g of Compound 1 as needles melting at 258°C.

Synthesis of Compound 6

20 g of 2-methylthiobenzoselenazole and 20 g of ethylene bromide were heated at 160°C for 4 hours. After cooling, the precipitated crystal was collected by filtration and recrystallized from ethanol-water mixture to obtain 18 g of compound 6 as needles melting at 288°C.

Compounds 8 and 9 and Compound 10 can be synthesized according to the process described in Chemical Abstracts 72, 31666 (1970), and ibid. 63, 11569 (1965), respectively.

It has been found that compound (D), when added to the hydrophilic macromolecular substance (A), shows an effect of lowering the solubility thereof in warm water (typically above 35°C.), due to a crosslinking reaction, and that said effect is enhanced in the presence of a metal ion and in alkaline conditions.

When an aqueous solution containing compound (D), hydrophilic macromolecular substance (A) and metal ion (B) is made alkaline, the solution immediately shows a crosslinking reaction to turn to the gelled state or a remarkable increase of viscosity, though without gelling, in certain cases. Gelling occurs where more cross-linkages occur than viscosity increasing state. The metal ion (B) is found to be effective even in trace amounts, and does not show any adverse effect so long as it is totally soluble in the system.

As regards the crosslinking reaction between substance (A) and the compound (D), the amount of the compound (D) should not be less than 0.2 parts (hereinafter amounts will be represented by parts by weight), preferably not less than 2 parts, per 1,000 parts of the macromolecular substance (A). As indicated, the amount of metal ion (B) can be very small, and is found to be effective in an amount of 0.002 parts with respect to 1,000 parts of compound (D), but is preferably present in an amount of 0.01 parts or more with respect thereto.

The above-mentioned quantitative relationships arise exclusively from the requirements for the crosslinking reaction, and the amounts to be employed in the practical cases vary depending upon the exact embodiment.

The process according to this invention requires, as stated above, the presence of: (A) hydrophilic macromolecular substance; (B) metal ion; (C) compound capable of maintaining the pH value of medium at not less than 8; and (D) compound represented by the general formula (I), but these four components are not necessarily all different from one another. Stated differently, a compound can be provided with the two or more functions of said four components. More specifically, it is possible that a compound can act as component (A) as well as component (C). For example, certain synthetic polymers containing primary amino radicals as mentioned above show a pH value higher than 8 in aqueous solution, and therefore can be employed as component (A) as well as component (C).

Of course, it is possible to subsequently render the obtained polymer image stronger by using a known hardener.

The following applications of this invention will be explained with reference to the attached drawings.

APPLICATION I

APPLICATION IN ELECTROLYTIC ELECTROPHOTOGRAPHIC PROCESS

The process of this invention can be applied to an electrolytic-electrophotographic process to obtain an image by means of the decrease of electrical resistance resulting from light exposure on a photoconductive material. Known electrolytic-electrophotographic process consist of the steps of projecting a light image on a photoconductive layer which is composed of a powdered photoconductive material such as cadmium sulfide, titanium oxide, zinc sulfide, zinc oxide, etc. uniformly dispersed in an insulative resin, and which is provided on an electroconductive support material, and subjecting the layer to electrolysis simultaneously with, or succeeding said projection, in an electrolytic bath containing suitable material capable of forming image on said layer by means of reduction or oxidation, thereby effecting an electrolytic reaction in accordance with the pattern formed due to the difference in electroconductivity resulting from photoconduction to obtain a visible image.

As an example of such electrolytic electrophotographic process there is disclosed in U.S. Pat. No. 3,010,883 a process of obtaining a copy by treating a recording material provided with a photosensitive layer of zinc oxide in an electrolytic bath containing metal salts which are capable of forming a colored metal image when reduced, e.g., silver nitrate, nickel chloride, cupric sulfate, etc., or an organic compound capable of generating color when reduced. There is also al-

ready known a modified process in which, for example, indium oxide is added alone, or together with zinc oxide to the photosensitive layer while the electrolytic bath has added thereto only salts of relatively basic metals which reduce the indium ion contained in the

photosensitive layer. Also known is a process in which water-soluble metal salts capable of giving a metal image when reduced are mixed with hydrophilic binder, such as gelatin, and applied onto the surface of photosensitive layer together with other electrolytes.

This invention provides extremely desirable results when applied to such an electrolytic electrophotographic process. In such an application it is possible to employ an ordinary photosensitive element for the electrolytic electrophotographic process, namely, one composed of a support material provided with suitable mechanical properties and a photosensitive layer provided thereon and consisting of powdered photoconductive material in an electroinsulative binder.

In order to apply the electric potential required for electrolytic reaction, the interface between the support material and the photosensitive layer is required to be highly electroconductive. Consequently, if the support material is composed of a plastic material etc., it is necessary to provide the surface thereof with a thin layer of aluminum or other metal though ordinarily vacuum deposited aluminum is used. Examples of other available support materials are electroconductive glass provided with a thin layer of tin oxide, paper containing carbon black, paper containing fine metal fibers, paper laminated with aluminum foil, etc. The use of a metal plate as the support is naturally desirable.

The photosensitive layer consists of a thin layer of an intimate mixture of, for example, photoconductive zinc oxide and an electroinsulative binder. The zinc oxide is preferably manufactured by the French method. The binding material has a significant influence on the electrophotographic properties and can be exemplified by styrene-butadiene copolymers (Pliolite S-5D and S-7; Goodyear Tire and Rubber). Fatty acid epoxy esters, vinyl chloride-vinyl acetate copolymers, polyvinyl acetate, etc. can also be utilized for this purpose. The binder can have added thereto plasticizers, inactive pigments (for example colloidal silica, talc, titanium dioxide, etc.), lubricants, etc., if desired. The addition of surface active agents is often desirable in order to regulate the coating properties. Sensitizing dyes are often added in order to widen the photosensitive wavelength range of the zinc oxide, which is basically limited to the ultraviolet to blue region. Other sensitizing materials may also be added as minor additives.

This invention can be applied to electrolytic electroconductive process by adding the components (A) hydrophilic macromolecular substance; (B) metal ion; and (D) the aforementioned compound to the surface of the photosensitive layer or to the electrolytic bath. The alkali generating compound (C), water in this case, renders the proximity of the cathode alkaline upon electrolysis. In this case it is possible to add all three components (A), (B) and (D) to the electro-

lytic bath, or to overlay the three components in layers on the photosensitive layer. Furthermore, it is possible to apply components (A) and (B) or (A) and (D) in layers on the photosensitive layer and to add component (D) or (B) into the electrolytic bath, respectively.

Furthermore, it is possible to apply component (A) onto the photosensitive layer and to add components (B) and (D) to the electrolytic bath. Another possibility of application of the components (A) and (B) or (A) and (D) and addition of the components (B) and (D) into the electrolytic bath. A further possibility is the application of the three components (A), (B) and (D) in layers on the photosensitive layer and the addition of the components (B) and/or (D) into the electrolytic bath.

FIG. 1 shows an enlarged cross section of a thus prepared photosensitive element 10, which is composed of a transparent or opaque support material 11, an electroconductive layer 12 and an insulative photoconductive layer 13, on which is provided a hydrophilic macromolecular layer 14 consisting, for example, of gelatin and aforementioned compound 1. Such a macromolecular layer 14 preferably has a thickness of 0.1 - 500 microns in the dry state.

FIG. 2 shows the step of imagewise light projection on the photosensitive element 10 shown in FIG. 1, in which a transparency original 21 consists of opaque areas 22 and translucent area 23 distributed according to the image. The uniform light from above (indicated by the arrows) is transmitted through the transparent area 23 of original plate 21 and the macromolecular layer 14 and reaches the photoconductive layer 13 to thereby form a low resistance area [a] and high resistance area [b]. Layer 14 may previously have added thereto a dye or pigment. If such a dye or pigment has an absorption within the sensitive wavelength range of layer 13, it is also possible to form said macromolecular layer 14 after the imagewise exposure of the photoconductive layer 14 to light.

FIG. 3 shows the step of effecting electrolysis on the photosensitive element 10 after imagewise exposure, thereon, where 31 is a container for electrolytic solution 32 consisting, for example, of an aqueous solution of metal ions (B). It has been found in this step that a slightly acidic electrolytic bath is capable of providing a sharper image. The photosensitive material 10 after imagewise exposure thereon and a counter electrode 33 are, respectively, connected with the cathode and anode of an electric source 34 which supplies a voltage of 0.3 - 100 volts DC for the electrolysis. During the course of electrolytic treatment, gelatin in area [a] of the macromolecular layer is rendered insoluble in water which is warm by means of a crosslinking reaction with metal ions (B) and compound (D) due to alkalinity generated by the electrolysis of water. Such a reaction does not proceed in unexposed area [b] in macromolecular layer 14 due to the absence of an increase in the pH value. It has also been found possible to obtain a colored macromolecular image by adding a compound capable of generating formazan dye on reduction, such as triphenyltetrazolium chloride, in the electrolytic bath. More simply, it is also possible to add a coloring component not causing undesirable effects upon the crosslinking reaction in the electrolytic bath by incorporating the colored component into the macromolecular image to render the image more easily visible.

Development by electrolytic treatment can be realized by applying an electric potential to the photosensitive surface through an electrode connected thereto (the cathode is connected when zinc oxide is used as the photosensitive material) in the electrolytic bath directly after or during the imagewise exposure. The electrolytic bath can be substituted for by absorbent materials capable of holding electrolytic solution in an amount sufficient to effect the electrolytic treatment, such as brushes, sponges, porous papers, etc. Contact between the electrolytic bath and the photosensitive layer can be made either at one time over the whole surface thereof or progressively in small portions thereof, such as by a roll covered with sponge.

FIG. 4 shows the step of treatment with hot water of the photosensitive material after the electrolytic treatment thereon, in which uncrosslinked area is removed by the hot water 42 supplied from the nozzle 41, thereby leaving area [a] as a water-insoluble macromolecular image 43 on the photosensitive layer 13 to thus obtain a negative image of the original image 21.

The macromolecular image 43 thus obtained can be utilized in various printing processes. For example, the image can be employed in dye transfer printing by impregnating the image with a water-soluble dye. Thus, the sheet holding the macromolecular image 43 thereon can be used as the gelatin relief for dye transfer printing. In this case, it is possible to apply a hardening treatment in order to reinforce the image. When the photosensitive material is composed of zinc oxide, it has also been found preferable to remove the zinc oxide with acid, etc., in order to obtain a clearer transfer image. The image can also be utilized in spirit printing by impregnating the image with a sufficient amount of a dye soluble in water and alcohol.

Furthermore, the macromolecular image can be utilized for offset printing since image 43 is hydrophilic whereas the photoconductive layer 13 is hydrophobic. Furthermore, it is possible to obtain a thick macromolecular image 43 by subjecting macromolecular layer 14 with a dry thickness larger than 10 microns to electrolytic treatment. Such an image constitutes a relief of considerable height in the water-containing state, and therefore can be utilized in braille printing or in letterpress printing with an aqueous printing ink.

It is possible to obtain a metal image by further treatment on the sheet provided with macromolecular image 43. Such treatment may comprise, as shown in FIG. 5, spraying a solvent 52 for the binder of the photoconductive layer 13 from a nozzle 51 thereby removing the photoconductive layer except for the area 53 protected by the macromolecular image 43, and then spraying an etching solution 62 from a nozzle 61 to thereby remove the thus exposed electroconductive layer as shown in FIG. 6. In this case the said electroconductive layer 12 and the etching solution 62 are, respectively, composed of a copper chloride and ferric chloride solution. Successive removal of macromolecular image 43 and the remaining photosensitive layer 53 provides a metal image 63 on the support material 11 as shown in FIG. 7. The metal image thus obtained can be used as a printed circuit when the support material is composed of an electroinsulative material. Such a metal image can also be utilized as a letterpress printing plate.

It is furthermore possible to obtain a printing plate by a process which consists of pressing the sheet holding the macromolecular image thereon as shown in FIG. 4.

against a metal plate 120 with the image facing the metal plate as shown in FIG. 12, and transferring the macromolecular image [e] onto the metal plate to obtain a resist image on the plate (the plate may be, for example, copper). The pressing can be accomplished by means of a roller 121. A successive etching treatment as shown in FIG. 13, followed by removal of the macromolecular image [e], provides a printing plates as shown in FIG. 14. The area [f] indicates the non-etched surface of the plate.

It is also possible to prepare a mimeographic printing plate according to this invention by an electrolytic electroconductographic process. A photosensitive element for preparing mimeographic printing plate is shown in FIG. 10 as composed of a support material 11, an electroconductive layer 12, a photoconductive layer 13 and a porous sheet 101 composed, for example, of Japanese paper impregnated with hydrophilic macromolecular material 100 and aforementioned compound (D). The Japanese paper layer can be provided on the photosensitive layer 13 prior to or after the imagewise exposure thereof, but it is preferred to provide the layer after imagewise exposure in order to obtain a mimeographic plate of higher quality. The area [d] indicates the unexposed portion of the photosensitive layer. The electrolytic bath employed in this case is preferred to be slightly acidic and to contain metal ions (B). The mimeographic printing plate as shown in FIG. 11 can be obtained by washing the element with hot water after electrolytic treatment to thereby remove unexposed areas, and peeling off the Japanese paper layer from the element in a solvent for the binder of the photosensitive layer 13. The plate is composed of uncross-linked area 111 permeable to printing ink and cross-linked area 112 constituting a barrier to ink.

In the case of applying the present invention to the electrolytic electroconductographic process, the temperature of the electrolytic bath is preferred not to exceed 45°C, since a temperature exceeding this limit will accelerate the decay of retentive photoconduction resulting from light irradiation and makes complete crosslinking reaction impossible.

APPLICATION II

APPLICATION IN AN ELECTROPHOTOGRAPHIC PROCESS

The present invention can also be applied to an electrophotographic process consisting of uniformly charging a photoconductive insulative layer in a dark place, then subjecting said layer to imagewise exposure and developing the thus obtained electrostatic latent image with an electroscopic powdered material (toner). Development can be carried out, for example, with a developer consisting of fine powders obtained by crushing compound (D) and a salt containing metal ion (B) and carrier particles for cascade development.

On the other hand, a layer of hydrophilic macromolecular substance (A) provided on a water-resistant support material is moistened with an alkaline aqueous solution and pressed against a xerographic plate holding developed toner image thereon. After pressing, the sheet provided with the macromolecular layer is peeled from the xerographic plate and treated with hot water. The macromolecular layer after treatment is found to be insolubilized exclusively in the area which has been in contact with the toner image. Generally, in this case at least one member in the four components (A), (B), (C) and (D) is incorporated in the toner thereby elec-

trophotographically making the four components present in the image area to cause the crosslinking reaction. Thus, the hydrophilic macromolecular image is obtained exclusively in the area where the four components are all present. Theoretically, it is possible to use any and at least one member of the four components in the toner, but practically the hydrophilic macromolecular substance (A) is preferred not to be used in the toner but to be applied in a layer on the support material in order to facilitate handling.

The electrophotographic process used in conjunction with the present invention can employ any conventional developing processes, such as cascade developing, magnetic brush developing powder cloud developing, liquid developing, toner sheet developing, etc. In addition, it is also possible to obtain a macromolecular image by bringing an aqueous alkali solution impregnated in a porous material, such as sponge, into contact for a short period with the surface holding the electrostatic latent image to thereby form the distribution pattern of alkaline material on the xerographic plate, and then press a sheet provided with a wet layer containing components (A), (B) and (D) against the surface of the xerographic plate.

APPLICATION III

APPLICATION TO AN ELECTROCONDUCTIVE RECORDING PROCESS

This invention can easily be applied to an electroconductive recording process to obtain a macromolecular image by means of a crosslinking reaction initiated by the alkalinity generated at the proximity of a cathode by an electric current. For example, in this case a recording layer of hydrophilic macromolecular substance (A) containing compound (D) and metal ion (B) provided on an electroconductive support material is moistened with water or water vapor prior to recording thereon and a metal needle is displaced while keeping contact therewith. An electric voltage modulated by means of an electric signal is applied to the metal needle in order to generate alkalinity on the layer in correspondence with the electric signal. The alkalinity causes the crosslinking reaction in the macromolecular layer according to the amount of electric current passed therethrough.

A water-insoluble macromolecular image can thus be obtained by treating the recording layer with hot water. The image thus obtained can be utilized for multiple copying by means of dye transfer process.

Metal ion (B) can be supplied from the metal needle instead of being incorporated as a water-soluble salt in said recording layer. For this purpose, the metal needle can be composed, for example, of silver, nickel, cobalt, zinc, etc. Metal ions are generated from the metal needle connected with the anode of the electric source and supplied into the recording layer. Excessive metal ion is again reduced to the metallic state and deposited on the surface of the recording layer, giving a colored macromolecular image in this case.

The metal needle can be used singly or in the form of pin matrix. Thus, according to this invention, it is possible to obtain a printing plate from a pin matrix type cathode ray tube.

APPLICATION IV

APPLICATION TO A THERMOGRAPHIC COPYING PROCESS

This invention can further be applied to a thermal copying process as shown in FIG. 8 showing a support

material 81 of low thermal conductivity and a thermosensitive recording layer 82. In this case, the thermosensitive recording layer 82 is composed of hydrophilic macromolecular substance (A), metal ion (B), a compound capable of generating alkali when decomposed (C) and compound (D). Alkaline source (C) can be, for example, urea, thiourea, ammonium carbonate, etc., which liberates alkali on decomposition by heating.

In this process recording layer 82, contacted tightly against an original 83, is exposed to uniform irradiation of infrared light for a short period. The image area 84 in the original which absorbs infrared light shows a local temperature increase, resulting in a local temperature increase by thermal conduction in the corresponding area [c] in the recording layer. In area [c], compound (C) is thermally decomposed to render the area alkaline, thereby causing a reaction between the hydrophilic macromolecular substance (A), metal ion (B) and compound (D) to insolubilize the macromolecular substance (A) against water. Thus a macromolecular image 91 is obtained on the support material 81 by treating the recording layer with hot water after the exposure to infrared light. The sheet holding the thus prepared image thereon can be utilized as a gelatin relief for dye transfer printing, as an offset printing plate, as a spirit printing plate, etc.

A recording layer containing the macromolecular substance (A), metal ion (B), alkali source (C), compound (D) and a colored powder such as a pigment or dye is suitable for direct recording with laser light. When the surface of such a recording layer is scanned with a signal-modulated laser light, the colored powdered material absorbs the light to elevate the temperature thereof, resulting in the decomposition of alkali source (C) and initiating the crosslinking reaction.

OTHER APPLICATIONS

This invention can naturally be applied to the direct scribing recording process. In such a case, a recording layer containing hydrophilic macromolecular substance (A), metal ion (B) and compound (D) is provided on a transparent support material, and the recording is directly inscribed on the layer with a pen, painting brush, felt pen, etc., containing an aqueous solution of alkali (C). This aqueous solution may be colored, if desired. After inscribing, the recording layer is treated with hot water to remove unrecorded areas, thereby leaving a macromolecular image on the transparent support. The sheet thus prepared can be utilized as a transparency for overhead projection as an original plate for making multiple transparencies by the dye transfer process.

Furthermore, this invention can be applied to electron beam recording. For example, when a recording element consisting of a recording layer containing the hydrophilic macromolecular substance (A), metal ion (B), compound (D) and a compound capable of generating alkali when decomposed under electron beam irradiation and a support material is subjected to electron beam irradiation, compound (C) is decomposed in the irradiated area to cause a hardening reaction.

It is also possible to obtain a hydrophilic macromolecular image by providing pressure-rupturable micro-capsules containing alkaline material (C) on the bottom surface of a paper sheet, placing thereunder another paper sheet provided with a layer containing components (A), (B) and (D) and rupturing the micro-capsules by means of scribing pressure, etc.

The process of this invention is thus characterized by the co-existence at imaging of the aforementioned four components (A), (B), (C), and (D).

This invention will be further explained by the following examples. It will be readily understood to those skilled in the art that the examples cited below can be subjected to variations and modifications as to the composition or combination of components, order of the process, etc. within the scope of this invention, and therefore, the examples should not be regarded as limiting this invention. Parts mentioned are by weight.

Example 1

The following composition was kneaded for 20 hours 15 in a porcelain ball mill:

Photoconductive zinc oxide (Sakai Chemical, Sazex)	100 parts
Pliolites S-5D (Goodyear Tire and Rubber) (styrene butadiene copolymer, the molar ratio of styrene and butadiene being 85:15)	25 parts
Toluene	75 parts
Methylethylketone	25 parts

The white paste thus prepared was diluted with toluene to a viscosity of 50 centipose, and then coated on a polyethylene terephthalate film previously provided with a vacuum-evaporated aluminum layer 1,000 angstroms thick to obtain a coating thickness of 16 micron after drying.

The photosensitive sheet thus prepared was subjected to imagewise exposure at ca. 10,000 lux for 5 seconds by means of a slide projector using a tungsten lamp.

After exposure, the sheet was subjected to electrolytic treatment in an electrolytic bath of the following composition, which was maintained at 30°C in order to prevent setting of the bath:

(Photographic grade) gelatin	6 parts
Compound-1	0.4 parts
Nickel chloride hexahydrate	9 parts
Distilled water	100 parts

The periphery of the sheet was covered with insulative adhesive tape prior to dipping into the electrolytic bath in order to prevent direct contact between the bath and the aluminum layer. The electrolysis was carried out by placing a nickel plate as an anode at a distance of 1.5 cm from the sheet of which the aluminum layer acted as cathode. A D.C. potential of 4 volts was applied therebetween. The sheet was taken from the bath after electrolysis for 10 seconds. In this condition the sheet was wet exclusively in the exposed areas which showed a pale gray color. The sheet was then washed with water, dried and finally wiped with a sponge impregnated with an aqueous solution (concentration 0.2 percent) of a blue dye (C.I. acid blue 54) to obtain a blue negative image. The optical density of the image was 0.57.

Example 2

The procedure of example 1 was repeated except that there was further added to the electrolytic bath 0.1 part of glacial acetic acid. Electrolytic treatment and dyeing as in Example 1 provided a sharper image of higher density. The optical density of the image was 0.57.

Example 3

In this example, a 5 percent aqueous solution of photographic gelatin was coated onto the photosensitive layer in Example 1, and cooled and dried to obtain gelatin layer 1.9 microns thick after drying. The photosensitive layer was successively subjected to imagewise exposure at ca. 10,000 lux for 8 seconds with a light source as in Example 1.

The composition of the electrolytic bath employed was as follows:

Nickel chloride hexahydrate	3 parts
Cobalt (II) chloride hexahydrate	2 parts
Compound-1	0.4 parts
Distilled water	100 parts

The sample was washed with hot water after electrolytic treatment as in Example 1. After drying, the sample was coated with an aqueous solution of formalin to harden the gelatin image and dipped into an aqueous solution of C.I. acid blue 54 as in Example 1. Then the

aqueous solution of Color Index acid blue 54. A transfer process as shown in Example 3 provided a dark blue transferred image. It was found that the gelatin layer was totally insoluble in hot water in the area subjected to maximum exposure.

Example 5

The procedure of Example 4 was repeated except that the electrolytic bath had further added thereto 0.2 parts of Compound 1. The results obtained were comparable to those of Example 4.

Example 6

In this example the photosensitive layer was dye sensitized by adding a dye solution of the following composition to the photosensitive composition of Example 1 at the solvent dilution thereof. The following table also indicates the resulting sensitivity to white light (tungsten lamp, color temperature ca. 3,000°K). The amounts in this table are with respect to 100 g of zinc oxide.

No.	Sensitizing Dye	Solvent For Dye	Relative Sensitivity
1	None (photosensitive layer of Example 1)	None	1
2	Rose bengal	Methanol 15 ml	18
3	Fluorescein Erythrosin B	Methanol 20 ml	45
4	Brilliant blue FCF 3,3'-di-carboxyethyl thiadicarbocyanine bromide	Methanol 15 ml	23

sample was pressed against a sheet provided with a gelatin layer which had been previously subjected to modanting treatment to thereby obtain a blue transferred image on the sheet. As a result it was found that gelatin in the exposed areas was insoluble in hot water with a maximum thickness of 0.2 microns.

Example 4.

The following composition was coated onto the photosensitive layer of Example 1.

Gelatin (Photographic grade)	5 parts
Compound-1	0.5 parts
Compound-4	0.1 parts
Distilled water	100 parts

The thickness after drying of the gelatin layer was 2.0 microns. The electrolytic bath employed was as follows:

Nickel chloride hexahydrate	3 parts
Cobalt (II) chloride hexahydrate	2 parts
Hydrochloric acid (30%)	0.02 parts
Distilled water	100 parts

After exposure and electrolysis as in Example 1, the photosensitive surface was washed with hot water at 45°C to leave thereon a pale-gray gelatin image which was so sharply raised that it could be felt with one's fingers.

The temperature of the warm water capable used generally ranges between about 30°C. and about 98°C. After drying, the sample was further treated with formalin to harden the gelatin image and dipped into an

Photosensitive layer No. 3 was further provided with a gelatin layer as shown in Example 4 and subjected to imagewise exposure through a negative photographic film placed in a photographic enlarger (enlarger for 35 mm film produced by Fuji Photo Film.) The exposure was carried out for 3.5 seconds with maximum lumiance at the exposed surface of 75 lux. Electrolytic treatment similar to that in example 4 provided a satisfactory positive gelatin image.

45

Example 7.

The procedure of Example 1 was repeated using an electrolytic bath of the following composition:

50	Polymer-1	5 parts
	Compound-1	0.4 parts
	Nickel chloride hexahydrate	9 parts
	Distilled water	100 parts

55 Results comparable to those in Example 1 were obtained.

Example 8.

The procedure of Example 1 was repeated using an electrolytic bath of the following composition:

60	Polymer-3	6 parts
	Compound-2	0.3 parts
	Cobalt chloride hexahydrate	9 parts
	Distilled water	100 parts

The procedure of Example 1 provided results comparable to those obtained in Example 1.

Example 9.

In this example, the gelatin layer of Example 4 was provided on the photosensitive layer so as to obtain a thickness after drying of 0.6 microns instead of 2 microns. The electrolytic bath and procedure shown in Example 4 provided a gelatin image, which was wiped, after washing the photosensitive layer, with an offset plate treating agent (Fuji Photo Film, Plano Developing Ink 801). Ink 801 adhered exclusively to the exposed photosensitive layer, leaving the gelatin image completely intact. The image thus treated could be used as an offset printing plate.

Example 10.

The following composition was kneaded for 20 hours in a porcelain ball mill.

Photoconductive zinc oxide (Sakai Chemical, Sazex)	100 parts
Pliolite S-5D (Goodyear Tire and Rubber)	28 parts
Toluene	80 parts
Methylethylketone	20 parts

The white paste thus prepared was diluted with toluene to an appropriate viscosity, then coated onto the copper surface of a laminated plate for printed circuits (Matsushita Electric Co.) composed of an epoxy resin support plate and copper layer provided thereon. The coating thickness was 16 microns after drying.

The photosensitive layer thus prepared was further coated with the following composition:

Photographic grade gelatin	5 parts
Polymer-3	2 parts
Compound-1	0.8 parts
Distilled water	100 parts

The coating thickness after drying was 3 microns. The electrolytic bath employed was as follows:

Cobalt (II) chloride hexahydrate	9 parts
Glacial acetic acid	0.02 parts
Distilled water	100 parts

The photosensitive element thus prepared was subjected to imagewise exposure through a negative original for printed circuits, electrolytic treatment, washing with hot water (45°C) and hardening with formalin as shown in Example 4, and further washed with ligroin to remove the bare photosensitive layer in unhardened areas. The element was then dipped into an acidic solution of ferric chloride (40° Be) for 15 minutes at 45°C, then washed with water. A sharp printed circuit was obtained by strongly wiping the hardened areas with benzene to remove the photosensitive layer and the hardened image provided thereon.

Example 11

The procedure of Example 10 was repeated except that the laminated printed circuit plate was further provided with a vacuum-evaporated aluminum layer of 750 angstroms on the copper layer to obtain a sharp printed circuit comparable to that obtained in Example 10. In this example the aluminum layer could be eliminated by washing with a 1N sodium hydroxide solution. Insertion of the aluminum layer between the photosensitive layer and the copper layer reduced the necessary exposure time to $\frac{1}{2} - \frac{1}{3}$ that in Example 10.

Example 12

The following mixture was dried and crushed:

Compound-1	5 parts
Nickel acetate	0.1 parts

The almost pure white powder obtained was well mixed with 100 parts of Xerox 914 Carrier (Fuji Xerox Co.) to obtain an electrophotographic dry developer.

10 A xerographic plate provided with an amorphous selenium layer 80 microns thick was subjected to a positive corona discharge in the dark to charge the layer to a potential of +500 volts. The xerographic plate was subjected to imagewise exposure to form an electrostatic latent image thereon, which was then developed with the above-mentioned dry developer by a cascade process to obtain a white toner image on the xerographic plate.

The following composition was separately coated on a sheet of polyethylene terephthalate previously irradiated with ultraviolet light (thickness: 120 microns):

Gelatin	5 parts
Sodium dodecylbenzene sulfonate (wetting agent)	0.05 parts
Distilled water	100 parts

25 The coating layer was first set by cooling and then dried by exposing it to warm air. The gelatin layer was swollen in a 0.1N sodium hydroxide solution at 15°C and tightly pressed against the surface of the xerographic plate holding the toner image thereon. The sheet was then peeled off and washed with water at 45°C to obtain a gelatin image corresponding to the toner image on the sheet.

Example 13

The following composition was coated onto a sheet of polyethylene terephthalate of 120 microns thick which had been previously irradiated with ultraviolet light to obtain a coating thickness of 3 microns after drying:

Carbon black	0.8 parts
Gelatin	8 parts
Cadmium sulfate	0.1 parts
Compound-2	0.6 parts
Distilled water	100 parts

30 50 A direct manual inscription was made on the layer thus prepared by means of a felt pen impregnated with 0.1N potassium hydroxide. The sheet was then treated with hot water at 50°C. to remove non-inscribed areas, leaving a sharp black image thereon suitable as a transparency for overhead projection. It was also possible to

55 reproduce this transparency by dipping the sheet in a dye solution and transferring the dye to other transfer sheets.

Example 14

The following composition was coated onto a sheet of polyethylene terephthalate (thickness 60 microns) previously subjected to ultraviolet irradiation so as to provide a dry thickness of 2 microns:

Gelatin	5 parts
Compound-1	0.5 parts
Nickel chloride hexahydrate	0.01 parts
Urea	0.8 parts
Distilled water	100 parts

The coating was dried, after setting thereof, by blowing air at 30°C thereon. The recording layer thus prepared was pressed against an original having a black image, subjected to infrared radiation from the rear side of said recording sheet and immediately dipped into warm water at 40°C. After drying the recording layer was dipped in a dye solution to obtain a positive reproduction of the original image.

Example 15

The photosensitive layer of Example 1 was subjected to imagewise exposure through a line positive image. Separately, a sheet of thin Japanese paper was dipped into the following solution kept at 28°C.

Gelatin	4 parts
Compound-1	0.3 parts
Manganese chloride hexahydrate	0.01 parts
Distilled water	100 parts

The wet Japanese paper sheet was superposed onto the photosensitive layer shown in Example 1 directly after imagewise exposure thereon and made to stick firmly thereto by setting the gelatin by means of blowing cold air thereon. The photosensitive layer was then subjected to the electrolytic treatment described in Example 1 in the electrolytic bath of Example 4, then washed with hot water, dipped into toluene and the Japanese paper sheet was peeled off the photosensitive layer. After drying, it was found that gelatin in unexposed areas (line image areas) was removed from the paper sheet. The thus treated paper sheet showed satisfactory performance as a stencil master (mimeographic printing plate). Thin cloth of synthetic fibers instead of Japanese paper gave comparable results.

Example 16.

An epoxy resin-zinc laminate plate for letter press printing plate use was coated with the white photosensitive paste shown in Example 10. After drying, the plate was further coated with the composition shown in Example 10 in a thickness as shown in Example 10. The photosensitive element thus prepared was subjected to imagewise exposure, washing with warm water (45°C), and hardening with formalin as shown in Example 4, and further treated with ligroin to remove the photosensitive layer present in the unexposed portions thereof. Then the plate was dipped into an etching solution (Itoh Chemical Co.) containing ferric chloride at 45°C for 15 minutes to dissolve zinc present in the unhardened areas. After washing with water, the photosensitive layer in the hardened areas was removed together with the hardened image by means of wiping with benzene to provide a zinc letterpress plate.

Example 17

A composition consisting of

Gelatin	5 parts
Acrylamide	0.4 part
Hexahydrated nickel chloride	0.02 part
Compound 1	0.1 part
Distilled water	100 parts

was coated to a thickness of 2 microns as a dry layer on a polyethylene terephthalate film to prepare an electron beam recording material. The recording material thus obtained was exposed to an electron beam image in vacuum and treated with warm water to obtain a gelatin image.

Example 18

A composition consisting of

5	Gelatin	5 parts
	Red pigment (brilliant carmine 6B)	1 part
	Compound-2	0.3 part
	Urea	0.8 part
	Ferric chloride	0.01 part
	Distilled water	100 parts

10 was coated to a thickness of 4 microns as a dry layer on a polyethylene terephthalate film to prepare a laser sensitive recording material. The recording material thus obtained was exposed to an argon ion laser light modified by a signal and treated with warm water at a temperature of 40°C to obtain a red gelatin image.

Example 19

The following compositions were heated at 40°C to form a uniform solution.

20	Gelatin	6 parts
	Compound-1	0.2 parts
	Cobalt chloride	0.01 parts
	Distilled water	100 parts

To the solution kept at 70°C, 10 parts of 5 percent acetone solution of carbontetrabromide was added under stirring. Carbon tetrabromide was dispersed in fine particles of about 2 microns. The solution was applied to a cellulose triacetate film of 100 microns. Dry thickness of the layer was 7 microns. The film was then immersed in 0.05N aqueous potassium hydroxide solution at 15°C for 2 seconds and dried. By the treatment with alkali the layer was hardened and rendered insoluble in warm water (60°C). The above-mentioned processes were carried out under a subdued light excluding ultra-violet radiation.

30 40 The film thus formed was exposed in contact with a transparent original to a light from a high pressure mercury lamp of 100 W at a distance of 35 cm. for 3 minutes. Then the film was washed with warm water of 60°C. The exposed portions of the layer were washed out, while the unexposed portions were remained. The film was immersed in a mixed solvent of acetone and water (1:1) by volume to remove carbontetrabromide present in the unexposed portions.

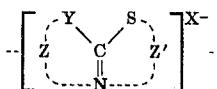
45 50 Numerous modifications of the invention will become apparent to one of ordinary skill in the art upon reading the foregoing disclosure. During such a reading it will be evident that this invention provides a unique imaging process for accomplishing the objects and advantages herein stated.

What is claimed is:

1. A process for forming an image in a system including a recording layer, said process comprising imagewise forming first and second portions in said system by

60 forming a water insoluble first portion in or on said recording layer by reacting a hydrophilic macromolecular substance (A) containing primary amino radicals, a metal ion (B) selected from the group consisting of ions of metallic atoms belonging to groups 6A, 7A, 8, 1B, and 2B of the periodic table of the IUPAC Comptes Rendus XXIII Conference, 1965, a compound (D) represented by the following general formula:

23



wherein

Z, Z' : non-metallic atoms constituting heterocyclic structure

X : anion, and

Y : atom selected from the group consisting of selenium and sulfur atoms

under conditions of a pH value not less than 8, while preventing the formation of a water insoluble reaction product in a second portion in or on said recording layer where said system lacks at least one of said substance (A), said ion (B), said compound (D), or said pH condition.

2. An imaging process as in claim 1 where said recording layer comprises a photoconductive insulating layer, said process including developing an electrostatic latent image formed on said photoconductive insulating layer with a finely powdered material consisting of at least one member selected from the group consisting of said hydrophilic macromolecular substance (A), said metal ion (B), said compound (D) and a compound (C) capable of maintaining the pH value of the surrounding medium at not less than 8 when brought into contact with water or a compound (C') which provides a compound (C) when decomposed and reacting the thus obtained powder image with the remaining members of said group to obtain a final image.

3. A process as in claim 1 where said recording layer contains all said substance (A), ion (B), compound (D) and a compound (C'), which after decomposure, is capable of maintaining the pH value of the surrounding medium at not less than 8 when brought into contact with water, said compound (C') maintaining the surrounding medium at a pH value not less than 8 when decomposed by electron beams, and selectively image-wise irradiating said recording layer with an electron beam to decompose said compound (C') and water insolubilize said recording layer at the electron beam exposed portions.

4. An imaging process as claim 1 where said first portion of the system is maintained at said pH value by introducing into the system a compound (C), which is capable of maintaining the surrounding medium at said pH value when brought into contact with water, and bringing said system into contact with water.

5. An imaging process as in claim 4 where said compound (C) is selected from the group consisting of oxides, hydroxides, carbonates of alkali metals and alkali earth metals and water soluble, organic bases.

6. An imaging process as in claim 1 where said pH value is maintained by applying to said recording layer an alkali solution.

7. An imaging process as in claim 6 where at least one of said substance (A), said ion (B) or said compound (D) is only imagewise present in or on said recording layer.

8. An imaging process as in claim 6 where an alkali solution is applied imagewise to said recording layer.

9. An imaging process as in claim 1 where said first portion of the system is maintained at said pH value by introducing into the system a substance (C') which provides by decomposition a compound, which is capable of maintaining the surrounding medium at said pH

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value when brought into contact with water, decomposing said substance, and contacting the system with water.

10. An imaging process as in claim 9 where said substance (C') is decomposed thermally.

11. An imaging process as in claim 10 where said substance (C') is at least one member chosen from urea, thiourea, and ammonium carbonate.

12. An imaging process as in claim 10 where said substance (C') is decomposed by electric current.

13. An imaging process as in claim 10 where said substance (C') is decomposed by laser beam.

14. An imaging process as in claim 10 where said substance (C') is decomposed by electron beam.

15. An imaging process as in claim 1 where said metal ion is selected from the group consisting of chromium, manganese, iron, cobalt, nickel, copper, zinc, palladium, silver, cadmium, mercury and gold.

16. An imaging process as in claim 15 where said metal ion is selected from the group consisting of manganese, cobalt, nickel, copper, zinc, silver and cadmium.

17. An imaging process as in claim 1 where said recording layer is a photosensitive element, said process including the steps of projecting a light image onto said photosensitive element comprising an electroconductive support and a photoconductive layer provided thereon and selectively passing an electric current through the exposed areas of said photoconductive

30 layer in an aqueous solution optionally containing at least one component of said substance (A), ion (B), and compound (D) at a point no earlier than simultaneously with said exposure, the remaining components (if any) of said system being present in at least one outer layer provided on said photoconductive layer, the medium adjacent the surface of the light exposed areas of said photoconductive layer being maintained at a pH value not less than 8 by said electric current to thereby enable the components of said system to react and form

40 a water insoluble image at the light exposed areas.

18. An imaging process as in claim 17 where said hydrophilic macromolecular substance (A) and said compound (D) are present in outer layers provided on said photoconductive layer, and said metal ion (B) is dissolved in said aqueous solution.

19. An imaging process as in claim 17 where said hydrophilic macromolecular substance (A), and metal ion (B), and said compound (D) are present in said aqueous solution.

20. An imaging process as in claim 17 where said electroconductive support layer is disposed on a further support layer, said process comprising the further steps of selectively removing said photoconductive layer and electroconductive support at the image area to expose said electroconductive support layer on said further support layer.

21. A process as in claim 1 where said recording layer contains at least said hydrophilic macromolecular substance (A), said metal ion (B), said compound (D), and a compound (C'), which after decomposure, is capable of maintaining the pH value of the surrounding medium at not less than 8 when brought into contact with water, said compound (C') maintaining the surrounding medium at a pH value not less than 8 when decomposed by an electric current, said recording layer being disposed on an electroconductive support layer, and scanning said recording layer with means for

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applying an electric current thereto, said scanning means optionally containing said metal ion (B), said electric current being modulated in accordance with the image to be formed on said recording layer so that wherever an image portion is to be formed, the intensity of the electric current is sufficient to decompose said compound (C') and thereby water insolubilize that portion of the recording layer.

22. A process as in claim 21 where said metal ion (B) is present in said recording layer. 10

23. A process as in claim 1 where said recording layer contains all said substance (A), ion (B), compound (D) and a compound (C'), which after decomposure, is capable of maintaining the pH value of the surrounding medium at not less than 8 when brought into contact with water, said compound (C') maintaining the sur-

rounding medium at a pH value not less than 8 when decomposed by heat, forming a heat image at said recording layer to thereby enable said component (A), (B), (C'), and (D) to react where the image portions of said heat image are present to thereby water insolubilize the recording layer at said image portions. 5

24. A process as in claim 23 including providing said recording layer with an additional component which raises the temperature of said surrounding medium when it absorbs light, said heat image forming step including scanning said recording layer with a modulated laser beam, the beam being so modulated that when an image portion is to be formed in said recording layer, the intensity of the beam is made sufficient to elevate the temperature so that said component (C') decomposes to thereby water insolubilize said recording layer at said image portion. 15

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