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(54) Image-forming method and material.

(57) In the process of forming an image on a light-sensitive recording material (e.g. a diazo type) a heat-developing or heat-fixing step is performed in the presence of a small amount of water, allowing employment of a temperature lower than the conventional minimum of 150° C. The water may be contained in the recording material in microcapsules which are ruptured thermally or mechanically, or as water of crystallization or hydration which is released by heating. Alternatively, the water may be applied to the recording material immediately preceding, or simultaneously with, the heating step in the form of a coating or as steam.

IMAGE-FORMING METHOD AND MATERIAL

This invention relates to a method of forming an image on a light-sensitive recording material utilizing a low temperature heat-development or heat-fixing step, and to a material for use in the method.

In one aspect the invention relates to an image-forming method comprising imagewise exposing a recording material to form a latent image or an image in the recording layer, then uniformly heating the entire recording layer to develop or fix the image so formed. The latent image or the image formed in the recording layer by the imagewise exposure may be a negative image or a positive image of the original, depending upon whether a light-sensitive organic substance present in the recording layer is rendered active or inactive with respect to a labelling organic substance by irradiation with light.

Labelling substances capable of discriminating between a light-sensitive organic substance and a photo-decomposition product of the aforesaid light-sensitive organic substance are well known as compounds which undergo reaction, change phase or change their permeability, etc. in the presence of either the light-sensitive organic substance or the photo-decomposition product during development. Therefore, in establishing a recording system which utilizes these compounds, compounds requiring less heat energy for the change enable a more efficient, less expensive and smaller system to be achieved.

However, recording materials applicable to the above-described system are required to resist change in their properties during storage regardless of the storage conditions and the storage period obtaining before recording takes place. However this requirement conflicts with another 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 spontaneous reaction between the light-sensitive organic substance and the labelling organic substance during storage before recording, which results in undesired premature development (generally called "fog" in many cases), or insufficient formation of color images required to be formed at high color 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. The first type is known as the wet-process development type and comprises a support having provided thereon a light-sensitive layer which contains a diazo compound and a coupling compound as major components, and which, after imagewise exposure, is developed with an alkaline aqueous solution. The second type is known as the dry-process development type and is developed with an ammonia gas instead of the alkaline aqueous solution of the wet-process type. The third type is known as the heat-developable type and includes the sub-type containing in the light-sensitive layer an ammonia gas generator such as urea capable of generating an ammonia gas upon being heated; the sub-type containing in the light-sensitive layer an alkali salt of an acid such as trichloreacetic acid which loses acidic properties upon being heated; and the sub-type using a higher fatty acid amide as a coloring aid which, upon being fused by heat, serves to activate the diazo compound and a coupling component.

Wet-process type recording materials incur several problems due to the use of a developing solution. For example, procedures for maintenance, such as replenishment, and discharge of the solutions are troublesome; the process requires large-scale equipment; the materials do not permit writing thereon immediately after recording due to their wetness; and recorded images cannot be stored for a long time.

Dry-process type materials involve the problems that they require replenishment of a development solution just as the wet-process type; that gas-absorbing equipment for preventing leakage of the ammonia gas generated is required, which leads to a large-sized copying apparatus; and, in addition, that an ammoniacal smell is given off immediately after recording.

On the other hand, heat-developable type materials have merits with respect to maintenance due to the fact that it is not necessary to use a development solution, in comparison to the wet-process type and the dry-process type. However, conventionally known heat-developable recording materials require a development temperature as high as 150°C to 200°C and require the temperature to be controlled in the range of about ±10°C; and thus require expensive apparatus. Diazo compounds, which are 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 to lower the development temperature (to 90 to 130°C) which attempts have, at the same time, caused a reduction in shelf life of the materials themselves.

As described above, heat-developable type recording materials still do not currently pre-dominate in the diazo-based recording systems in spite of their expected merits in comparison with the wet-process type and the dry-process type systems.

Now, in order to obtain a desired color density by heating a material comprising a support having provided thereon a layer containing a diazo compound, a coupling component and a color forming aid, it is required that the respective components are instantly melted, diffused and reacted with each other upon being heated to produce a colored dye. A material designed to form a high color density, even at low temperatures, for providing such a high density naturally tends also to undergo this reaction prematurely during storage at room temperature before recording, which results in the phenomenon of coloration (fog) of the background which must remain white.

An aim of the present invention is, therefore, to provide a recording method and a recording material capable of providing a high coloration density even by low-temperature development; and capable of forming an image having excellent long-term storage stability (i.e., undergoing less of a decrease in color density and less of an increase in background density when stored in a dark or light place).

A further aim of the present invention is to provide an image-forming method using a light-sensitive heat-developable recording material, wherein latent image- or image-forming by imagewise exposure and a heat-development or heat-fixing are combined with each other, which method is simple and permits use of easily maintainable equipment and materials.

A still further aim of the present invention is to provide a recording material having good shelf life, i.e., which undergoes less background coloration (fog) during storage before recording; has a simplified stratum structure, and is capable of being easily prepared, yet which can be developed or fixed at a lower temperature.

A fundamental step in achieving the aim of the present invention is to heat by a heating means a recording material comprising a support having coated thereon a dispersion of fine particles containing a light-sensitive organic substance, a photo-decomposition product of the light-sensitive organic substance, and a labelling organic substance capable of chemically or physically discriminating the product from the substance. In order to attain high-speed recording, the respective ingredients must instantly be fused, diffused and reacted to form a recorded image upon being heated. In this heating process, there are the following three approaches for minimizing the heat energy necessary: (1) conducting heat to the recording material without loss; (2) utilizing, without loss, heat conducted to the recording material for forming a recorded image; and (3) establishing a recorded image-forming system permitting low-temperature development. With respect to approaches (1) and (2), it has been proposed to render the surface of the recording material smoother thereby to effect complete contact with a heating means, and to use a support which has been made heat-insulating so as not to lose heat from the support side. These techniques, however, are still inadequate to achieve the objects of the present invention.

As a result of intensive investigations to establish a record image-forming system permitting low-temperature development, the inventors have achieved the present invention.

That is, as long as a recording material is to be used based on the use of heat to change a substance, it has been necessary to discover a means for melting a substance at a low temperature. It is well known that the melting point of a mixture of substances is lower than the melting points of the respective substances. With this in mind, the inventors have tested innumerable compounds to determine whether they can decrease the melting points of substances relating to recorded image formating and, as a result, they have discovered that simple water is surprisingly most effective.

The aims of the invention are attained by a method of forming an image, which comprises uniformly heating in the presence of a slight amount of water a recording material comprising a support having provided thereon a dispersion of fine particles containing a light-sensitive organic substance and a photo-decomposition product of the light-sensitive organic substance, the dispersion further containing a labelling organic substance capable of chemically or physically discriminating the light-sensitive organic substance and photo-decomposition product from each other. The water may be contained in the recording material, or may be added to the recording material immediately before or simultaneously with a heat-development or heat-fixing step.

The present invention also provides a recording material comprising a support having provided thereon a dispersion of fine particles containing a light-sensitive organic substance and a photo-decomposition product of the light-sensitive organic substance, the dispersion further containing a labelling organic substance capable of chemically or physically discriminating the light-sensitive organic substance and photo-decomposition product from each other; the support may have provided thereon a source capable of releasing water.

In the present invention, the slight amount of water may be supplied from outside the recording material, or may be previously provided in the recording material so that it may be supplied internally on external stimulation, with both methods serving to achieve the aims of the present invention. In the former case of supplying the slight amount of water from outside the recording material, it is preferred to uniformly coat the water immediately in front of (with respect to the direction of travel of the material), or at the same position as, a heating means; or to preheat with steam using a slit for uniformly blowing steam onto the recording material immediately in front of, or at the same position as, the heating means.

In the latter case of providing the small amount of water within the material (e.g., water contained in microcapsules, or water contained in a compound as water of crystallization or as water of hydration), so as to enable water to be supplied internally upon external stimulation, physical pressure may be applied to the recording material to cause rupture of the water-containing microcapsules immediately in front of, or at the same position as, the heating means; or more preferably heat may be applied to the material by a heating means to thereby cause release of water from microcapsules or from compounds containing water of crystallization or water of hydration within their molecules, without the need to provide any additional step or equipment.

Advantage is obtained when polyurea or polyurethane is present among the organic substances relating to recorded image formation. Therefore, a recording material wherein a light-sensitive organic substance is contained in microcapsules having capsule walls made of at least one high polymer selected from polyureas and polyurethanes is preferable in the present invention.

Light-sensitive organic substances usable in the present invention include the following compounds which, however, do not limit the present invention in any way:-

Diazo compounds, aromatic diazonium salts, diazosulfonate compounds and diazoamino compounds described in Takahire Tsunoda and Tsugio Yamaoka, "Photo-Decomposition and Chemical Structure of Light-sensitive Diazonium Salts", Journal of Photographic Society of Japan, 29(4), pp. 197-205 (1965), and photo-oxidizing agents described in Photo. Sci. Eng., 5, 98 (1961), JP-B-43-29047 (the term "JP-B" as used herein means an "unexamined Japanese patent publication"), etc; photo-oxidizing agents including, for example, carbon tetrafluoride, N-bromosuccinimide, tribromomethylphenylsulfone, 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 quinone, and thioxanthenone.

Labelling compounds which may be used in the present invention include the following compounds which, however, do not limit the present invention in any way:-

Coupling components such as phenols, naphthols, and active methylene compounds can be used as labelling compounds to be associated with the diazo compounds; examples thereof include resorcinol, phloroglucinol, 2-hydroxy-3-naphthoic acid anilide, and 1,3-bis-(pivaloylacetaminomethyl)benzene.

Labelling compounds to be associated with the photo-oxidizing agents include leuco dyes having one or two hydrogen atoms which, when the atoms are removed therefrom or when additional electrons are added thereto, are colored to form dyes. Examples of such labelling compounds include aminotriarylmethanes, aminoxanthenes, amino-1,9-dihydroacridine, aminophenoxazine, aminodihydrophenazine, leucoindamine, hydrazine, and phenethylaniline, as described, e.g., in U.S. Patent 3,445,234.

In the present invention, the slight amount of water to be supplied immediately before or simultaneously with heat-development may conveniently be supplied by any means that can uniformly dampen the light-sensitive layer, and the amount of water to be supplied to the light-sensitive layer is preferably controlled to be 0.1 g/m^2 to 20 g/m^2, more preferably 0.1 g/m^2 to 10 g/m^2, still more preferably 0.1 g/m^2 to 5 g/m^2.

Supply of this water immediately before or simultaneously with the heat-development serves the aims of the present invention. If the same amount of water is allowed to exist in the light-sensitive layer during storage before recording in the form which is available without any stimulation, there results a serious increase in background density. If this water is supplied to the light-sensitive layer after heat-development, an additional increase in color density is not observable. Thus, the water is preferably provided immediately before or simultaneously with heating.

In supplying the slight amount of water to the recording material by coating, a suitable coating process may be selected from among ordinary spray coating, dip coating, coating by using a coating bar and, in addition, those processes which are described, for example, in Yuji Harasaki; Coating Technology, published by Asakura Shoten, p. 253, (1987).

In supplying the slight amount of water to the recording material by a coating process, it may be supplied as an aqueous solution of a known anionic or nonionic surface active agent. Preferred surface active agents include sodium alkylbenzenesulfonates, sodium alkylsulfonates, sodium dioctyl sulfosuccinate, and polyalkylene glycol (for example, polyoxyethylene nonylphenyl ether).

Microcapsules containing the light-sensitive organic substance used in the present invention may be prepared according to a process described, for example, in JP-A-59-190886 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") (corresponding to U.S. Patent 4,650,740). Polyurea and polyurethane forming the walls of the 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 micro-capsules preferably have an average size of 0.3 µm to 12 µm and a wall thickness of 0.01 µm to 0.3 µm.

In the present invention, the slight amount of water may be previously encapsulated in microcapsules, and water-containing microcapsules may be prepared by processes described, for example, in U.S. Patents 4,020,210, 3,856,699 and 3,427,250.

Examples of compounds having water of crystallization or water of hydration within their molecules are described, for example, in the aforesaid U.S. Patent 4,020,210.

As supports to be used in the present invention, any paper support used for ordinary pressure-sensitive paper, heat-sensitive paper, dry-process or wet-process diazo recording paper, etc. may be used. In addition, there may be used neutral papers having a pH of 6 to 9 sized with a neutral sizing agent such as alkylketene dimer; papers having the relation between Stokigt sizing degree and meter basis weight satisfying the condition described in JP-A-116687 and having a Bekk smoothness of 90 seconds or more; papers having an optical surface roughness of 8 µm or less and a thickness of 30 to 150 µm as described in JP-A-58-136492; papers having a density of 0.9 g/cm^3 or less and an optical contact ratio of 15% or more as described in JP-A-58-69091; papers made from pulps which have 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 JPA-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 which have been corona discharge-treated to improve coating properties as described in JP-A-59-35985.

Synthetic resin films which can be used as a support in the present invention can be selected from among known materials which are not deformed by heat in the developing or fixing step and which have good dimensional stability. Examples of the films include polyester films such as polyethylene terephthalate film or polybutylene terephthalate film; films of cellulose derivatives such as cellulose triacetate film; and polyolefin films such as polystyrene film, polypropylene film or polyethylene film. These may be used as a single film or as a laminate thereof. As to thickness of the support, films of 20 to 200 µm in thickness may be used.

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

As has been described in detail above, a recording material according to the present invention has a good shelf life, and provides a high color density and a good image stability even when treated by a heat-development or heat-fixing process at a low temperature. The heat-developing or heat-fixing temperature may suitably be selected depending upon the properties of substances, such as a light-sensitive organic substance to be used, and the development conditions, and temperatures of 150° C, or lower, i.e. lower than those which it has conventionally been possible to select, may be freely selected.

The heat-developing or heat-fixing temperature to be employed in the present invention is selected by taking into consideration such factors as that images after processing should be completely dried; that curling should not become too serious a problem; and that the recording rate should be fast enough. Based on these considerations heat-development or heat-fixing temperatures of 60° C to 140° C can be employed.

A diazo type recording material is now described as one preferred embodiment utilizing the present invention which, however, does not limit the present invention in any way.

A diazo compound and a coupling component to be contained in the light-sensitive layer of a diazo type recording material in accordance with the present invention are those which form a color upon coming into contact with each other upon heating. As the diazo compound, those photo-decomposable compounds which decompose when receiving light of a specific wavelength before a coloration reaction can be used.

The photo-decomposable diazo compounds to be used in the present invention are mainly aromatic diazo compounds, more specifically aromatic diazonium salts, diazosulfonate compounds and diazoamino compounds. Usually, the wavelength for the photo-decomposition of the 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 (Takahiro Tsunoda and Tsugio Yamaoka, "Photo-Decomposition 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 of ArN_2X (wherein Ar represents a substituted or unsubstituted aromatic ring, N_2 represents a diazonium group, and X represents an acid anionic.

In the present invention, multi-color heat-developable recording materials may be obtained by using diazo compounds having different photo-decomposable wavelengths or undergoing photo-decomposition at different rates.

Specific examples of the diazo compounds to be used in the present invention include 4-diazo-1-di-methylaminobenzene, 4-diazo-2-butoxy-5-chloro-1-di-methylaminobenzene, 4-diazo-1-methylbenzylaminobenzene, 4-diazo-1-ethylhydroxyethylaminobenzene, 4-diazo-1-di-ethylamino-3-methoxybenzene, 4-diazo-1-morpholinobenzene, 4-diazo-1-morpholino-2,5-dibutoxybenzene, 4-diazo-1-toluylmercapto-2,5-diethoxybenzene, 4-diazo-1-piperadino-2-methoxy-5-chlorobenzene, 4-diazo-1-(N,N-di-octylaminocarbonyl)-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), tetrafluoroboric acid, tetraphenylboric acid, hexafluorophosphoric acid, aromatic carboxylic acid, aromatic sulfonic acid, and metal halide (e.g., zinc chloride, cadmium chloride or tin chloride).

As the coupling component to be used in the diazo type recording materials in accordance with the present invention, there are those compounds which couple with the diazo compounds in a basic atmosphere to form a dye. Examples of the coupling component include active methylene compounds having a methylene group adjacent to a carbonyl group, phenol derivatives, and naphthol. Specific examples thereof include resorcinol, phloroglucinol, sodium 2,3-di-hydroxynaphthalene-6-sulfonate, 1-hydroxy-2-naphthoic acid morpholinopropylamide, 1,5-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,3-dihydroxy-6-sulfanylnaphthalene, 2-hydroxy-3-naphthoic acid morpholino propylamide, 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 of them to obtain an image having any desired hue.

A basic substance is preferably added as a color forming aid to the diazo recording material in accordance with the present invention 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 substances or those substances which produce alkali upon being heated may be used.

The basic substances include nitrogen-containing compounds such as organic and inorganic ammonium salts, organic amines, amides, urea, 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 in combination of two or more of them.

Other color forming aids such as phenol compounds, naphthol compounds, alkoxy-substituted benzenes, alkoxy-substituted naphthalenes, hydroxy compounds, amide compounds, and sulfonamide compounds may also be added to light-sensitive layers in order to rapidly and completely conduct heat-development by applying a low energy. These compounds are considered to decrease the melting point of the coupling component or basic substance or to improve the heat permeability of the microcapsule walls, thus providing a high coloration density.

Color forming aids which can be used in the present invention further include heat-fusible substances which have melting points of 50 to 150° C and which are solid at room temperature and are fused 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 ester compounds. The substances are preferably selected based on the intended recording temperature of the desired product.

Microcapsules containing the diazo compound of the present invention can be prepared by the process as described, for example, in JP-A-190886 (corresponding to U.S. Patent 4,650,740). The diazo compounds are preferably coated in amounts of 0.05 to 5.0 g/m^2.

As microcapsules containing the diazo compound of the present invention, these are particularly preferre are substantially no solvent microcapsules obtained by dispersing and emulsifying in a solution of hydrophilic protective colloid a solution of a diazonium salt and a compound capable of forming, different compounds capable of reacting with each other to form, a high-molecular material in a non-aqueous solvent having a boiling point of 40 to 95° C under atmospheric pressure, and raising the temperature of the system while decreasing the pressure within the reaction vessel to distil off the non-aqueous solvent, whereby the wall-forming substance is allowed to migrate to the surface of the oil droplets and a polymer-producing reaction based on polyaddition and polycondensation is allowed to proceed at the surface of the oil droplets to form a wall membrane.

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 preferably used in an amount of 0.1 to 30 parts by weight per part by weight of the diazo compound.

The coupling component, basic substance and other color forming aids to be used in the present invention are preferably solid-dispersed together with a water-soluble high molecular material by means of, for example, a sand mill. As a preferred water-soluble high molecular material, those water-soluble high molecular materials 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 diazo compound, coupling component and color forming aids are added to the water-soluble high molecular material solution in proportions of 5 to 40 wt%, respectively. Sizes of dispersed particles are preferably not more than 10 µm.

To the recording material of the present invention may be added free radical generating agents (compounds capable of generating free radicals upon being irradiated with light) used in photo-polymerizable compositions for the purpose of reducing the yellowing of background after recording. Examples of the free radical generating agents include aromatic ketones, quinones, benzoins, benzoin ethers, azo compounds, organic disulfides, and acyloxime esters. 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 bonds (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 monomers or prepolymers. Examples thereof include unsaturated carboxylic acids and salts thereof, esters of unsaturated carboxylic acids with aliphatic polyhydric alcohols, amides of unsaturated carboxylic acids with aliphatic polyamide compounds, 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 compound.

The aforementioned free radical generating agents and the vinyl monomers are preferably enclosed in the microcapsules together with the diazo compounds.

In addition to the above-described substances, 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 the diazo type recording material of the present invention, a coating solution containing microcapsules which contain a diazo compound, etc., 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 with a coating method 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 having a coated amount of 2.5 to 30 g/m^2 as a solid. In the recording material of the present invention, microcapsules, coupling components, basic substances, etc. may be contai-ned in 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 the support for diazo type recording material of the present invention, any of the aforementioned supports may be used.

Formation of image on the diazo type recording material of the present invention 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-forming portions by irradiation with light, various fluorescent lamps, xenon lamps, mercury lamps, etc. can be used as light sources. Light sources which have an emission spectrum almost according with the absorption spectrum of the diazo compound used in the recording material are preferable, since portions other than image-forming portions can be effectively photo-fixed by such light. In the second step, the recording material is uniformly dampened. In the third step of development which involves heating the whole surface of the light-sensitive layer of the recording material using a heating means such as a heat pen, a thermal head, infrared rays, high frequency radiation, a heat block or a heat roller, may be used.

As has been described in detail above, the diazo type recording material of the present invention possesses a good shelf life by containing a diazo compound in microcapsules and enables development at low temperatures by providing the second step of uniformly damping the whole light-sensitive layer of aforesaid recording material with water between the first step of imagewise exposing the recording material to form a latent image in the aforesaid light-sensitive layer and, at the same time, to fix portions other than the image- forming portions by irradiation with light and the third step of heat-development by a heating means. Heat-developing temperature may be suitably selected depending upon properties of the diazo compounds and the like to be used and development conditions, and temperatures of 150°C or lower, i.e., lower than those which it has conventionally been possible to select as the heat-developing temperature for recording materials having high storage stability, may freely be selected.

The present invention is now illustrated in greater detail by reference to the following Examples which, however, is not to be construed as limiting the present invention in any way. Unless otherwise indicated, all parts, percents and ratios are by weight.

EXAMPLE 1

Preparation of the diazo compound-containing capsule solution for Recording Material A:

3.45 parts of 1-morpholino-2,5-dibutoxybenzene-4-diazonium hexafluorophosphate and 18 parts of an adduct of xylilenediisocyanate with trimethylolpropane (3:1) were added to a mixed solvent of 6 parts of tricresyl phosphate and 5 parts of ethyl acetate, and heated to dissolve. The resulting diazo compound solution was mixed with an aqueous solution of 5.2 parts of polyvinyl alcohol dissolved 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 the mixture was heated to 60°C with stirring. After two hours, a solution of microcapsules containing the diazo compound as the core substance for Recording Material A was prepared.

Preparation of the diazo compound dispersion for Recording Material B:

3 parts of 1-morpholino-2,5-dibutoxybenzene-4-diazonium hexafluorophosphate and 100 parts of 10% aqueous solution of polyvinyl alcohol were mixed and dispersed for a whole day.

Preparation of the coupling component dispersion for Recording Materials A and B:

10 parts of 2-hydroxy-3-naphthoic acid anilide (coupling component) 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.

Preparation of Recording Material A:

50 parts of the thus-obtained coupling component dispersion, and 10 parts by weight of a 40% calcium carbonate dispersion were added to 50 parts of the above-obtained solution of microcapsules containing the diazo compound for Recording Material A 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.

Preparation of Recording Material B:

The procedure of preparation of Recording Material A was repeated except that the diazo compound dispersion for Recording Material B was used in place of the diazo compound-containing capsule solution for Recording Material A to prepare Recording Material B.

Recording Materials A and B 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 using a 2-B pencil) superimposed thereon. The fluorescent lamp used had a maximum value at 420 nm in emission spectrum. Then, the test original was removed and the material was heated for 3 seconds using a heat block heated to 120° C. The same procedures were separately repeated except for changing the heating temperature to 80° C or 100° C. On the other hand, water was coated in an amount of 2 g/m^2 on Recording Materials A and B after exposure and before heating, followed by heating it in the same manner using the heat block. In order to test shelf life, Recording Materials A and B were stored for 24 hours at 40° C, 90% RH before being exposed, and after that, the materials were exposed by light, coated with water and developed at respective temperatures in the same manner. Image densities of colored portions and background portions of respective materials obtained by the tests were measured using a Macbeth densitometer. Table 1 shows the results of tests wherein the heating temperature was changed, and Table 2 shows the results of tests on the storage property before recording.

As is shown in Table 1, development in the presence of dampening water enables a high image density to be obtained even when a low temperature is employed for development. Advantages of the present invention become apparent from the results shown in Table 1, and the storage properties can be seen from the results shown in Table 2.

Table 1

Heat-Developing Temperature		Image Density		Background Density	
		A	B	A	B
80° C	*	1.25	1.08	0.12	0.20
	-	0.56	0.37	0.12	0.18
100° C	*	1.28	1.15	0.14	0.21
	-	0.97	0.88	0.13	0.20
120° C	*	1.28	1.21	0.14	0.23
	—	1.25	1.16	0.13	0.21

In the above Table 1, (*) indicates tests using dampening water, and (-) indicates tests using no dampening water.

Table 2

Heat-Developing Temperature		Background Density			
		40° C, 90% RH		60° C, 30% RH	
		A	B	A	B
80° C	*	0.13	0.58	0.13	0.34
	-	0.12	0.37	0.12	0.31
100° C	*	0.16	0.71	0.15	0.42
	-	0.15	0.65	0.15	0.38
120° C	*	0.16	0.78	0.16	0.45
	—	0.15	0.75	0.15	0.43

In the above Table 2, (*) indicates tests using dampening water, and (-) indicates tests using no dampening water.

EXAMPLE 2

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/trimethylole 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 emuylsified and dispersed at 20°C to obtain an emulsion having an average particle size of 1 µm. 100 parts of water were 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-phenylpyrazolidine-3-one (Phenidone A) were 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/mz) using a coating rod, and then dried to prepare Recording Material C.

Recording Material C was exposed with a jet lamp (ultra high pressure mercury lamp, manufactured by Oak K.K.) through a test original having line image to form an image. The density of the thus formed image was measured with Macbeth densitometer, and the value 1.26 was obtained.

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

Separately, the image formed sample was heated for 3 seconds using a heat block heated to 80°C, 100°C and 120°C, in the same manner as in Example 1, respectively. On the other hand, water was coated in an amount of 1 g/m^2 on Recording material C after exposure and before heating, followed by heating it using the heat block in the same manner as in Example 1. The density of background of the samples heated using a heat block and then allowed to stand in a bright room for 6 hours was measured.

The result are shown in Table 3.

Table 3

Heat-Developing Temperature		Background Density
80°C	*	0.16
	-	1.14
100°C	*	0.14
	-	0.97
120°C	*	0.14
	—	0.16

In the above Table 3, (*) indicates tests using dampening water, and (-) indicates tests using no dampening water.

Claims

1. A method of forming an image, which comprises heating a recording material comprising a support having provided thereon a fine particle dispersion containing in imagewise disposition a light-sensitive organic substance and photo-decomposition product of the light-sensitive organic substance, said dispersion further containing a labelling organic substance capable of chemically or physically discriminating between the light-sensitive organic substance and the photo-decomposition product, characterised in that the recording material is uniformly heated in the presence of a slight amount of water.

2. A method as claimed in claim 1, wherein the recording material is heated with a heating means and is coated with the slight amount of water immediately before with respect to the direction of travel of the recording material, or at the same position as, said heating with said heating means.

3. A method as claimed in claim 1, wherein the recording material is heated with steam and with a heating means, the heating with steam occurring immediately before with respect to the direction of travel of the recording material, or at the same position as, the heating with said heating means.

4. A method as claimed in claim 1, wherein said support has provided thereon microcapsules containing water, and the recording material is pressed with a pressing means sufficiently to cause release of water from the microcapsules and is heated with a heating means, said pressing means being disposed immediately before with respect to the direction of travel of the recording material, or at the same position as. said heating means.

5. A method as claimed in claim 1, wherein said support has provided thereon a composition capable of releasing water upon application of heat, and the recording material is heated sufficiently to cause release of water from the water-releasing composition.

6. A method as claimed in any preceding claim, wherein the amount of water present is from 0.1 to 20 g/m^2.

7. A method as claimed in any preceding claim, wherein said light-sensitive organic substance is contained in microcapsules.

8. A method as claimed in any preceding claim, wherein said light-sensitive organic substance is a diazo compound, said labelling organic substance is an organic coupler, and after imagewise exposure to form a latent image with the photo-decomposition product, the light-sensitive layer is dampened and developed by heat using a heating means.

9. A recording material comprising a support having provided thereon a dispersion of fine particles of a light-sensitive organic substance and of a labelling organic substance capable of chemically or physically discriminating between a light-sensitive organic substance and a photo-decomposition product of said light-sensitive organic substance, characterised in that a slight amount of water is also provided on the support.

10. A recording material as claimed in claim 9, wherein the water is contained in microcapsules.

11. A recording material as claimed in claim 9, wherein the water is present as water of crystallization or water of hydration.

12. A recording material as claimed in any one of claims 9 to 11, wherein said light-sensitive organic substance is a diazo compound, and said labelling substance is a coupling organic substance.

13. A recording material as claimed in any one of claims 9 to 12, wherein said light-sensitive organic substance is contained in microcapsules.

14. A recording material as claimed in claim 13, wherein the walls of the microcapsules containing said light-sensitive compound comprise a high molecular weight substance formed by polymerization of a substance around a core substance after emulsification of the core substance.

15. A recording material as claimed in claim 14, wherein said high molecular weight substance comprises at least one of polyurethane and polyurea.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 89305124.3

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	<u>US - A - 3 525 619</u> (SCHELER et al.) * Claims *	1,4,5, 8-12	G 03 C 5/34 G 03 C 5/18
Y	<u>DE - A1 - 3 636 333</u> (FUJI PHOTO FILM) * Abstract; page 4, lines 28-36; page 9, lines 4-29 *	1,7, 12-15	
D,A	<u>US - A - 4 650 740</u> (USAMI et al.) * Claim 1; column 2, lines 10-16 *	1,8	
A	<u>FR - A1 - 2 382 026</u> (LES LABORATOIRES DE PHYSICO CHIMIE APPLIQUEE ISSEC) * Claim 1 *	1,8	
A	<u>US - A - 4 452 876</u> (SCHAEFFER et al.) * Claims; example 1 *	1,3,8	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	24-08-1989	BÖHM

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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