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(54) Image-forming by heating recording material containing light-sensitive organic substance.

(57) A recording material contains on a 20 - 200 µm thick paper or plastics support a 2 - 30 µm layer of a dispersion of particles of a light-sensitive organic substance which forms a decomposition product when light-exposed and an organic substance which reacts imagewise (e.g. a diazo compound and its coupler or a photo-oxidizing agent and a leuco dye); at least one of these may be microencapsulated. The material is imagewise exposed, e.g. from a fluorescent lamp, and overall heated in two steps, firstly at a temperature (e.g. 60 - 90 °C) at which no formation or fixing of the image occurs and then at a higher temperature (e.g. 80 - 150 °C) to cause the reaction to form a visible image.

The first heating can be at the time of the imagewise exposure, e.g. by the heat from the lamp. The material is transferrd between the heating steps as fast as possible. The use of the first heating allows less energy to be used for the development step.

Diazo material used can contain other components such as a color forming aid or substance fusible at 50 - 150 °C.

Visible images are formed of good colour density, low background fog and good shelf life before use.

IMAGE-FORMING BY HEATING RECORDING MATERIAL CONTAINING LIGHT-SENSITIVE ORGANIC SUBSTANCE

This invention relates to image-forming on a light-sensitive recording material and, more particularly, on a recording material having a good shelf life and yet giving a high color density of image and a good image preservability, by conducting thermal development or thermal fixing even at a low temperature.

This invention relates to an image-forming method by exposing the aforesaid recording material in conformity with an original image to form a latent image or an image in the recording layer, then wholly heating the recording layer to develop or fix the image. The latent image or the image formed in the recording layer by the imagewise exposure is a negative image or a positive image of the original depending upon whether a light-sensitive organic substance used in the recording layer is rendered active or inactive against a labelling organic substance by irradiation with light.

The labelling substance capable of discriminating a light-sensitive organic substance and a photo decomposition product of said light-sensitive organic substance from each other have been known as compounds which undergo reaction, change in phase or in substance permeability, etc. Therefore, in establishing a recording system utilizing these mechanisms, compounds requiring less heat energy for the change enable the realization of a cheaper and more compact system.

However, recording materials to be applied to the above-described system are required to undergo the least change in properties during storage regardless of storage conditions and storage period before recording which, however, contradicts the requirement that the heat energy required for recording be minimized. That is, recording materials capable of being developed or fixed at lower temperatures more easily undergo mutual change between the light-sensitive organic substance and the labelling organic substance during storage before recording, which results in inconvenient formation of recorded images which essentially should not be recorded (generally called "fog") or coloration failure in recorded portions which should be colored with high density.

As an example of recording materials utilizing the above-described recording system, a diazo type recording material is described below.

Recording materials utilizing light-sensitivity of diazo compounds are roughly grouped into three types. First type recording materials are those which are known as wet-process development type, which comprise a support having a provided thereon a light-sensitive layer containing a diazo compound and a coupling component as major components and which, after imagewise exposure in superposition with an original, is developed with an alkaline aqueous solution. Second type materials are those which are known as dry-process development type and which are developed with ammonia gas; this is different from the wet-process type. The third type are those which are known as thermally-developable type including a type containing in the light-sensitive layer an ammonia gas generator such as urea capable of generating ammonia gas upon being heated, a type containing in the light-sensitive layer an alkali salt of an acid such as trichloroacetic acid which loses acidic properties upon being heated and a type using a higher fatty acid amide as a coloring aid which, upon being molten by heat, serves to activate a diazo compound and a coupling component.

Wet-process type recording materials have several problems due to the use of a developing solution, namely the procedures for maintenance such as replenishing and discharging of the solution are troublesome, the process requires large-sized equipment, it does not permit writing immediately after recording due to the wetness, and the recorded images cannot be stored for a long time. Dry-process type ones involve the problems that they require replenishment of a developer as is the same with the wet-process type, that gas-absorbing equipment for preventing leaking of ammonia gas generated is required, which leads to a large-sized recording apparatus, and, in addition, that an ammoniacal smell is given off immediately after recording. On the other hand, thermally developable type ones have advantages with respect to maintenance due to the lack of need for a developing solution, (in contrast to the wet-process type and the dry-process type). However, conventionally known thermally developable recording materials require a developing temperature as high as 150° C to 200° C and require the temperature to be controlled in the range of about ±10° C (if not, insufficient development results or the color tone is changed), the apparatus thus being expensive. Diazo compounds to be used for such a high-temperature development are also required to be highly heat-resistant. Such compounds, however, are disadvantageous for obtaining a high density. Many attempts have been made for operating at a lower temperature (to 90° C - 130° C) which, however, at the same time causes reduction in the shelf life of the materials themselves.

As is described above, thermally developable type recording materials still are not currently predominant in the diazo recording system in spite of their expectable merits with respect to maintenance in comparison with the wet-process type and the dry-process type.

Now, in order to obtain a desired color density of image by heating a material containing a diazo compound, a coupling component, and a color forming aid, it is required that respective components are instantly molten, diffused, and reacted with each other upon being heated to produce a colored dye. A material designed to form enough color even when heated to low temperatures for providing a high density naturally has the possibility of undergoing this reaction also during storage at room temperature before recording which results in a phenomenon of coloration of the background, which must remain white.

In order to solve these seemingly inconsistent problems with the recording material comprising a support having provided thereon a thermally developable light-sensitive layer contain a diazo compound, a coupling component and a coloring aid, it has been proposed as a fundamental solution to microencapsulate the diazo compound. However, this microencapsulation technique still fails to provide sufficient effects.

An object of the present invention is to provide a recording method capable of providing a high coloration density of the visible image even by low-temperature development, or capable of providing high image stability even by low-temperature fixing.

Another object of the invention is to provide such a method using inexpensive apparatus whose maintenance is simple.

A further object of the invention is to provide a recording method in which the material used has good shelf life, i.e., forms little background coloration (fog) and suffers only a small decrease in color density after storage before the recording.

According to the invention we provide an image-forming method, which comprises uniformly heating a recording material comprising a support having coated thereon a layer of a dispersion of fine particles containing (a) a light-sensitive organic substance, (b) a photo-decomposition image product of said light-sensitive organic substance and (c) a labelling organic substance capable of chemically or physically discriminating these substances from each other, and wherein the heating is carried out in two heating steps at different temperatures successively, wherein the temperature of the first heating step is set at a temperature at which no image-forming reaction or no image-fixing reaction take place and the second step causes development of a visible image.

The first heating step serves to preliminarily heat the whole of the recording material, thus allowing subsequent thermal development at a low temperature. In addition, it is preferable to previously microencapsulate at least one of the light-sensitive organic substance, photodecomposition product thereof and the labelling organic substance and to form the capsule walls of at least one polymer selected from polyureas and polyurethanes.

In order to attain high-speed recording, the dispersed ingredients must instantly be molten, diffused and reacted with each other to form a recorded image upon being heated. In order to minimize heat energy in this heating process, it is important to conduct heat to the recording material without waste and to utilize, without waste, the heat conducted to the recording material. The recording material used in the invention generally comprises a support of 20 to 200 µm in thickness having provided thereon a 2 - 30 µm thick coated layer. Therefore, in order to heat the coated layer to conduct the recorded image-forming reaction therein, conventionally heat energy several times as much as that necessary for the coated layer must be used for heating the support. This has been an obstacle to recorded image formation at low temperature and at high speed.

Light-sensitive organic substances to be used in the present invention include for example: diazo compounds, aromatic diazonium salts, diazo-sulfonate compounds and diazoamino compounds described in Takahiro Tsunoda et Tsugio Yamaoka, "Photolysis and Chemical Structure of Light-Sensitive Diazonium Salts", Journal of the Photographic Society of Japan, 29(4), 1970205 (1965); photo-oxidizing agents such as carbon tetrabromide, N-bromosuccinimide, tribromomethyl phenyl sulfone, azide polymer, 2-azidobenzoxazole, benzoylazide, 2-azidobenzimidazole, 3-ethyl-1-methoxy-2-pyridothiacyanine perchlorate, 1-methoxy-2-methylpyridinium p-toluenesulfonate, 2,4,5-triarylimidazole dimer, benzophenone, p-aminophenyl ketone, polynuclear quinones, and thioxanthenone as described, for example, in Photo. Sci. Eng., 5, 98 (1961), JP-B-43-29407 (the term "JP-B" as used herein means an "examined Japanese patent publication").

Labelling compounds to be used in the present invention on heating can be known types of components which react to form a coloured image, such as:

Coupling compounds such as phenols, naphthols or active methylene compounds can be used as labelling compounds to be associated with the diazo compounds, examples thereof being resorcin, phloroglucin, 2-hydroxy-3-naphthoic acid anilide and 3-bis-(pivaloylacetaminomethyl)benzene.

Labelling compounds to be used with the photo-oxidizing agents include leuco dyes having one or two hydrogen atoms which, when the hydrogen atoms are removed therefrom or when additional electrons are added thereto, are colored to form dyes. Examples thereof include aminotriarylmethanes, amino-1,9-dihydroacridines, aminophenoxazines, aminodihydrophenazines, leucoindamines, hydrazines and phenethylanilines, described in US Patent 3,445,234.

Microcapsules containing the light-sensitive organic substance used in the invention may be prepared according to a process described, for example, in JP-A-59-190886 (ther term "JP-A" as used herein means an "unexamined published Japanese patent application") (corresponding to U.S. Patent 4,650,740). Polyureas and polyurethanes forming the wall of microcapsules may be obtained by polymerizing corresponding monomers according to the process described above, with the amounts of monomers to be used being selected so that the resulting microcapsules have an average size of 0.3 µm to 12 µm and a wall thickness of 0.01 to 0.3 µm.

As supports to be used in the present invention, any of paper supports used for ordinary pressure-sensitive paper, heat-sensitive paper and dry-process or wet-process diazo recording paper may be used. In addition, there may be used neutral papers of 6 to 9 in pH sized with a neutral sizing agent such as alkylketene dimer, papers satisfying the relation between Stöckigt sizing degree and meter basis weight as described in JP-A-57-116687 and having a Bekk smoothness of 90 seconds or more, papers having an optical surface roughness of up to 8 µ and a thickness of 30 to 150 µm as described in JP-A-58-136492, papers having a density of up to 0.9 g/cm^3 and an optical contact ratio of 15% or more as described in JP-A-58-69091, papers made of pulps having been beaten to a degree of 400 cc or more according to Canadian Standard Freeness (JIS P8121) to prevent penetration of a coating solution as described in JP-A-58-69097 (corresponding to U.S. Patent 4,484,205), papers made by using a Yankee machine whose glossy side is intended to be coated to improve color density and resolving power as described in JP-A-58-65695, and papers having been corona discharge-treated to improve their coatability as described in JP-A-59-35985.

As synthetic resin film to be used as a support in the present invention, a suitable one may freely be selected from among known materials which are not deformed by heat in the developing step and have a sufficient dimensional stability. As such films, there may be illustrated, for example, polyester films such as polyethylene terephthalate film and polybutylene terephthalate film; films of cellulose derivatives such as cellulose triacetate film; and polyolefin films such as polystyrene film, polypropylene film and polyethylene film. These may be used as a single film or as a laminate thereof. As to the thickness of the support, films of 20 to 200 µm in thickness are used.

Heating means to be employed in the present invention include, for example, a heat pen, thermal head, infrared rays, high frequency rays, a heat block or heat roller.

As a light source to be used in the present invention for exposing the recording material, there may be used fluorescent lamps, xenon lamps and mercury lamps.

In the image-forming method of the present invention, a recording material having been subjected to imagewise exposure in conformity with an original to form a latent image or an image is passed successively through two heating steps of different temperatures from each other to thereby develop the latent image or fix the image. Temperatures to be employed in the two heating steps may be suitably selected depending upon the properties of the materials to be used such as light-sensitive organic substances, and developing conditions. However, the temperature to be employed in the first heating step must be set at the temperature at which the image-forming reaction which may causes fog, or the image-fixing reaction which may causes decrease in color density, does not take place. Temperatures of 60 to 80 or 90 °C are preferably employed for the first heating step. Temperatures of 80 to 150 °C which are the lowest temperatures necessary for causing the recorded image-forming reaction or recorded image-fixing reaction are preferably employed for the second heating step. The temperature of the recording material is preferably maintained between the first and the second steps and, if not, the recording material is preferably transferred from the first step to the second step as fast as possible, within about 60 seconds.

In the image-recording method of the present invention, the step of exposing the recording material and the first heating step may be conducted at the same time before the second heating step.

A diazo type recording material is now described as one preferable embodiment of the material used in the present invention.

A diazo compound and a coupling component to be incorporated in the light-sensitive layer of a diazo type recording material used in the present invention are those which, upon being heated, come into contact with each other to form color. As the diazo compound, those photo-decomposable compounds which are to be decomposed when receiving light of a specific wavelength before color-forming reaction are used.

The photo-decomposable diazo compounds to be used in the present invention mainly include aromatic diazo compounds, more specifically aromatic diazonium salts, diazosulfonate compounds and diazoamino compounds. Usually, the wavelength for the photo-decomposition of diazo compounds is said to be the wavelength of the absorption maximum thereof. Absorption maximum wavelengths of diazo compounds are known to range from about 200 nm to about 700 nm depending upon their chemical structures (see Takahiro Tsunoda et Tsugio Yamaoka, "Photolysis and Chemical Structure of Diazonium Salts", *Journal of the Photographic Society of Japan*, 29(4), pp. 197-205 (1965)). That is, when diazo compounds are used as *photo-decomposable compounds*, they are decomposed by light of a wavelength corresponding to their chemical structure. In addition, the hue of a dye after the reaction may be changed even when the coupling reaction is conducted with the same coupling component, by changing the chemical structure of the diazo compound.

The diazo compounds are compounds represented by the general formula ArN_2X wherein Ar represents a substituted or unsubstituted aromatic ring, N_2 represents a diazonium group, and X represents an acid anion.

Multi-color thermally developable recording materials may be used which contain several diazo compounds having different photo-decomposable wavelengths or undergoing photo-decomposition at different rates.

Specific examples of the diazo compounds which can be used include 4-diazo-1-dimethylaminobenzene, 4-diazo-2-butoxy-5-chloro-1-dimethylaminobenzene, 4-diazo-1-methylbenzylaminobenzene, 4-diazo-1-ethylhydroxyethylaminobenzene, 4-diazo-1-diethylamino-3-methoxybenzene, 4-diazo-1-morpholinobenzene, 4-diazo-1-morpholino-2,5-dibutoxybenzene, 4-diazo-1-toluylmercatpto-2,5-diethoxybenzene, 4-diazo-1-piperazino-2-methoxy-5- chlorobenzene, 4-diazo-1-(N,N-dioctylaminocarbonyl)benzene, 4-diazo-1-(4-*tert*-octylphenoxy)benzene, 4-diazo-1-(2-ethylhexanoylpiperidino)-2,5-dibutoxybenzene, 4-diazo-1-(2,5-*di*-*tert*-amylphenoxy-α-butanoylpiperidino)benzene, 4-diazo-1-(4-methoxy)phenylthio-2,5-diethoxybenzene, 4-diazo-1-(4-methoxy)benzamido-2,5-diethoxybenzene and 4-diazo-1-pyrrolidino-2-methoxybenzene.

Specific examples of acids capable of forming diazonium salts with the above-described diazo compounds include $C_nF_{2n+1}COOH$ (wherein *n* represents an integer of 1 to 9), $C_mF_{2m+1}SO_3H$ (wherein *m* represents an integer of 1 to 9), boron tetrafluoride, tetraphenylboron, hexafluorophosphoric acid, aromatic carboxylic acids, aromatic sulfonic acids and metal halides (e.g., zinc chloride, cadmium chloride and tin chloride).

As the coupling component to be used in the diazo type recording materials in the present invention, there are those compounds which couple with the diazo compounds in a basic atmosphere to form color and which are exemplified by so-called active methylene compounds having a methylene group adjacent to a carbonyl group, phenol derivatives, naphthol derivatives, etc. Specific examples thereof include resorcin, phloroglucin, sodium 2,3-dihydroxynaphthalene-6-sulfonate, 1-hydroxy-2-naphthoic acid morpholinopropylamide, 1,5-dihydroxy naphthalene, 2,3-dihydroxynaphthalene, 2,3-dihydroxy-6-sulfanylnaphthalene, 2-hydroxy-3-napthoic acid morpholinopropylamide, 2-hydroxy-3-naphthoic acid octylamide, 2-hydroxy-3-naphthoic acid anilide, benzoylacetanilide, 1-phenyl-3-methyl-5-pyrazolone, 1-(2,4,6-trichlorophenyl)-3-anilino-5-pyrazolone, 2-[3-α-(2,5-di-*tert*-amylphenoxy)butanamidobenzamido]phenol, 2,4-*bis*-(benzoylacetamino)toluene and 1,3-*bis*(pivaloylacetaminomethyl)benzene.

These coupling components may be used alone or in combination of two or more them to obtain any hue as desired.

A color-forming aid may be added to the diazo type recording material in the present invention for the purpose of controlling color forming reaction. As one such color-forming aid, a basic substance is preferably added, if necessary, for the purpose of accelerating the coupling reaction by rendering the system basic upon thermal development.

As the basic substance, slightly water-soluble or water-insoluble basic substance or those substances which produce alkali upon being heated may be used.

Examples of the basic substance include organic or inorganic ammonium salts, organic amines, amides, urea and derivatives thereof, thiourea and derivatives thereof, thiazoles, pyrroles, pyrimidines, piperadines, guanidines, indoles, imidazoles, imidazolines, triazoles, morpholines, piperidines, amidines, formamidines and pyridines. These basic substances may be used either alone or as a mixture of two or more of them.

As another color forming aid to be used in a diazo type recording material in the present invention, phenol derivatives, naphthol derivatives, alkoxy-substituted benzenes, alkoxy-substituted naphthalene, hydroxy compounds, amide compounds, or sulfonamide compounds may also be added to light-sensitive layers in order to rapidly and completely conduct thermal development by applying only a low energy. These compounds are considered to decrease the melting point of coupling component or basic substance or improve heat permeability of microcapsule wall, thus providing a high color density of image.

Color forming aids to be used in a diazo type recording material in the present invention further include heat-fusible substances which have a melting point of 50 to 150°C and which are solid at ordinary temperatures and are molten by heat to dissolve the diazo compound, the coupling component or the basic substance. Specific examples of these compounds include fatty acid amides, N-substituted fatty acid amides, ketone compounds, urea compounds and esters.

Microcapsules containing the diazo compound or coupling component in the present invention may be prepared according to a process described, for example, in JP-A-59-190886 (corresponding to U.S. Patent 4,650,740). Polyureas and polyurethanes forming the wall of microcapsules may be obtained by polymerizing corresponding monomers according to the process described above, with the amounts of monomers to be used being decided so that the resulting microcapsules have an average size of 0.3 μm to 12 μm and a wall thickness of 0.01 to 0.3 μm. The diazo compound is coated in an amount of preferably 0.05 to 5.0 g/m^2.

As microcapsules containing the diazo compound in the present invention, substantially solvent-free microcapsules obtained by dispersing and emulsifying a solution of a diazonium salt and one and the same or different compounds capable of reacting with each other to form a high-molecular substance in a non-aqueous solvent having a boiling point of 40 to 95 °C under ordinary pressure, in a solution of hydrophilic protective colloid, and raising the temperature of the system with decreasing the pressure within the reactor to distill off the non-aqueous solvent, whereby the wall-forming substance is allowed to migrate to the surface of oil droplets, and polymer-producing reaction based on polyaddition and polycondensation is allowed to proceed at the surface of the oil droplets to form wall membrane, are particularly preferable for obtaining a good shelf life.

In the diazo type recording material in the present invention, the coupling component is used in an amount of preferably 0.1 to 30 parts by weight per part by weight of the diazo compound, and the basic substance is used in an amount of 0.1 to 30 parts by weight per part by weight of the diazo compound.

The diazo compound, coupling component, basic substance and the other color forming aids to be used in the diazo type recording material in the present invention but not to be contained in the microcapsules are preferably solid-dispersed together with a water-soluble high polymer by means of, for example, a sand mill. As a preferable water-soluble high polymer, those water-soluble high polymers which are used upon preparation of microcapsules may be used. (See, for example, JP-A-59-190886 (corresponding to U.S. Patent 4,650,740).) In this case, the compounds are added to the water-soluble high polymer solution in proportions of 5 to 40 % by weight, respectively. Sizes of dispersed particles are preferably not more than 10 μm.

To the diazo type recording material in the present invention may be added free radical generating agents (compounds capable of generating a radical upon being irradiated with light) used in photopolymerizable compositions for the purpose of reducing background yellowing after recordings. As the free radical generators, there include aromatic ketones, quinones, benzoins, benzoin ethers, azo compounds, organic disulfides, acyloxime esters etc. They are added in an amount of preferably 0.01 to 5 parts by weight per part by weight of the diazo compound.

For the purpose of similarly reducing yellowing, polymerizable compounds having ethylenically unsaturated bond (hereinafter referred to as "vinyl monomers") may also be used. Vinyl monomers are compounds which have at least one ethylenically unsaturated bond (e.g., a vinyl group or a vinylidene group) and are in the chemical form of monomer or prepolymer. Examples thereof include unsaturated carboxylic acids and salts thereof, esters between unsaturated carboxylic acids and aliphatic polyhydric alcohols, amides between unsaturated carboxylic acids and aliphatic polyamines, and the like. The vinyl monomers are used in an amount of 0.2 to 20 parts by weight per part by weight of the diazo compounds.

The afore-mentioned free radical generating agents and the vinyl monomers are preferably contained in the microcapsules together with the diazo compounds.

In addition to the above-described materials, citric acid, tartaric acid, oxalic, acid, boric acid, phosphoric acid, pyrophosphoric acid, etc. may be added to the diazo type recording material of the present invention as acid stabilizers.

In preparing a diazo type recording material for the present invention, a coating solution comprising microcapsules containing a diazo compound or a coupling component, a basic substance and other additives is prepared, and this coating solution is coated on a support such as paper or synthetic resin film by a coating process such as bar coating, blade coating, air knife coating, gravure coating, roll coating, spray coating or dip coating, then dried to provide a light-sensitive layer containing 2.5 to 30 g/m^2 of solids. In a diazo type recording material, the diazo compound, the coupling component, the base, etc. may be contained in one and the same layer as described above, or may be incorporated in different layers to form a multi-layer constitution. The light-sensitive layer may be coated on an interlayer provided on a support as described, for example, in JP-A-61-54980.

As supports to be used in the diazo type recording material any of the aforementioned supports may be used.

In forming an image on the diazo type recording material in the present invention, a recording material having been subjected to imagewise exposure in conformity with an original to form a latent image is passed successively through two heating steps of different temperatures from each other to thereby develop the latent image, or is subjected to the imagewise exposing step and the first heating step at the same time, then to the second heating step for development.

Formation of an image on the diazo type recording material by conducting the imagewise exposure and the first heating step at the same time and subsequently conducting the second heating step is preferably conducted in the following manner. In the first step of conducting exposure in conformity with an original image to form a latent image in the light-sensitive layer and fix other portions than the image portions by irradiation with light, fluorescent lamps, xenon lamps, mercury lamps, etc. are used as a light source. Light sources which have an emission spectrum almost coinciding with absorption spectrum of diazo compound in the recording material are preferable, since portions other than image portions can be effectively photofixed. In order to imagewise expose the recording material at the preferred first temperature of from 60° C to 90° C, a method can be used of exposing and conveying the recording material while it is directly wound around a fluorescent lamp in superposition with an original and controlling the tube wall temperature of the fluorescent lamp by forcibly feeding cooling air; or of exposing and conveying the recording material while it is wound around a glass tube in which various light sources are inserted in superposition with an original, while controlling the temperature within the glass tube by feeding cooling air. In the second step of development by overall heating, any of the aforementioned heating means may be used.

The present invention thus can provide a diazo type recording having a good shelf life and yet having a high color density of image, even by low-temperature development.

The invention is now illustrated in greater detail by the following examples, wherein all parts, percentages and ratios are by weight.

EXAMPLE 1

3.45 Parts of 1-morpholino-2,5-dibutoxybenzene-4-diazonium hexafluorophosphate and 18 parts of an adduct between xylilenediisocyanate and trimethylolpropane (3:1) were added to a mixed solvent of 6 parts of tricresyl phosphate and 5 parts of ethyl acetate, and heated to dissolution. The resulting diazo compound solution was mixed with an aqueous solution of 5.2 parts of polyvinyl alcohol in 58 parts of water, and emulsified at 20° C to obtain an emulsion of 2.5 µm in average particle size. 100 Parts of water was added to the thus-obtained emulsion and, under stirring, the mixture was heated to 60° C. After two hours, a solution of microcapsules retaining the diazo compound as the core substance was obtained.

Then, 10 parts of 2-hydroxy-3-naphthoic acid anilide and 10 parts of triphenylguanidine were added to 200 parts of a 5% polyvinyl alcohol aqueous solution, and dispersed for about 24 hours using a sand mill to obtain a dispersion of 3 µm in average particle size.

50 Parts of a dispersion of the coupling component and the triphenylguanidine and 10 parts of a 40% calcium carbonate dispersion were added to 50 parts of the thus-obtained solution of microcapsules containing the diazo compound to prepare a coating solution. This coating solution was coated in a dry weight of 10 g/m^2 on a woodfree paper (75 g/m^2) having a smooth surface using a coating bar, then dried at 50° C for 1 minute to prepare Recording Material A.

Recording Material A was exposed with a fluorescent lamp through a test original (wherein a uniformly black disk of 3 cm in diameter was drawn on tracing paper with a 2B pencil) superposed thereon. The fluorescent lamp used had a maximum at 420 nm in emission spectrum. Then, the material was heated for 0 second, 2 seconds, 4 seconds or 6 seconds using a heat block heated to 70° C, and immediately heated for 2 seconds using a heat block heated to 120° C to form an image. Color densities of image portions and fog densities of background portions were measured using a Macbeth densitometer. Table 1 shows the results of the tests.

Table 1

Heating Time in the First Heating Step	Color Density of Image	Color Density of Background
(Second)		
0	1.02	0.12
2	1.11	0.12
4	1.21	0.13
6	1.22	0.14

EXAMPLE 2

An apparatus was prepared wherein a fluorescent lamp of 55 mm in diameter having a maximum at 420 nm in the emission spectrum was used in the exposing station, a recording material is to be exposed and conveyed in a state of being wound around the lamp at a wrapping angle of 270°, a heat roller of 50 mm in diameter was used in a developing station, and the recording material is heated and conveyed in a state of being wound around the roller at a wrapping angle of 270°. A 300 mm path was provided between the exposing station and the thermally developing station. An air of a constant temperature was forcibly applied to the tube wall of the fluorescent lamp in the exposure station, temperature of the tube wall being controlled by controlling the temperature of the air.

Recording Materials A obtained in Example 1 were subjected to the above-described apparatus to form images. Recording Materials A were exposed with a fluorescent lamp through a test original (wherein a uniformly black disk of 3 cm in diameter was drawn on tracing paper with a 2B pencil) superposed thereon. In this occasion, illuminance of the fluorescent lamp was adjusted to 10 mW/cm^2 (measured by means of an illumination meter, UVD-405PD made by Ushio Inc.) and a conveying speed at 300 mm/sec. Temperatures of the tube wall of fluorescent lamp were set at 50°C, 60°C, 70°C, 80°C and 90°C, respectively, and temperatures of the heat roller were set at 100°C, 120°C and 140°C, respectively, to form images. Densities of colored portions and background portions were measured by means of a Macbeth densitometer. Results thus obtained are tabulated in Table 2.

Similar tests were conducted with recording materials having been stored for 3 days at 40°C and 90 %RH, and the results are tabulated in Table 3.

Table 2

Temperature of Tube Wall (°C)	Developing Temperature (°C)	Color Density of Image	Color Density of Background
50	100	1.01	0.12
50	120	1.09	0.12
50	140	1.25	0.13
60	100	1.19	0.12
60	120	1.24	0.12
60	140	1.26	0.13
70	100	1.25	0.12
70	120	1.26	0.12
70	140	1.26	0.13
80	100	1.26	0.13
80	120	1.26	0.13
80	140	1.26	0.14
90	100	1.26	0.16
90	120	1.27	0.17
90	140	1.27	0.17

Table 3

Temperature of Tube Wall (°C)	Developing Temperature (°C)	Color Density of Image	Color Density of Background
50	100	0.98	0.14
50	120	1.05	0.14
50	140	1.22	0.15
60	100	1.17	0.14
60	120	1.22	0.14
60	140	1.23	0.15
70	100	1.21	0.14
70	120	1.23	0.14
70	140	1.23	0.15
80	100	1.23	0.14
80	120	1.23	0.14
80	140	1.24	0.15
90	100	1.23	0.18
90	120	1.24	0.19
90	140	1.24	0.19

It is seen from Tables 2 and 3 that the recording materials in the present invention possess a good shelf life, and that the image-forming method of the present invention enables one to decrease the thermally developing temperature by about 20 to 40 °C.

EXAMPLE 3

3 parts of leuco crystal violet, 3 parts of 2,2′-bis(o-chlorophenyl)-4,4′,5,5′-tetraphenylbiimidazole, 0.6

part of tribromomethylphenylsulfone, 0.4 part of 2,5-di-tert-octylhydroquinone and 24 parts of 75% ethyl acetate solution of xylenediisocyanate/trimethylol propane adduct were dissolved the mixed solvent of 22 parts of methylene chloride and 24 parts of tricresyl phosphate. The resulting solution was added to 63 parts of 8% aqueous solution of polyvinyl alcohol, and emulsified and dispersed at 20°C to obtain an emulsion having an average particle size of 1 μm. 100 parts of water was added to the emulsion obtained above and stirred at 40°C for 3 hours. Then, the mixture was cooled to room temperature and filtered to obtain a capsule dispersion.

30 parts of 1-phenylpyrazoline-3-one (Phenidone A) was added to 150 parts of 4% aqueous solution of polyvinyl alcohol, and the mixture was dispersed by means of a horizontal sand mill to obtain Phenidone A dispersion having an average particle size of 1 μm.

240 parts of the thus-obtained capsule dispersion, 180 parts of the above Phenidone A dispersion, 20 parts of 20% silica dispersion (Siloid 404, manufactured by Fuji Devison Chemical Co., Ltd.) and 10 parts of 3% aqueous solution of polyethylene glycol lauryl ether were mixed to obtain the coating solution. The resulting coating solution was coated in a dry weight of 10 g/m^2 on a woodfree paper (76 g/m^2) using a coating rod, and then dried to prepare Recording Material B.

Recording Material B was exposed with a fluorescent lamp as in Example 1 to form an image. The color density of the thus formed image was measured with Macbeth densitometer, and the value 1.26 was obtained.

When the thus image formed sample was allowed to stand in bright room for 6 hours, the density of the background (not image formed portion) was risen to 1.24, that is, the image cannot be distinguished from the background.

Separately, Recording Materials B were exposed and fixed with the same apparatus as prepared in Example 2. Temperatures of the tube wall of the fluorescent lamp and of heat roller were set at the temperatures as shown in Table 4. The densities of the image and the background of samples obtained using the apparatus and then allowed to stand in bright room for 6 hours were measured. Results thus obtained are shown in Table 4.

It is seen in Table 4 that increase in color density of background is prevented even by low temperature fixation, even at 100°C, by providing two heating steps according to the present invention, while conventional methods require the heat developing temperature of about 140°C or more to prevent increase in color density of background which is caused by light such as a room right.

Table 4

Temperature of Tube Wall	Developing Temperature	Color Density of Image	Color Density of Background
(°C)	(°C)		
50	100	1.26	0.95
50	120	1.26	0.31
50	140	1.25	0.16
60	100	1.25	0.28
60	120	1.26	0.18
60	140	1.26	0.16
70	100	1.26	0.16
70	120	1.25	0.14
70	140	1.26	0.14
80	100	1.26	0.15
80	120	1.26	0.14
80	140	1.26	0.14
90	100	1.26	0.14
90	120	1.25	0.14
90	140	1.26	0.14

Claims

1. An image-forming method, which comprises uniformly heating a recording material comprising a support having coated thereon a layer of a dispersion of fine particles containing (a) a light-sensitive organic substance, (b) a photo-decomposition image product of said light-sensitive organic substance and (c) a labelling organic substance capable of chemically or physically discriminating these substances from each other, and wherein the heating is carried out in two heating steps at different temperatures successively, wherein the temperature of the first heating step is set at a temperature at which no image-forming reaction or no image-fixing reaction take place and the second step causes development of a visible image.

2. A method as claimed in Claim 1, wherein the step of imagewise exposing and the first of the heating steps are conducted at the same time.

3. A method as claimed in Claim 1 or 2, wherein at least one of the substances (a), (b) and (c) is enclosed in microcapsules, with the capsule wall of said microcapsules being made of at least one high polymer selected from among polyureas and polyurethanes.

4. A method as claimed in any preceding claim, wherein said first heating step is conducted at a temperature of from 60° C to 90° C.

5. A method as claimed in any preceding claim, wherein said second heating step is conducted at a temperature of from 80° to 150° C.

6. A method as claimed in any of Claims 1 to 5, wherein said light-sensitive substance (a) is a diazo compound, and said labelling substance (c) is a coupling component.

7. A method as claimed in any of Claims 1 to 5, wherein said light-sensitive substance (a) is a photo-oxidizing agent and the labelling substance (c) is a leuco dye having 1 or 2 hydrogen atoms which can form a dye by addition of electrons or removal of hydrogen atoms.

8. A method as claimed in any preceding claim, wherein the support has a thickness of 20 - 200 μm and the layer thereon has a thickness of 2 - 30 μm.

9. A method of forming a visible image from a light-sensitive material containing a layer of a color-sensitive organic substance and a color developer therefor, wherein the material is imagewise exposed to light which causes local decomposition of said substance and subsequently is heated to a temperature to cause development and/or fixing of a visible color image, characterized in that immediately prior to said heating the material is heated to a lower temperature which does not cause color development or fixing.

10. A method as claimed in Claim 9, wherein said layer contains a diazo compound and a coupler therefor.