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3,674,483

REPRODUCTION METHOD

Marcel Nicolas Vrancken, Hove, Eric Maria Brinckman, Mortsel, and Frans Clement Heugebaert, Kontich, Belgium, assignors to Agfa-Gevaert, Mortsel, Belgium
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ABSTRACT OF THE DISCLOSURE

A method of recording information using a recording material having a water-permeable recording layer consisting essentially of a continuous phase of at least one proteinaceous hydrophilic colloid binder having distributed therethrough finely divided particles of a hydrophilic inorganic photoconductive compound in one embodiment and finely divided particles of a non-photoconductive hydrophilic pigment, plus an organic photoconductive dye, in another embodiment, wherein the recording layer is image-wise exposed to active electromagnetic radiation and then developed by contacting the same with an aqueous liquid to produce a visible change in the recording layer by penetration or removal of the water-permeable unexposed regions of the layer by the aqueous liquid. The ratio by weight of hydrophilic particles to hydrophilic colloid is about 1:1 to 5:1 and the proportion of the organic photoconductive dye is at least about 0.05% by weight of the hydrophilic non-photoconductive particles.

The present invention relates to photographic recording and reproduction of information and to recording and reproduction materials suited therefor.

More particularly this invention relates to a process for producing an irreversible change in physical behaviour in the areas where a photosensitive material is subjected to a sufficient degree of electromagnetic radiation. The photosensitive element, which will be described more in detail hereinafter undergoes by the action of active electromagnetic radiation a decrease of permeability and removability by water. This means that in said element an image or signal in the form of electromagnetic radiation is recorded as a pattern of differences in permeability for and removability by water.

It is an object of the present invention to provide several embodiments of such type of recording.

It is another object of the present invention to produce a coloured copy or relief pattern of an original.

It is a further object of the present invention to produce a printing master e.g. a planographic or screen printing master. Other objects will become apparent of the description.

The present invention resides in a method for recording respectively reproducing information, which method comprises (1) information-wise exposing to active electromagnetic radiation a recording material comprising at least one waterpermeable recording layer essentially consisting of dispersed finely divided hydrophilic particles and one or more photoconductive compounds and (a) hydrophilic colloid(s), said photoconductive compounds and hydrophilic dispersed material and hydrophilic col-

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loid(s) being present in the recording layer in such an amount and the exposure being of such an intensity that the irradiated portions of the recording layer undergo a reduction in waterpermeability and removability with water in the irradiated portions, and (2) developing the so formed image by allowing to penetrate a liquid into the non-irradiated or insufficiently irradiated portions of the recording layer bringing about a visible change in these portions or by removal of the non-irradiated or insufficiently irradiated portions of the recording layer.

According to a special embodiment, the finely divided hydrophilic particles are itself photoconductive and consequently need not to be surrounded by other photoconductive substances.

The dispersed hydrophilic particles should be for the most part in very near proximity with each other (only separate from each other over a very small distance) in order that neighbouring particles in any given area of the recording layer can coagulate when the layer in that area, which is sensitive to electromagnetic radiation, is sufficiently irradiated.

A preferred recording material for use according to the present invention consists of or incorporates a water-permeable recording layer or sheet containing a finely divided hydrophilic photoconductive substance and/or non-photoconductive substance surrounded with a photoconductive substance in a hydrophilic proteinaceous binder, preferably in a ratio by weight of at least 1:1 in respect of said binder.

The finely divided hydrophilic substance is preferably composed wholly or mainly of (a) hydrophilic photoconductive inorganic substances(s), which is (are) preferably applied from an aqueous dispersion.

The photoconductive substances which can be applied in the present invention may be n-type as well as p-type semiconductors or combination of both types.

A change of the conductivity, possibly also charging capacity, electron-accepting or electron-emission power, in other words a change of the potential level of the photoconductive particles in respect of the dispersed material in the surrounding medium is assumed as being the cause that a coagulation of the said dispersed hydrophilic particles and probably also a reduction in water-solubility (flocculation) of the surrounding hydrophilic colloid takes place. This assumption is based on the knowledge that theoretically flocculation and coagulation are the same phenomena. Indeed, in a suspended solid system both phenomena are characterized by interparticular surface reactions annihilating or decreasing the repelling forces between separate dispersed particles (ref. Ind. Eng. Chem., C. P. Priesing, vol. 54, No. 8, 1962, p. 38-45 "A Theory of Coagulation Useful for Design").

Stability of colloidal particles in aqueous dispersions is attributed to hydration and electrostatic charge.

The dispersed particles present to the dispersing medium an electronic or electrostatic capacity, which means that they can lose, gain or share electrons by forming bonds such as ionic, covalent, hydrogen, dipolar, or induced dipolar bonds. These bonds can be classified in terms of bond energies (given as kilocalories per mole). Ionic crystal bonds are the strongest, viz more than 150 to 200, covalent bonds about 50 to 100, hydrogen bonds 1 to 10, and dipolar bonds less than 5. Similar to dipolar bonds are bonds being the result of induced polarization (London-van der Waals forces) in molecules and atoms,

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which normally are electrically neutral. Such bonds are also of low energy. In most coagulation processes, covalent bonds or ordered ionic crystal lattices are neither made nor broken, although the system is subject to ionic equilibrium in solution.

The electrical capacity formed around a dispersed particle is built up by the electrical double layer surrounding the particle. A fixed layer of electrostatic charges, e.g. of ions, surrounds the dispersed particle, which may originate from within the colloidal mass itself, or may be formed thereon by a preferential adsorption thereto of a dispersing agent.

In flocculation four forces act on both the dispersed phase and the coagulant, viz Brownian motion, gravity, coulombic charge and agitation.

Colloidal stability depends on several parameters, the most important being the water-adsorbing character of substances, valence and concentration of ions surrounding the dispersed particle having an electrical double layer. It is assumed that at least one of said parameters is changed by the exposure of the photoconductive compounds surrounding the hydrophilic dispersed material and/or being itself the hydrophilic dispersed material. Probably a discharge or reduction of charge present in the electrical double layer of the dispersed particles results in the coagulation of said particles. Another explanation of the reduction in water solubility of the recording layer may be based on the assumption that the hydrophilic colloid binder molecules, which are preferably of the proteinaceous type and are strongly solvated (with water) undergo a dehydration by building up an irreversible hydration layer around the irradiated hydrophilic dispersed photoconductive substances.

It is also possible that in the irradiated recording layer portions the photoconductor increases the electrolyte concentration above a critical value so that the conditions of coagulation for the hydrophilic binder are attained.

Having stated in general the concepts of this invention and having given a probable explanation of the working mechanism laying on the basis of the water-permeability-impermeability differentiation in the recording element by active information-wise electromagnetic radiation, we will give now a more detailed description of the composition and structure of various photosensitive elements, which form or make part of recording and reproduction materials suited for being used according to the present invention.

The water-permeable recording layer used in the present invention, preferably contains a water-soluble binding agent. In that respect caseine and gelatin are preferred hydrophilic colloids.

Proteinaceous binding agents of the same origin as gelatin and which replace gelatin for lowering the cost of the recording material can be used too. In that respect animal glue is to be mentioned particularly. Useful but not especially interesting are further hydratable polymeric polyhydroxy compounds e.g. cellulose derivatives such as hydroxyethylcellulose.

In the recording layer preferably gelatins with a high gel strength, preferably having a Bloom number greater than 180 are used.

The photoconductive substances may be sensitive to any type of electromagnetic radiation e.g. X-rays, ultraviolet light, visible light and/or infra-red light. If they are not sensitive for visible light they can be spectrally sensitized for that part of the spectrum by means of properly selected spectrally sensitizing agents.

Suitable hydrophilic photo-sensitive semiconductive compounds have been found in the group of heavy metal compounds of an element of the group 6B of the periodic table of elements.

Representatives of the said group of photoconductive metal compounds by means of which particularly useful results have been obtained are photoconductive heavy metal oxides and sulphides of the following list: ZnO, ZnS, PbO, TiO₂, Cr₂O₃, MnO₂, Pb₃O₄ and CdS.

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The particle size of the dispersed hydrophilic material, preferably photoconductive hydrophilic metal compounds, is preferably as fine as possible. The specific surface expressed in sq.m. per g. of the photoconductive powders is as high as possible, preferably at least 0.3 sq.m. per g. The average particle diameter is preferably below 0.1 μ to 50 μ .

Preferably such type of photoconductive zinc oxide is used, that is applied in electrophotographic recording materials, more preferably white photoconductive zinc oxide prepared by the oxidation of zinc vapour (according to the French process).

The zinc oxide particles have e.g. an average grain size of 0.1 to 50 μ .

In the preparation of a recording layer suited for use according to the present invention photoconductive lead(II) oxide yields excellent results. There are two types of lead(II) oxide viz red lead(II) oxide having a tetragonal crystal structure and yellow lead(II) oxide having an orthorhombic crystal structure. Lead(II) oxide powders consisting mainly of orthorhombic lead(II) oxide are preferred for the purpose of the present invention.

Further good results are obtained by means of titanium(IV) oxide especially the type useful for a recording process as described in United Kingdom patent specification 1,043,250. This specification relates to a method of producing a visible image in a copy medium comprising a radiation-sensitive metal-containing semiconductor compound, which becomes conductive on the impingement of radiation thereon, which method comprises exposing said medium to an image pattern of activating radiation, thereby reversibly activating said semiconductor compound to render it capable of causing chemical reaction at portions of said medium corresponding to said image pattern of radiation, and then developing reversibly activated portions of said medium by contacting at least said portions with a liquid redox system reacting on contact at said reversibly activated portions to form reaction products defining a visible image corresponding to said image pattern.

Titanium(IV) oxide particles having particularly good properties for use according to the present invention have an average particle size not greater than 250 millimicrons. Such finely divided titanium(IV) oxide is preferably produced by processes involving the pyrolysis of titanium(IV) chloride (see United Kingdom patent specification 1,101,516).

Titanium(IV) oxides having an average particle size between 25 and 100 millimicrons are preferably used. By "average particle size" we mean the particle size at the peak of the frequency distribution graph of a mixture of particles having decreasingly numbers of larger particles and of smaller particles.

The inorganic photoconductive compound(s) is or (are) preferably used in a ratio by weight varying between 1:1 and 5:1 in respect of the hydrophilic binder.

The inorganic photoconductive semiconductor materials can be sensitized by a number of techniques known in the art such as doping with foreign ions, dye sensitization and heating.

According to a preferred embodiment the recording layer contains as photoconductive substances photoreducible dyes. The photoreducible dyes intended here are incapable of being reduced in the absence of light by a thiol polymer such as gelatin to which sulfhydryl groups were added, (so-called thiolated gelatins), but capable of being reduced by the sulfhydryl groups of the polymer when photo-excited with visible light.

For such type of dyes reference is made to the U.S. patent specification 3,145,104. These photo-reducible dyes include members of the fluorescein class, the thiazine class, the acridine class and the porphyrin class. Suitable photoreducible dyes are e.g. rose bengal, phloxine, erythrosine, eosine, fluorescein, acriflavine, thionine, riboflavine, and methylene blue. The dyes soluble in an aqueous medium are preferred.

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Photoconductive substances that are compatible (form a solid state solution) with the hydrophilic binder can be used advantageously in combination with dispersed non-photoconductive hydrophilic substances such as hydrophilic non-photoconductive pigments e.g. waterinsoluble hydrophilic salts e.g. barium sulphate, hydrophilic carbon black, and hydrophilic metal or non-photoconductive metal oxide particles.

The non-photoconductive hydrophilic pigments are preferably surrounded with organic photoconductive dyes that are spectrally sensitizing agents for photoconductive zinc oxide.

Such dyes are found in the class of: xanthene dyes preferably fluorescein dyes, thiazine dyes, and acridine dyes. A large number of these dyes are characterized by their fluorescein and are described e.g. in the U.S. patent specification 2,875,047.

For the photoconductive properties of fluorescein dyes such as eosine reference is made e.g. to "Semiconductive properties of organic dyes" by A. T. Vartanyan, Izvest. Akad. Nauk, U.S.S.R., Ser. Fiz. 16 (1952), pp. 169-185, cf. C.A. 45, 3709 i).

The dyes are preferably applied in dissolved form. Preferably they are dissolved in water and added in that state to the dispersion of the hydrophilic particles in the hydrophilic binder.

A very good sensitivity is obtained with fluorescein dyes such as eosine, erythrosine and rose bengal.

The photoreducible photoconductive dyes can be used in an amount as low as 0.05% by weight in respect of the hydrophilic dispersed particles, which are preferably dispersed photoconductive pigments.

Apart from the increase of the spectral sensitivity by means of spectral sensitizing dyes for the dispersed hydrophilic photoconductive substances or the use of coloured photoconductive substances for obtaining spectral sensitivity in the visible light range it is possible to increase the total sensitivity of recording layers suited for use according to the present invention by means of waterattracting substances, e.g. waterattracting polyols more preferably glycerol. Other useful polyol compounds are e.g. sorbitol and ethylene glycol. Ionic hygroscopic or slightly hygroscopic compounds or compounds crystallizing with a fairly large number of crystal water (hydratable ionic compounds) e.g. lithium chloride, potassium bromide, sodium chloride, sodium sulphate and lead acetate give also rise to an increase in photosensitivity.

Preferred recording layers contain glycerol and gelatin in a ratio of by weight from 10 to 80%. Optimal results are obtained by using 40% by weight of glycerol in respect of a proteinaceous colloid such as gelatin and casein.

An increase in photo-sensitivity in the visible spectrum range is further obtained with visible light absorbing pigments that are not necessarily photoconductive.

Preferred are finely divided hydrophilic visible light absorbing inorganic pigments such as hydrophilic carbon black, prussion blue, coloured hydrophilic oxides and sulphide of carbonates of heavy metals, particularly of those heavy metals having an atomic weight between 45 and 210, such as iron(III) oxide, cadmium sulphide, manganese oxides, or these heavy metals themselves in finely divided state such as silver, bismuth, lead, iron, cobalt, and nickel. As organic dyestuffs in pigments form preferably organic dyes, which are dispersible in a hydrophilic colloid medium, are used, e.g. water-insoluble azo dyes, anthraquinone dyes and phthalocyanine dyes.

The recording element used according to the present invention may further contain dyes that can be bleached, plasticizers, fillers, e.g. silica, coating aids, e.g. wetting or spreading agents, substances influencing the gloss or ageing, metal particles, e.g. metal particles that can be etched, reaction components or dyes that can be distilled preferably below 80° C., developing nuclei for e.g. complexed silver halide, photo-sensitive substances that directly on exposure or by a development can form a visible image

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e.g. photosensitive silver halide, diazonium compounds etc., possibly in the presence of developing agents or colour coupling agents. Further this layer may comprise latent hardening agents for the binder, which harden the binder at elevated temperatures.

The amount by weight of dispersed hydrophilic substance (which can be a photoconductive substance itself) in respect of the hydrophilic binder is one of the main features determining the photo-sensitivity.

From the following table sensitivity values as a function of layer-composition can be learned.

The recording layers contained 40% by weight of glycerol in respect of the hydrophilic binder.

The recording layers were exposed through a grey step wedge (which can be a photoconductive substance itself) with a 1500 w. quartz-iodine lamp held at a distance of 65 cm. of the recording layers.

Under the same circumstances all the exposed materials were subjected to a wash-off development in an automatically operating wash-off apparatus as described in the published Dutch patent application 6807686. The light-energy corresponding with the first non-washed-off step is a measure for the sensitivity.

Note that the exposure light is poor in ultra-violet rays and the photoconductive zinc oxide is mainly U.V. light-sensitive.

TABLE

Test No.	Ingredients of the recording layer g./m. ²			Sensitivity	
	Casein	Photoconductive zinc oxide (0.17 μ)	Hydrophilic carbon black (0.1 μ)	Lux. sec. 10 ⁶	Joule/cm. ²
1	1	5	-----	>90	>1,150
2	1	5	1	6.5	75
3	1	2.5	1	57	700
4	1	5	0.025	3.6	46
5	1	2.5	0.025	9	125
6	1	1	0.025	28	350
7	1	-----	0.025	>>90	>>1,150

According to their purpose the materials comprising a photosensitive element according to this invention may be composed differently. By way of example the photosensitive layer containing the photocoagulable composition may be applied to a hydrophilic layer, which occasionally serves as a support. By hydrophilic layer is understood a layer that is wettable by water or by aqueous solutions. Such a layer may be porous or water-permeable. By way of example this hydrophilic layer may be composed mainly of natural or synthetic colloids that are soluble or dispersible in water. Examples of such layers are a gelatin layer, a light-sensitive silver halide emulsion layer, a water-permeable nuclei-containing colloid layer for application of the silver complex diffusion transfer process, a baryta-coating comprising gelatin and barium sulphate, a gelatin layer containing pigments or dissolved dyes, or containing reaction components capable to produce a colour reaction, a gelatin layer containing developing substances for silver halide or complexed silver halide, or a gelatin layer containing finely divided metal that can be etched away, e.g. silver.

Further, the recording layer according to the present invention can be applied between two hydrophilic layers, a hydrophilic and a hydrophobic layer, between two permeable layers, or between a permeable and in impermeable layer.

A layer or sheet being in contact or water-permeable relationship with the photosensitive layer may contain all kinds of ingredients, e.g. ingredients that can be of practical interest to provide adherence to the recording layer. In other words such a layer may act as a subbing layer.

Other ingredients may be of interest to develop the recorded image, e.g. pigments, dyes, reaction components for the formation of dyes, developing substances, reaction components or dyes, which can be distilled preferably below 80° C., light-sensitive substances, e.g. silver halide or diazonium salts, developing nuclei suited for use in the silver halide diffusion transfer process, catalysts for colour reactions, and/or conductive particles, e.g. metal particles.

Depending on the use of the recording material the support of the recording layer may be rigid or flexible.

When flexibility is preferred a sheet element such as e.g. a paper sheet, a plastic film, a metal foil or the like is used. When flexibility is unimportant, plates of metal, glass, plastics, fiber board, cardboard or the like may be used. The support may be permeable as well as impermeable e.g. it may be water-permeable such as a wire screen or a web of textile.

Suitable water-impermeable supports are made of hydrophobic resins, e.g. of cellulose ester derivatives, polyesters, polystyrene, hydrophobic metal, hydrophilic metal coated with a hydrophobic layer e.g. an oxide layer, glass and the like. In order to improve the adherence of the recording layer to its support one or more subbing layers may be applied.

Recording according to the present invention can proceed in different ways according to the method in which radiation is supplied to the recording element.

Indeed, the exposure can be of any type known in the art, although a direct exposure (non-reflectographic exposure) is preferred. During the exposure the recording material may be heated to speed up or improve the information-wise impermeabilization of the recording layer.

According to one embodiment, a transparent original bearing light-absorbing indicia is recorded by bringing the photosensitive element of a recording material according to the present invention into contact with said original, and exposing said photosensitive element with electromagnetic radiation modulated by the contacting original. The irradiation is of such spectral composition, intensity and duration that the information contained in the original is recorded in terms of water-permeability differences and removability differences (e.g. by wash-off) of the recording layer.

According to another embodiment of photographic recording there is no direct contact between the photosensitive material and the original. In that case, an opaque or transparent original is projected onto the recording material (episcopically or diascopically projection). Thus, the present invention offers the possibility of making enlarged photographs by projection-exposure.

Before giving some examples for practising the method of the present invention, a short survey is given of different systems that are suited for the manufacture of copies and masters for the reproduction of originals starting from an electromagnetic-radiation-imaged recording material according to the present invention. This survey is intended for illustrating the possibilities and advantages of the invention without limiting therefore the scope of this invention.

According to a first system, the image-wise differentiation in permeability is utilised for applying by image-wise diffusion image-forming substance or substances in the recording element by a liquid treatment or from the recording element to a receiving material respectively, said image-wise diffusion being possible as a consequence of the permeability differentiation.

By way of example for the first system said imaged recording material is dipped into an aqueous dye solution, whereby the dye diffuses in the recording element (layer or sheet) only on the areas that remained permeable and sufficiently hydrophilic. Of course, instead of a dye solution, a solution of a catalyst for initiating a colour reaction between components in the recording material or a solution of a colourless reaction component capable of

giving a colour reaction with a colourless or slightly coloured reaction component in the recording material can be used.

By way of another example for the first system it is possible to incorporate into the recording element coloured substances which can be bleached out by a bleaching agent diffusing in the areas of the recording material that remained permeable. According to an alternative of that system, a conductive substance, e.g. a metal that can be etched away such as colloidal silver, and that is homogeneously dispersed in the recording element, is image-wise etched away by an etching liquid diffusing into the permeable areas. The photosensitive layer can be applied to an etchable base material, e.g. a resin sheet coated with aluminium. When using this material it is possible by image-wise etching to produce a planographic, lettertype or intaglio printing master.

In a second embodiment of image-formation wherein diffusion is applied, the image-forming substance incorporated into the recording material is transferred by diffusion from the areas that remained permeable to an image-receiving material. So, it is possible, e.g. to incorporate a soluble dye into the recording element or into a layer being in a liquid-permeable relationship therewith, said dye being capable of diffusing therefrom image-wise to a receiving material when the photographically exposed recording element is wetted.

Self-evidently, instead of a dye a colourless reaction component or catalyst for the formation of a colour reaction with a reaction component in the receiving material can be incorporated into the recording element.

So, it is also possible to incorporate into the recording material silver salts that can be complexed and that in their dissolved form can diffuse to a receiving material containing reduction nuclei or development nuclei, whereupon according to the areas of the recording material that remained permeable, silver is deposited image-wise.

In these diffusion methods the image-forming substances such as a dye, a metal that can be etched away, or reaction components need not be present in the recording element itself; they can also be incorporated into a layer or support being in a water-permeable relationship therewith.

According to a second system the portions of the information-wise electromagnetically irradiated recording material that remained sufficiently water-permeable and water-soluble are eliminated e.g. by washing out or degrading of the hydrophilic binder. By that technique a direct visible copy of the information is obtained when the recording element comprises already before its exposure a dye, e.g. a (coloured) pigment and/or a dissolved dyestuff.

By applying said second system, a gravure master can be produced by starting from the imaged recording layer, which is applied to a metal support that can be etched. After elimination of the portions of the recording layer that remained permeable and hydrophilic, e.g. by washing out and after making the portions of the recording layer left sufficiently resistant to the etching solution, the uncovered metal can be etched away image-wise. In this way e.g. printed circuits can be produced. After the elimination, e.g. by intensively rubbing the portions of the recording layer left after the wash-off development, the etched metal plate according to the depth and measure of etching can be used as a planographic printing master, a gravure master, or a letter press master.

By applying said second system also a stencil or screen-printing master can be manufactured by starting from an information-wise electromagnetically irradiated recording material according to the invention. For this technique either one or both sides of a screen material are coated with a recording layer, or the screening material makes part of a self-supporting sheet as described hereinbefore. As screen material Japan paper (Yoshino

paper), nylon fabrics with a size of mesh of 0.2 to 0.08 mm. and woven bronze wire are especially suited.

For the screen-printing technique it is known that only on the open (permeable) areas of the fabric (screen material) ink can pass and deposit on the material to be printed corresponding to these areas. The image-wise open areas are obtained according to the present invention by washing out or degrading the recording layer composition in the areas where this layer or sheet remained permeable and hydrophilic.

According to a third system the image portions that remained permeable and hydrophilic are transferred onto a receiving material by squeezeing and tearing out.

This type of transfer is possible if the cohesion of the matter of the receiving material is larger than that of the matter in the permeable portion of the recording layer, and if the adhesion between said permeable portion and the receiving material is larger than the cohesion of the matter of said permeable areas.

This transfer successfully occurs when separating after pressing together a wetted information-wise electromagnetically irradiated recording element according to the present invention from a receiving material preferably having a hydrophilic and/or porous surface, e.g. a paper sheet.

The contrary type of transfer is possible if the cohesion of the matter of a transfer material is less than that of the matter in the permeable portions of the recording layer, and if the adhesion between said permeable portions and the transfer material is larger than that of the matter of said transfer material. E.g. a dye layer of a carbon paper being little hydrophobic on its surface, such as is used in the process according to the French patent specification 1,466,223, after being pressed onto the moistened heat- or pressure-imaged material, can be transferred image-wise to the permeable and hydrophilic areas of the recording material on separating it therefrom. Before pressing the recording layer into contact with the dye layer, the hydrophilic binder of the recording layer can be swollen so that a relief image is formed that makes possible a closer contact with the dye layer.

According to this third system it is thus possible to manufacture hectographic masters since the pulled out material can contain a hectographic dye that is soluble in the transfer liquid or can contain a reaction component forming a dye with a reaction component present, e.g., in the transfer liquid or transfer material.

According to a fourth system it is possible by using a low melting dye in the recording element, to transfer this dye by heating the recording element after wash-off development in contact with a receiving material.

The following examples are presented to illustrate but not to limit the preferred means for carrying out the invention.

The present ratios are "by weight" if not otherwise indicated.

EXAMPLE 1

24 g. of a commercial massicot (yellow lead(II) oxide containing 30 p.p.m. of bismuth and having an average particle size of 5μ) were ball-milled for 1 h. in the presence of 32 ccs. of demineralized water.

To the obtained dispersion was added the following solution consisting of:

Gelatin	-----g--	15
Demineralized water	-----ml--	113
Glycerol	-----g--	12
12.5% solution of saponine in demineralized water	-----ml--	1

The composition was coated onto a subbed cellulose triacetate support at such a rate that after drying, a re-

cording layer of 40μ thick was obtained. The light-sensitive material was contact-exposed for 5 min. through a screened halftone transparency by means of a Philips HPR 125 lamp placed at a distance of 30 cm. Thereupon the exposed light-sensitive layer was treated with water of 40° C. resulting in the removal of the non-exposed portions of the recording layer. The residual portions of the recording layer were treated with a 5% aqueous solution of sodium sulphide in order to increase the optical density of the portions containing non-exposed yellow lead(II) oxide. The thus treated material was rinsed and a stable, black, very dense negative print of the original was obtained.

EXAMPLE 2

24 g. of lead(II) oxide as described in Example 1 were ball-milled for 1 h. in the presence of 60 ccs. of demineralized water and 4 g. of sodium hexametaphosphate as dispersing agent.

To the obtained dispersion was added the following solution consisting of:

Gelatin	-----g--	15
Demineralized water	-----ml--	85
Glycerol	-----ml--	6
A 12.5% solution of saponine in demineralized water	-----ml--	6

The composition was coated onto a subbed cellulose-triacetate support at such a rate that after drying a recording layer of 18μ thickness was obtained. The recording material was placed with its support into contact with a negative halftone transparency of an original and through the transparency exposed for 20 min. with a Philips HPR 125 lamp placed at a distance of 30 cm. Next, the exposed material was treated as described in Example 1. A black positive halftone print of the original was obtained.

EXAMPLE 3

24 g. of the lead(II) oxide as described in Example 1, were ball-milled for 1 h. in the presence of 32 ccs. of demineralized water, 2 g. of sodium hexametaphosphate and 2 g. of an aqueous carbon black dispersion, which contains per 100 g.; 43 g. of carbon black having an average particle size of 0.1μ , 23 g. of water, 18 g. of ethylene glycol and 6 g. of nonylphenylpoly(ethylene oxide)_n ($n=9$).

To the obtained dispersion was added the following solution consisting of:

Gelatin	-----g--	15
Demineralized water	-----ml--	113
Glycerol	-----g--	6
12.5% aqueous solution of saponine	-----ml--	1

The whole composition was coated onto a subbed cellulose triacetate support at such a rate that after drying a recording layer of 21μ thickness was obtained. The density measured by transmission was 1.72. The exposure was the same as for the material described in Example 2. The exposed material was treated with water of 40° C. resulting in a gradual washing away of the unexposed portions of the recording layer. Finally a black positive halftone image was obtained.

EXAMPLE 4

24 g. of lead(II) oxide as described in Example 1 were ball milled for 1 h. in the presence of 32 ccs. of demineralized water.

To the obtained dispersion was added the following solution consisting of:

Gelatin	-----g--	15
Demineralized water	-----ml--	113
Ethylene glycol	-----g--	2
12.5% aqueous solution of saponine	-----ml--	1

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The whole composition was coated onto a subbed cellulose triacetate support at such a rate that after drying a recording layer of 30μ thickness was obtained. The obtained recording layer was laid with its support onto a microfilm line image to be copied and exposed through the film in a Buroza 600 diazotype copying apparatus (from Atlas, Delft, the Netherlands) at a copying speed of 30 cm. per minute.

The exposed material was treated as described in Example 1. A black negative copy of the microfilm image was obtained.

EXAMPLE 5

24 g. of lead(II) oxide as described in Example 1 and 2 g. of sodium hexametaphosphate were ball-milled for 1 h. in the presence of 32 ccs. of demineralized water.

To the obtained dispersion was added the following solution consisting of:

Gelatin	-----g--	15
Demineralized water	-----ml--	113
Sorbitol	-----g--	12
12.5% solution of saponine in demineralized water	-----ml--	1

The whole composition was coated onto a subbed cellulose triacetate at such a rate that after drying a recording layer of 20μ thickness was obtained. Exposure through a transparent line original was carried out as described in Example 4.

The exposed recording layer was treated with water of 35°C . till all the non-exposed portions were washed off. A treatment of the exposed remaining portions with a 5% aqueous solution of sodium sulphide resulted in a black negative copy of the original.

EXAMPLE 6

24 g. of lead(II) oxide as described in Example 1, 2 g. of sodium hexametaphosphate and 60 ccs. of demineralized water were ball-milled for 1 h.

To the obtained dispersion was added the following solution consisting of:

Gelatin	-----g--	15
Demineralized water	-----ccs--	85
Glycerol	-----g--	6
12.5% solution of saponine in demineralized water	-----cc--	1

The whole composition was coated onto a subbed cellulose triacetate support at such a rate that after drying a recording layer of 26μ thickness was obtained.

The recording material was image-wise exposed through a transparent line original in a diazotype copying apparatus as in Example 5 at a copying speed of 8 cm. per min.

The exposed recording layer was moistened with water of 15°C . and after 2 min. the recording layer was pressed against a sheet of porous paper (filter paper).

At a speed of 8 cm. per sec. the whole sandwich was led between two pressure rollers at a temperature of 48°C .

Thereupon the filter paper was peeled off from the recording layer and for a while dipped into a 5% aqueous solution of sodium sulphide. A good black copy of the original was obtained on the filter paper.

EXAMPLE 7

24 g. of zinc sulphide having an average particle size of 5μ and 2 g. of sodium hexametaphosphate were ball-milled for 1 h. in the presence of 60 ccs. of demineralized water.

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To the obtained dispersion was added the following solution consisting of:

Gelatin	-----g--	15
Demineralized water	-----ml--	85
Glycerol	-----g--	6
12.5% solution of saponine in demineralized water	-----ml--	1

The whole composition was coated onto a subbed cellulose triacetate support at such a rate that after drying a recording layer of 68μ thickness was obtained.

The recording material was laid with its support onto a transparent line original and exposed through the latter for 30 min. by means of a 500 watt tungsten filament lamp placed at a distance of 25 cm. Thereupon the non-exposed portions were washed-off with water of 35°C . A negative copy of the original was obtained. In said copy the image parts have a white opaque aspect due to the zinc sulphide of the recording layer.

EXAMPLE 8

15 g. of titanium(IV) oxide (TiO_2) containing 60% by weight of anatase in its crystal structure and having an average particle size of 15-40 nm. was ball-milled for 1 h. in the presence of 1 g. of sodium hexametaphosphate and 60 ccs. of demineralized water.

To the obtained dispersion the following ingredients were added:

15% solution of gelatin in demineralized water	-----g--	100
Glycerol	-----g--	6
12.5% solution of saponine in demineralized water	-----ml--	1

The whole composition was coated onto a subbed cellulose triacetate support at such a rate that a recording layer with 15.5 g. of titanium(IV) oxide per sq. m. was obtained.

After drying, the recording material was image-wise exposed through a transparent line original in a diazotype copying apparatus as in Example 5. Copying was effected by conveying the whole sandwich twice through the apparatus at a speed of 8 cm. per min.

Thereupon the non-exposed portions of the recording layer were washed out with water of 35°C . A white opaque negative copy of the original was obtained.

EXAMPLE 9

24 g. of lead(II) oxide as described in Example 1, and 2 g. of sodium hexametaphosphate were ball-milled for 1 h. in the presence of 60 ccs. of demineralized water.

To the obtained dispersion the following ingredients were added:

15% solution of animal glue in demineralized water	-----g--	100
Glycerol	-----g--	6
12.5% solution of saponine in demineralized water	-----ml--	1

The whole composition was coated onto a subbed cellulose triacetate support at such a rate that after drying a recording layer of 25μ thickness was obtained.

The recording material was image-wise exposed through a transparency of a line image in a diazotype copying apparatus as in Example 5, at a copying speed of 30 cm. per min.

The non-exposed portions of the recording layer were washed out with water of 35°C . An opaque yellow-grey negative copy of the original was obtained. The greyish tone of the copy was the result of a print-out effect whereby some lead metal is formed on exposure.

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EXAMPLE 10

A poly(ethylene terephthalate) support of 0.1 mm. thickness was coated with the following subbing layer composition in a proportion of 18 g./sq. m.:

20% aqueous dispersion of copolymer of vinylidene chloride, n-tert-butylacrylamide and itaconic acid (molar ratio 88/10/2) -----	12
40% aqueous dispersion of polyethylene having a particle size of less than 0.1 μ and an average molecular weight comprised between 15,000 and 30,000 -----	12
30% aqueous dispersion of colloidal silica -----	12
Ethyl alcohol -----	100
Water -----	864

This subbing layer was dried at 30° C. On this layer a light-sensitive layer from the following composition was coated in a proportion of 30 g./sq.m.:

10% aqueous solution of gelatin which has a Bloom strength of 260 -----	100
5% aqueous solution of isooctylphenyl poly(ethylene oxide) _n (n=9) -----	10
Water -----	200
Chromium(III) oxide -----	75

The chromium(III) oxide was added whilst strongly stirring as a powder having an average particle size of 5 μ . The light-sensitive material thus obtained was vacuum-contact exposed for 20 minutes through a developed silver halide emulsion layer containing a negative halftone print by using a 1500 watt quartz iodine lamp mounted in a reflector and placed at a distance of 30 cm. above the vacuum frame.

After exposure, the material was rubbed with a soft sponge abundantly moistened with water of 30° C. The nonexposed parts were thus wiped off and a relief image was obtained.

When in the composition of the light-sensitive layer the Cr₂O₃ was replaced by MnO₂, Pb₃O₄ or CdS (same amounts and same particle size) analogous results were obtained.

EXAMPLE 11

24 g. of zinc sulphide having an average particle size of 5 μ and 1 g. of sodium hexametaphosphate were ball-milled for 1 h. in the presence of 60 ccs. of demineralized water.

To the obtained dispersion the following ingredients were added:

1% solution in demineralized water of commercial hydroxyethylcellulose with a degree of substitution (DS) of 0.85 and a molecular degree of substitution MS of 1.33, the viscosity of which as a 2% solution in water of 20° C. is 3500 cp. ---ccs---	100
70% solution of sorbitol in water -----g---	6
12.5% solution of saponine in demineralized water -----cc---	1

The whole composition was coated onto a subbed cellulose triacetate support at such a rate that after drying a recording layer of 18 μ thickness was obtained.

The recording material was laid with its support onto a transparent line original and exposed through the latter for 3 h. by normal daylight. Thereupon the non-exposed portions were washed away with water of 35° C. A negative copy of the original was obtained. In said copy the image parts had a white opaque aspect owing to the zinc sulphide in the recording layer.

EXAMPLE 12

A poly(ethylene terephthalate) base of 0.1 mm. thickness provided with a subbing layer for gelatin coatings

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was coated with the following composition in a proportion of 60 g./sq.m.

20% aqueous gelatin solution -----	100
50% aqueous dispersion of photoconductive zinc oxide (average particle size 0.17 μ) -----	200
Glycerol -----	8
Permanent Gelb H.R. Colanyl Teig C.I. 20,000 (a yellow diazo dye dispersion marketed by Farbwerke Hoechst A.G., Frankfurt am Main, Germany) -----	4
Permanent Carmin FBB Colanyl Teig C.I. 11,000 (a carmin red monoazodye dispersion marketed by Farbwerke Hoechst A.G., Frankfurt am Main, Germany) -----	20
Heliogen Grün G.N. Colanyl Teig (a green pigment dye dispersion marketed by Badische Anilin- & Soda-Fabrik A.G., Ludwigshafen (Rhine), Germany) -----	26
Ethanol -----	45
Water -----	177

The layer was dried at 20° C. and contact-exposed for 5 minutes through a negative line original in a flat contact-exposure apparatus containing white fluorescent light tubes each of 20 w. placed below a glass plate of 45 cm. x 65 cm. and yielding a 20,000 lux light output. After exposure the layer was rubbed with a soft sponge while it was abundantly wetted with running water of 30° C. The non-exposed parts were washed-off and a sharp positive copy was obtained.

EXAMPLE 13

A poly(ethylene terephthalate) base of 0.1 mm. thickness provided with a subbing layer was coated with the following composition in a proportion of 60 g./sq.m.:

10% aqueous solution of gelatin having a Bloom gel strength of 240 and an isoelectric point of 8.6 -----	200
50% aqueous dispersion of photoconductive zinc oxide (average particle size 0.17 μ) (French process type) -----	200
Glycerol -----	8
Ethanol -----	45
1.5% aqueous solution of isotetradecylsulphate -----	20
Mixture of aqueous dispersion of coloured pigments in the ratio as mentioned in Example 1 -----	50

The pH of the coating composition was adjusted to 10 with 5 N aqueous sodium hydroxide. After drying at 20° C. the material was exposed and treated as described in Example 1. The same result was obtained.

EXAMPLE 14

A poly(ethylene terephthalate) base provided with a subbing layer as described in Example 12 was coated with the following composition in a proportion of 50 g./sq.m.:

10% aqueous solution of a gelatin with a Bloom gel strength of 185 -----	200
50% aqueous dispersion of photoconductive zinc oxide (average particle size 0.17 μ) -----	200
Permanentschwarz P.R. Colanyl Neu (trade name for an aqueous carbon dispersion sold by Hoechst A.G., Frankfurt am Main, Germany) -----	20
Lithium chloride -----	8
Ethanol -----	45
Water -----	100

This layer was dried at 25° C. and exposed for 3 min. through a negative line original with a quartz iodine lamp of 1500 w. at a distance of 60 cm. After exposure the material was kept in the dark for 30 min. and then treated with water of 30° C. The non-exposed parts were washed-off and a positive image was obtained. When lithium chloride was replaced by a same amount of

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sodium chloride or sodium sulphate the same results and when replaced by a same amount of lead acetate still better results were obtained.

EXAMPLE 15

40 g. of barium sulphate as used in baryta-coatings of photographic silver halide materials were ball-milled for 1 h. in the presence of 160 ml. of demineralized water and 5 ml. of sodium hexametaphosphate.

To the obtained dispersion the following composition was added whilst stirring:

10% solution of casein in demineralized water (pH of the solution: 9) -----ml---	100
Glycerol -----ml---	2
Potassium bromide -----g---	4
5% aqueous solutions of nonylphenyl poly(ethylene oxide) _n (n=9) -----ml---	10
Erythrosine (C.I. 45,430) -----g---	0.25
Demineralized water -----ml---	100

The obtained composition was coated on a subbed celluloseacetate support at such a rate that after drying a layer of 6 μ thick was obtained.

The recording material was vacuum-contact exposed for 10 min. through a transparent line original using a 1500 watt quartz-iodine lamp mounted in a reflector and placed at a distance of 65 cm. above the vacuum-frame.

After exposure the material was rubbed with a soft sponge abundantly moistened with water of 20° C. The non-exposed parts were thus wiped off and a coloured relief image was obtained.

What we claim is:

1. A method for recording information, which method comprises (1) image-wise exposing to substantially visible or ultra-violet light a recording material comprising at least one water-permeable recording layer essentially consisting of finely divided particles of a hydrophilic inorganic photoconductive compound of the group consisting of the oxides and the sulfides of zinc, lead, titanium, chromium, manganese and cadmium dispersed in at least one proteinaceous hydrophilic colloid binder, said photoconductive compound undergoing a change in conductivity upon exposure to said substantially visible or ultra-violet light, said photoconductive particles and hydrophilic colloid binder being present in the recording layer in a ratio by weight of about 1:1 to 5:1, the exposure being of such an intensity and duration that the hydrophilic colloid in the exposed regions of said recording layer becomes substantially impermeable to water as a consequence of the response of said photoconductive particles to said exposing light, and (2) forming said impermeabilized regions into a visible relief image by removing the unexposed layer regions of unchanged permeability by washing away the same with an aqueous liquid or by wetting said recording layer with an aqueous liquid and transferring the permeable regions to a separate substrate by pressing the recording layer against a substrate for which the liquid-permeated regions are adherent.

2. A method according to claim 1, wherein the hydrophilic particles are applied from an aqueous dispersion.

3. A method according to claim 1, wherein the hydrophilic particles size from below 0.1 μ to 50 μ .

4. A method according to claim 1, wherein the hydrophilic binder is soluble in water.

5. A method according to claim 1, wherein the photoconductive compound is selected from the group consisting of photoconductive zinc oxide, zinc sulphide, titanium(IV) oxide, lead(II) oxide, red lead oxide (Pb₃O₄), chromium(III) oxide, and cadmium sulphide.

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6. A method according to claim 1, wherein the recording layer contains a water-attracting polyol or hygroscopic ionic compound.

7. A method according to claim 6, wherein the recording layer contains glycerol.

8. A method according to claim 1, wherein the recording layer is treated with an aqueous solution of a dye-stuff, or a dye-forming component.

9. A method according to claim 1, wherein the recording layer is applied to a screen base, and a screen printing master is produced by washing out the portions of said layer that remained sufficiently water-permeable after the exposure-wise exposure to said radiation.

10. A method of recording information which comprises (1) image-wise exposing to active electromagnetic radiation a recording material consisting essentially of a continuous phase of a proteinaceous hydrophilic colloid binder having uniformly distributed therethrough finely divided particles of a non-photoconductive hydrophilic pigment and a photoconductive fluorescein, thiazine, acridine or porphyrin dye compatible with said hydrophilic binder, said particles and said binder being present in a ratio by weight of about 1:1 to 5:1 and said dye in the amount of at least about 0.05% by weight of said particles, said exposure being of such an intensity and duration that the irradiated portions of the layer become substantially impermeable to water, and (2) developing the resultant image by contacting the recording layer with an aqueous liquid permeating the unexposed regions of the layer and removing the thus-permeated regions while the exposed regions of the layer remain intact.

11. The method of claim 10 wherein said unexposed regions are removed by contacting the recording layer with sufficient liquid to wash said regions away.

12. The method of claim 10 wherein said unexposed regions after being contacted with said aqueous liquid are transferred from said recording layer to a receiving material by pressing the recording layer against a receiving material for which the water-permeated regions of the recording layer are adherent.

13. The method of claim 10 wherein said radiation is substantially visible light.

14. A method according to claim 10, wherein said photoconductive dye has spectral sensitizing properties with respect to photoconductive zinc oxide.

15. A method according to claim 10, wherein the said dye is a photoreducible dye.

16. A method according to claim 15, wherein the photoreducible dye is soluble in an aqueous medium.

17. A method according to claim 15, wherein as photoreducible dyes a fluorescein dye is used.

18. A method according to claim 17, wherein as photoreducible fluorescein dye, eosine and/or erythrosine is used.

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GEORGE F. LESMES, Primary Examiner

J. P. BRAMMER, Assistant Examiner

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96—1, 1.5, 1.8, 27, 35, 48; 250—65

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,674,483 Dated July 4, 1972

Inventor(s) Marcel N. VRANCKEN et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Heading of the Patent, in the claim of priority,
insert after "28,778/68", -- and British Application No.
53.677/68, November 12, 1968 --.

Signed and sealed this 24th day of April 1973.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents