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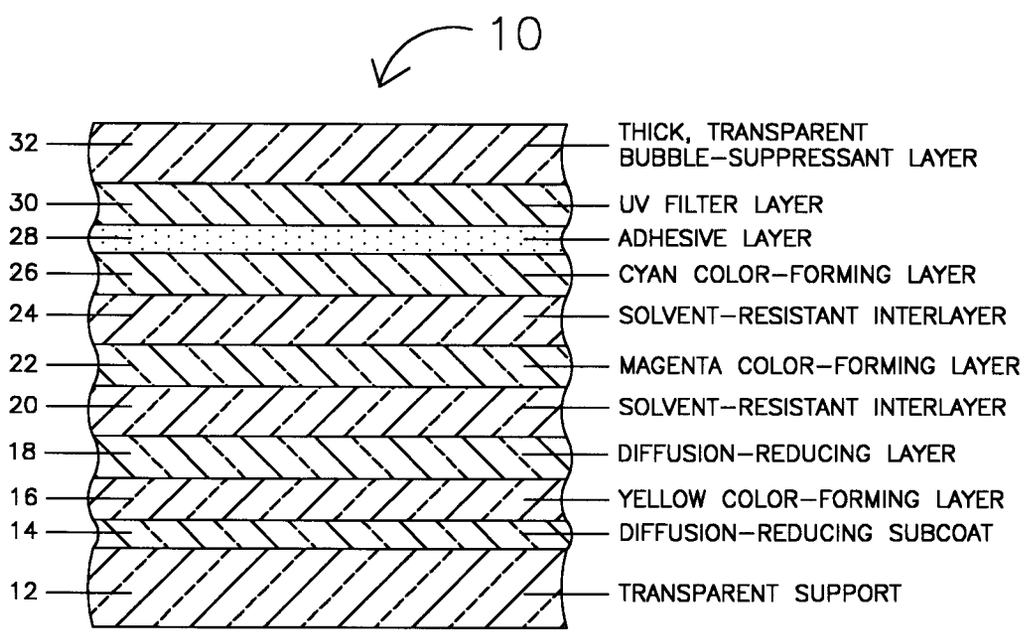
(54) Imaging medium with reduced dye diffusion.

(57) An imaging medium comprises a color-forming layer comprising a color-forming composition adapted to undergo a change of color upon exposure to actinic radiation, the color-forming composition being dispersed in a first polymer having a glass transition temperature of at least 50 °C; and at least one diffusion-reducing layer in contact with one face of the color-forming layer, the or each diffusion-reducing layer comprising a second polymer, having a glass transition temperature of at least 50 °C, and being essentially free from the color-forming composition. Post-imaging diffusion of the colored materials formed during imaging is reduced by the use of the high glass transition temperature polymer in the color-forming layer and the provision of the diffusion-reducing layer(s), so that the images formed are stable upon storage.



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This invention relates to a imaging medium with reduced dye diffusion, and to an imaging process using such an imaging medium.

Imaging media are known which have at least one color-forming layer comprising a color-forming composition adapted to undergo a rapid change of color (from colorless to colored, from colored to colorless, or from one color to another) upon increase in the temperature of the color-forming layer above a color-forming temperature for a color-forming time. The color change in such media need not be supplied by applying heat directly to the medium; the color-forming composition may comprise a color-forming compound which undergoes a change of color upon heating above a color-forming temperature, and an absorber capable of absorbing actinic radiation and thereby generating heat in the color-forming layer. When such a medium is exposed to appropriate actinic radiation, this radiation is absorbed by the absorber, thereby heating the color-forming compound and causing it to undergo its color change. Many such thermal imaging media have the advantage over conventional silver halide media of not requiring a post-exposure developing step. Such thermal imaging media also have the advantage that they are essentially insensitive to visible light, so that they can be handled under normal lighting conditions.

For example U.S. Patents Nos. 4,602,263 and 4,826,976 both describe thermal imaging systems for optical recording and particularly for forming color images. These thermal imaging systems rely upon the irreversible unimolecular fragmentation of one or more thermally unstable carbamate moieties of an organic compound to effect a visually discernible color shift. U.S. Patent No. 4,720,449 describes a similar imaging system in which the color-developing component is a substantially colorless di- or triarylmethane imaging compound possessing within its di- or triarylmethane structure an aryl group substituted in the ortho position to the meso carbon atom with a moiety ring-closed on the meso carbon atom to form a 5- or 6-membered ring, said moiety possessing a nitrogen atom bonded directly to the meso carbon atom and the nitrogen atom being bound to a group with a masked acyl substituent that undergoes fragmentation upon heating to liberate the acyl group for effecting intramolecular acylation of the nitrogen atom to form a new group in the ortho position that cannot bond to the meso carbon atom, whereby the di- or triarylmethane compound is rendered colored. Other thermal imaging systems using di- or triarylmethane compounds are described in U.S. Patents Nos. 4,720,450 and 4,960,901, while U.S. Patent No. 4,745,046 describes a thermal imaging system using as color-forming co-reactants a substantially colorless di- or triarylmethane compound possessing on the meso carbon atom within its di- or triarylmethane structure an aryl group substituted in the ortho position with a nucleophilic moiety which is ring-closed on the meso carbon atom, and an electrophilic reagent which upon heating and contacting the di- or triarylmethane compound undergoes a bimolecular nucleophilic substitution reaction with the nucleophilic moiety to form a colored, ring-opened di- or triarylmethane compound. Finally, International Patent Application No. PCT/US89/02965, published under No. WO90/00978 on February 8, 1990, describes a thermal imaging system in which the color-forming component is a colorless precursor of a preformed image dye substituted with (a) at least one thermally removable protecting group that undergoes fragmentation from the precursor upon heating and (b) at least one leaving group that is irreversibly eliminated from the precursor upon heating, provided that neither the protecting group nor the leaving group is hydrogen, said protecting and leaving groups maintaining the precursor in its colorless form until heat is applied to effect removal of the protecting and leaving groups, whereby the colorless precursor is converted to an image dye.

The aforementioned patents describe a preferred form of imaging medium for forming multicolor images; in this preferred imaging medium, three separate color-forming layers, capable of forming yellow, cyan and magenta dyes respectively, are superposed on top of one another. Each of the three color-forming layers has an infra-red absorber associated therewith, these absorbers absorbing at differing wavelengths, for example 760, 820 and 880 nm. This medium is imagewise exposed simultaneously to three lasers having wavelengths of 760, 820 and 880 nm. (In the present state of technology, solid state diode lasers emitting at about 760 to 1000 nm provide the highest output per unit cost. Since most of the color-forming materials (also hereinafter referred to as "leuco dyes", with the understanding that the leuco dye may comprise more than one compound) described in the aforementioned patents do not have high extinction coefficients within this wavelength range, it is necessary to include the infra-red absorbers with the leuco dyes in order to ensure efficient absorption of the laser radiation and hence efficient heating of the leuco dye.) The resultant imagewise heating of the color-forming layers causes the leuco dyes to undergo color changes in the exposed areas, thereby producing a multicolored image, which needs no development.

This preferred type of imaging medium is capable of very high resolution images; for example, the medium can readily be imaged using a laser to produce a 2000 line 35 mm slide. However, it has been found that, although the quality of the images produced is initially high, sometimes upon storage the sharpness of the image degenerates; for example, narrow lines with sharp, well-defined edges in the original image may become broader and show fuzzy edges after the image has been stored at room temperature

for weeks or months. Such fuzziness in the image is of course highly undesirable in a high resolution imaging system.

It has now been found that this loss of image sharpness can be reduced or eliminated by controlling the glass transition temperature of the color-forming layer and an adjacent layer.

Accordingly, this invention provides an imaging medium comprising:

a color-forming layer comprising a thermal color-forming composition adapted to undergo a change of color upon increase in the temperature of the color-forming layer above a color-forming temperature for a color-forming time, the color-forming composition being dispersed in a first polymer having a glass transition temperature of at least 50 °C; and

a diffusion-reducing layer in contact with one face of the color-forming layer, the diffusion-reducing layer comprising a second polymer, having a glass transition temperature of at least 50 °C, and being essentially free from the color-forming composition.

This invention also provides a process for forming and storing a image, the process comprising:

providing an imaging medium of the invention;

imagewise heating the color-forming layer above the color-forming temperature for the color-forming time, thereby causing the color-forming composition to undergo the change of color in heated regions, produce a colored material in these heated regions, and thereby form an image;

storing the image for a period of at least about one week without substantial diffusion of the colored material outwith the color-forming layer and the diffusion-reducing layer.

The accompanying drawing shows a schematic cross-section through a preferred imaging medium of the present invention.

As already mentioned, the imaging medium of the present invention comprises a color-forming layer comprising a color-forming composition dispersed in a first polymer having a glass transition temperature of at least 50 °C, and a diffusion-reducing layer in contact with one face of the color-forming layer, having a glass transition temperature of at least 50 °C, and being essentially free from the color-forming composition.

As with the imaging media described in the aforementioned U.S. Patents, in the imaging medium of the present invention the color-forming composition desirably comprises a color-forming compound which undergoes a change of color upon heating above a color-forming temperature, and an absorber capable of absorbing actinic radiation and thereby generating heat in the color-forming layer. This type of imaging medium can be imaged by actinic radiation rather than by direct heating, and a high resolution image is more easily achieved using actinic radiation, for example a focussed laser.

In some cases, it will be desirable to provide two diffusion-reducing layers in contact with opposed faces of the color-forming layer, so that the color-forming composition cannot diffuse in either direction from the color-forming layer. However, in some cases (for example, where the color-forming layer is directly in contact with a support into which the colored material formed upon imaging does not migrate to a significant extent during storage of the image), a single diffusion-reducing layer may suffice. Note, however, that some high glass transition polymers used in the color-forming layer do not adhere well to some supports (for example, poly(methyl methacrylate) does not adhere well to poly(ethylene terephthalate)), and if a conventional subcoat is employed to increase adhesion of the color-forming layer to the support, diffusion of colored material into the subcoat after imaging may occur, with consequent loss of image sharpness. If a subcoat is needed to increase adhesion of the color-forming layer to the support, it is desirable to provide a diffusion-reducing subcoat between the color-forming layer and the support, this diffusion-reducing subcoat serving as both a subcoat and a diffusion-reducing layer. An example of such a diffusion-reducing subcoat is shown in the accompanying drawing and described in detail below.

Obviously, in a multicolor imaging medium one or more than one color-forming layer may be provided with a diffusion-reducing layer or layers in accordance with the present invention.

The first polymer used in the imaging medium of the present invention desirably has a glass transition temperature of at least 75 °C, and preferably at least 95 °C. This polymer is preferably an acrylic polymer, desirably poly(methyl methacrylate), which has a glass transition temperature of about 110 °C. The or each diffusion-reducing layer desirably has a glass transition temperature of at least 55 °C, and preferably comprises an acrylic polymer, styrene-acrylic polymers being especially preferred. Appropriate styrene-acrylic polymers are readily available commercially, and good results have been obtained using the acrylic latices sold as Joncryl 138 and 538 by S.C. Johnson & Son, Inc., Racine WI 53403, United States of America. However, layers formed solely from these Joncryl latices do show some tendency to crack during coating, and to reduce this tendency towards cracking, it has been found desirable to include in the diffusion-reducing layer a minor proportion of a water-soluble acrylic polymer, such as that sold under the tradename Carboset 526 by The B.F. Goodrich Co., Akron Ohio 44313, United States of America. Although the glass transition temperatures of the diffusion-reducing layer can be higher than those of these specific

polymers, difficulties may be encountered in producing media containing a plurality of adjacent layers, all of which have very high glass transition temperatures, and such media may not be very stable against cracking during storage, and thus it is generally convenient to use a very high glass transition temperature material (T_g > 95 °C) for the color-forming layer and a material of lower glass transition temperature (T_g < 75 °C) for the diffusion-reducing layer or layers.

The or each diffusion-reducing layer must of course be thick enough to ensure that the color-forming composition cannot diffuse therethrough and thus migrate to other layers of the imaging medium where it may produce undesirable effects. On the other hand, it is desirable to avoid excessively thick diffusion-reducing layers, since such thick layers may adversely affect the resolution of the imaging medium. The optimum thickness of diffusion-reducing layer in any specific imaging medium may readily be determined empirically. In general, it is preferred that the diffusion-reducing layer have a thickness of at least 1μm.

It is known to those skilled in the relevant art that the tendency of dyes to migrate through polymers are reduced as the glass transition temperature of the polymer increases; for example, it is known that in dye diffusion thermal transfer imaging, the image-receiving layer should normally have a low glass transition temperature so that dye can readily diffuse thereinto. However, it should be noted that the advantages of the present invention are not achieved simply by placing the color-forming composition in a layer of a polymer having a high glass transition temperature; provision of the diffusion-reducing layer having a glass transition temperature of at least about 50 °C is also necessary to substantially reduce or overcome the problem of post-imaging diffusion of colored material. The diffusion-reducing layer or layers should also be essentially free from (and preferably completely free from) the color-forming composition, since any color-forming composition present in the diffusion-reducing layer(s) may tend to migrate laterally during storage after imaging, with deleterious effects on the sharpness of the image produced.

The color-forming composition used in the present imaging medium may be any of those described in the aforementioned patents, or in various copending Applications. Thus, the color-forming composition may be:

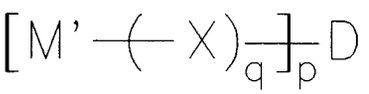
a. an organic compound capable of undergoing, upon heating, an irreversible unimolecular fragmentation of at least one thermally unstable carbamate moiety, this organic compound initially absorbing radiation in the visible or the non-visible region of the electromagnetic spectrum, said unimolecular fragmentation visibly changing the appearance of the organic compound (see U.S. Patent No. 4,602,263);

b. a substantially colorless di- or triarylmethane imaging compound possessing within its di- or triarylmethane structure an aryl group substituted in the ortho position to the meso carbon atom with a moiety ring-closed on the meso carbon atom to form a 5- or 6-membered ring, said moiety possessing a nitrogen atom bonded directly to said meso carbon atom and said nitrogen atom being bound to a group with a masked acyl substituent that undergoes fragmentation upon heating to liberate the acyl group for effecting intramolecular acylation of said nitrogen atom to form a new group in the ortho position that cannot bond to the meso carbon atom, whereby said di- or triarylmethane compound is rendered colored (see U.S. Patent No. 4,720,449);

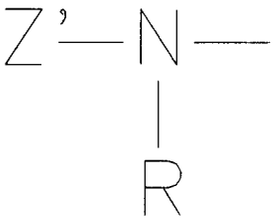
c. a colored di- or triarylmethane imaging compound possessing within its di- or triarylmethane structure an aryl group substituted in the ortho position to the meso carbon atom with a thermally unstable urea moiety, said urea moiety undergoing a unimolecular fragmentation reaction upon heating to provide a new group in said ortho position that bonds to said meso carbon atom to form a ring having 5 or 6 members, whereby said di- or triarylmethane compound becomes ring-closed and rendered colorless (see U.S. Patent No. 4,720,450);

d. in combination, a substantially colorless di- or triarylmethane compound possessing on the meso carbon atom within its di- or triarylmethane structure an aryl group substituted in the ortho position with a nucleophilic moiety which is ring-closed on the meso carbon atom, and an electrophilic reagent which upon heating and contacting said di- or triarylmethane compound undergoes a bimolecular nucleophilic substitution reaction with said nucleophilic moiety to form a colored, ring-opened di- or triarylmethane compound (see U.S. Patent No. 4,745,046);

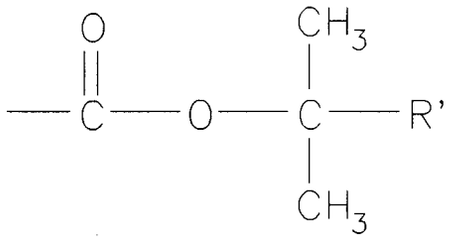
e. a compound of the formula



wherein M' has the formula:

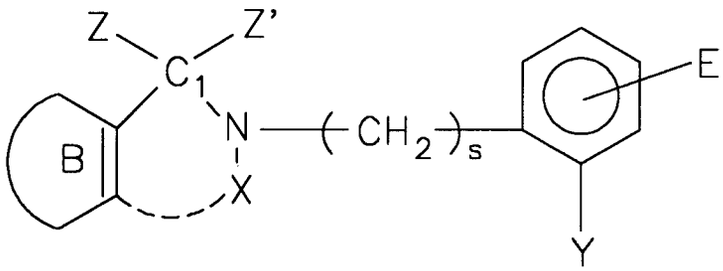


wherein R is alkyl; $-SO_2R^1$ wherein R^1 is alkyl; phenyl; naphthyl; or phenyl substituted with alkyl, alkoxy, halo, trifluoromethyl, cyano, nitro, carboxy, $-CONR^2R^3$ wherein R^2 and R^3 each are hydrogen or alkyl, $-CO_2R^4$ wherein R^4 is alkyl or phenyl, $-COR^5$ wherein R^5 is amino, alkyl or phenyl, $-NR^6R^7$ wherein R^6 and R^7 each are hydrogen or alkyl, $-SO_2NR^8R^9$ wherein R^8 and R^9 each are hydrogen, alkyl or benzyl; Z' has the formula:



wherein R' is halomethyl or alkyl; X is -N=, $-SO_2-$ or $-CH_2-$; D taken with X and M' represents the radical of a color-shifted organic dye; q is 0 or 1; and p is a whole number of at least 1; said Z' being removed from said M' upon the application of heat to effect a visually discernible change in spectral absorption characteristics of said dye (see U.S. Patent No. 4,826,976);

f. a substantially colorless di- or triarylmethane compound of the formula:



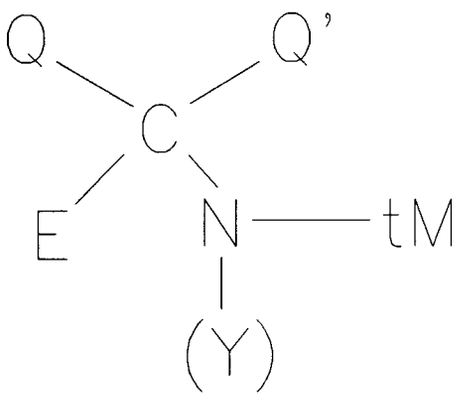
wherein ring B represents a carbocyclic aryl ring or a heterocyclic aryl ring; C_1 represents the meso carbon atom of said di- or triarylmethane compound; X represents -C(=O)-; $-SO_2-$ or $-CH_2-$ and completes a moiety ring-closed on said meso carbon atom, said moiety including the nitrogen atom bonded directly to said meso carbon atom; Y represents -NH-C(=O)-L, wherein L is a leaving group that departs upon thermal fragmentation to unmask -N=C=O for effecting intramolecular acylation of said nitrogen atom to open the N-containing ring and form a new group in the ortho position of ring B that cannot bond to said meso carbon atom; E is hydrogen, an electron-donating group, an electron-withdrawing group or a group, either an electron-donating group or an electron-neutral group that undergoes fragmentation upon heating to liberate an electron-withdrawing group; s is 0 or 1; and Z and Z' taken individually represent the moieties to complete the auxochromic system of a diarylmethane or triarylmethane dye when said N-containing ring is open, and Z and Z' taken together represent the bridged moieties to complete the auxochromic system of a bridged triarylmethane dye when said N-containing ring is open (see U.S. Patent No. 4,960,901);

g. a colorless precursor of a preformed image dye substituted with (a) at least one thermally removable protecting group that undergoes fragmentation from said precursor upon heating and (b) at least one leaving group that is irreversibly eliminated from said precursor upon heating, provided that neither said

protecting group nor said leaving group is hydrogen, said protecting and leaving groups maintaining said precursor in its colorless form until heat is applied to effect removal of said protecting and leaving groups whereby said colorless precursor is converted to an image dye (see the aforementioned International Patent Application No. PCT/US89/02965);

h. a mixed carbonate ester of a quinophthalone dye and a tertiary alkanol containing not more than about 9 carbon atoms;

i. a leuco dye represented by:



wherein:

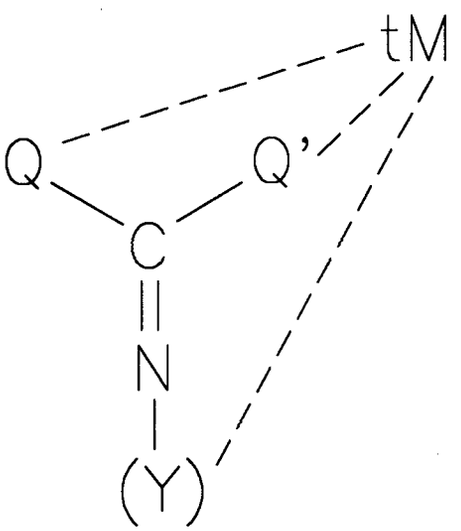
E represents a thermally removable leaving group;

tM represents a thermally migratable acyl group;

Q, Q' and C taken together represent a dye-forming coupler moiety wherein C is the coupling carbon of said coupler moiety;

and, (Y) taken together with N represents an aromatic amino color developer,

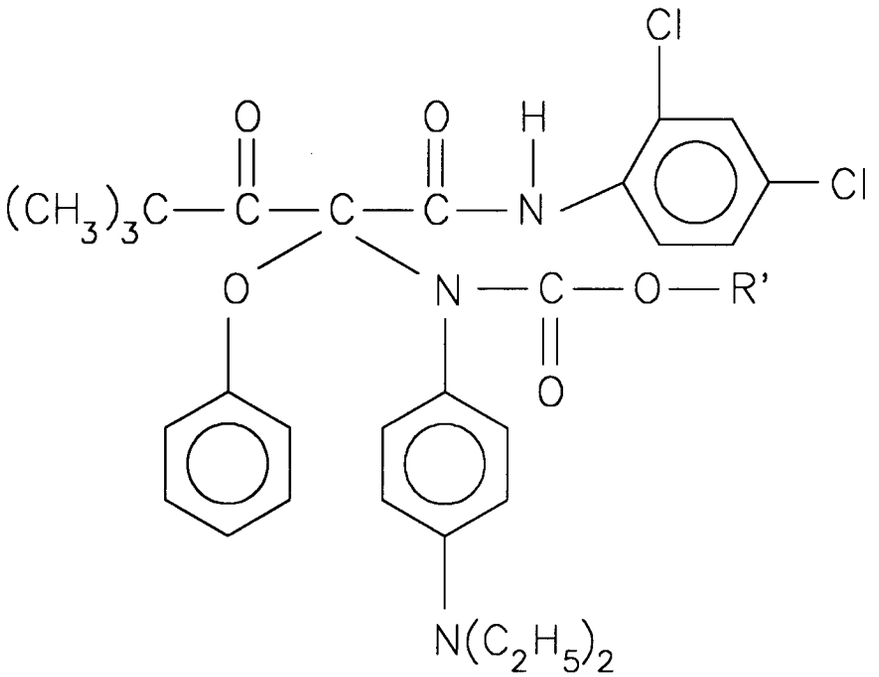
one of said Q, Q' and (Y) containing an atom selected from the atoms comprising Group 5A/Group 6A of the Periodic Table, said groups E and tM maintaining said leuco dye in a substantially colorless form until the application of heat causes said group E to be eliminated from said leuco dye and said group tM to migrate from said N atom to said Group 5A/Group 6A atom thereby forming a dye represented by:



wherein said dotted lines indicate that said tM group is bonded to said Group 5A/Group 6A atom in one of said Q, Q' and (Y) (see U.S. Application Serial No. 696,196, filed May 6, 1991, and corresponding applications in other countries).

Of these color-forming compounds, it has been found that the colored material formed from those leuco dyes described in the aforementioned International Application No. PCT/US89/02965 are especially prone to

migrate within an imaging medium after imaging, and thus the present invention is especially useful with these imaging dyes. Among this class of imaging dyes, one especially preferred leuco dye is that of the formula:



(hereinafter referred to as "Leuco Dye A").

As already noted, the aforementioned patents describe a multicolor imaging medium having two or more (usually three) different color-forming layers which produce different colors. In a preferred form of such an imaging medium, the color-forming layers are separated by solvent-resistant interlayers. Accordingly, a preferred form of the present imaging medium comprises:

a support;

a first color-forming layer superposed on the support;

a diffusion-reducing layer superposed on the first color-forming layer;

a second color-forming layer superposed on the second diffusion-reducing layer, the second color-forming layer comprising a second color-forming composition adapted to undergo a change of color upon increase in the temperature of the color-forming layer above a second color-forming temperature for a second color-forming time, the color change undergone by the second color-forming layer being different from that undergone by the other color-forming layer; and

an interlayer interposed between the diffusion-reducing layer and the second color-forming layer, the interlayer having a glass transition temperature less than 50 °C.

Except for the high glass transition temperature color-forming layer and diffusion-reducing layers, the other layers of the imaging medium of the present invention, and the techniques used for forming and exposing the medium, can be those used in the aforementioned U.S. Patents Nos. 4,602,263; 4,720,449; 4,720,450; 4,745,046; 4,826,976; and 4,960,901. Thus, in carrying out the imaging method of the present invention, heat may be applied or induced imagewise in a variety of ways. Preferably, selective heating is produced in the color-forming layer itself by the conversion of electromagnetic radiation into heat, and preferably the light source is a laser beam emitting source such as a gas laser or semiconductor laser diode. The use of a laser is not only well suited for recording in a scanning mode but by utilizing a highly concentrated beam, radiant energy can be concentrated in a small area so that it is possible to record at high speed and high resolution. Also, it is a convenient way to record data as a heat pattern in response to transmitted signals, such as digitized information, and a convenient way of preparing multicolor images by employing a plurality of laser sources that emit at differing wavelengths.

Most of the aforementioned preferred leuco dyes do not absorb strongly in the infra-red. Since, at present, imaging processes are preferably carried out using an infra-red laser, in a preferred embodiment, the heat-sensitive element contains an infra-red absorbing substance for converting infra-red radiation into

heat, which is transferred to the leuco dye to initiate the color-forming reaction and effect the change in the absorption characteristics of the leuco dye from colorless to colored. Obviously, the infra-red absorber should be in heat-conductive relationship with the leuco dye, for example, in the same layer as the leuco dye or in an adjacent layer. Though an inorganic compound may be employed, the infra-red absorber preferably is an organic compound, such as a cyanine, merocyanine, squarylium, thiopyrylium or benzpyrylium dye, and preferably, is substantially non-absorbing in the visible region of the electromagnetic spectrum so that it will not contribute any substantial amount of color to the D_{min} areas, i.e., the highlight areas of the image. The light absorbed by the respective infra-red absorbers is converted into heat and the heat initiates the reaction to effect the formation of the colored materials in the color-forming layers.

In the production of such multi-color images, the infra-red absorbers are desirably selected such that they absorb radiation at different predetermined wavelengths above 700 nm sufficiently separated so that each color-forming layer may be exposed separately and independently of the others by using infra-red radiation at the particular wavelengths selectively absorbed by the respective infra-red absorbers. As an illustration, the color-forming layers containing yellow, magenta and cyan leuco dyes may have infra-red absorbers associated therewith that absorb radiation at 760 nm, 820 nm and 880 nm, respectively, and may be addressed by laser sources, for example, infra-red laser diodes emitting at these respective wavelengths so that the three color-forming layers can be exposed independently of one another. While each layer may be exposed in a separate scan, it is usually preferred to expose all of the color-forming layers simultaneously in a single scan using multiple laser sources of the appropriate wavelengths. Instead of using superimposed imaging layers, the leuco dyes and associated infra-red absorbers may be arranged in an array of side-by-side dots or stripes in a single recording layer.

Where imagewise heating is induced by converting light to heat as in the embodiments described above, the imaging medium may be heated prior to or during exposure. This may be achieved using a heating platen or heated drum or by employing an additional laser source or other appropriate means for heating the medium while it is being exposed.

In addition to the color-forming and diffusion-reducing layers, the imaging medium of the present invention may comprise additional layers, for example, a subbing layer to improve adhesion to a support, interlayers for thermally insulating the color-forming layers from each other, an anti-abrasive topcoat layer, an ultra-violet screening layer having an ultraviolet absorber therein, or other auxiliary layers. To give good protection against ultra-violet radiation, ultra-violet screening layers are desirably provided on both sides of the color-forming layer(s); conveniently, one of the ultra-violet screening layers is provided by using as the support a polymer film containing an ultra-violet absorber, and such absorber-containing films are available commercially. The leuco dyes are selected to give the desired color or combination of colors, and for multicolor images, the compounds selected may comprise the subtractive primaries yellow, magenta and cyan or other combinations of colors, which combinations may additionally include black. The leuco dyes generally are selected to give the subtractive colors cyan, magenta and yellow, as commonly employed in photographic processes to provide full natural color.

The support employed may be transparent or opaque and may be any material that substantially retains its dimensional stability during image formation. Suitable supports include paper, paper coated with a resin or pigment, such as calcium carbonate or calcined clay, synthetic papers or plastic films, such as polyethylene, polypropylene, polycarbonate, cellulose acetate, poly(ethylene terephthalate) and polystyrene. If it is desired to image through the support, the support must of course be sufficiently transparent that it does not interfere with the imaging process, and in this case it is also desirable that the support be substantially non-birefringent.

Usually the or each color-forming layer contains a binder and is formed by combining the leuco dye, the infra-red absorber and the binder in a common solvent, applying a layer of the coating composition to the support and then drying. Rather than a solution coating, the layer may be applied as a dispersion or an emulsion. The coating composition also may contain dispersing agents, plasticizers, defoaming agents, hindered amine light stabilizers and coating aids. In forming the color-forming layer(s) and the interlayers or other layers, temperatures should be maintained below levels that will cause the color-forming reaction to occur rapidly so that the leuco dyes will not be prematurely colored or bleached.

Examples of binders that may be used include poly(vinyl alcohol), poly(vinyl pyrrolidone), methyl cellulose, cellulose acetate butyrate, styrene-acrylonitrile copolymers, copolymers of styrene and butadiene, poly(methyl methacrylate), copolymers of methyl and ethyl acrylate, poly(vinyl acetate), poly(vinyl butyral), polyurethane, polycarbonate and poly(vinyl chloride). It will be appreciated that the binder selected should not have any adverse effect on the leuco dye incorporated therein and may be selected to have a beneficial effect. Also, the binder should be substantially heat-stable at the temperatures encountered during image formation and it should be transparent so that it does not interfere with viewing of the color image. Where

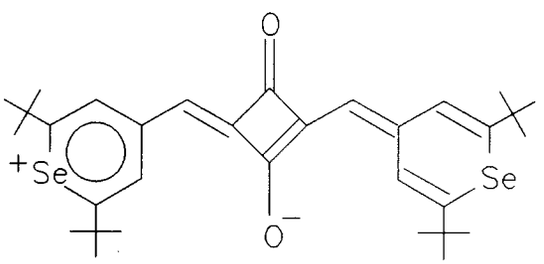
electromagnetic radiation is employed to induce imagewise heating, the binder also should transmit the light intended to initiate image formation.

A preferred embodiment of the invention will now be described, though by way of illustration only, with reference to the accompanying drawing, which is a schematic cross-section through an imaging medium of the present invention. The thicknesses of the various layers shown in the drawing are not to scale.

The imaging medium (generally designated 10) shown in the drawing is intended for use in the production of transparencies and comprises a substantially transparent support 12 formed of 4 mil (101 μm) poly(ethylene terephthalate) (PET) film incorporating an ultra-violet absorber. Appropriate PET films are readily available commercially, for example as P4C1A film from DuPont de Nemours., Wilmington, Delaware, United States of America.

The imaging medium 10 also comprises a diffusion-reducing subcoat 14 approximately 1 μm thick formed from a 10:1 w/w mixture of a water-dispersible styrene acrylic polymer (Joncryl 538 sold by S.C. Johnson & Son, Inc., Racine WI 53403, United States of America) and a water-soluble acrylic polymer (Carboset 526 sold by The B.F. Goodrich Co., Akron Ohio 44313, United States of America). As explained above, the presence of the minor proportion of water-soluble acrylic polymer reduces the tendency for the layer 14 to crack during the coating process. The diffusion-reducing subcoat 14, which has a glass transition temperature of approximately 55 °C, and serves the function of a conventional subcoat, namely increasing the adhesion of the color-forming layer 16 (described in detail below) to the support 12. The subcoat 14 also serves to reduce or eliminate migration of colored material from the color-forming layer 16 after imaging; as noted above, if a conventional subcoat were employed in place of the diffusion-reducing subcoat 14, diffusion of the colored material from the layer 16 into the subcoat after imaging might cause loss of sharpness of the image. The subcoat 14 is coated onto the support 12 from an aqueous medium containing the water-dispersible and water-soluble polymers.

A yellow color-forming layer 16 is in contact with the diffusion-reducing subcoat 14. This color-forming layer 16 is approximately 5 μm thick and comprises approximately 47.5 parts by weight of the aforementioned Leuco Dye A, 1.6 parts by weight of an infra-red absorber of the formula:



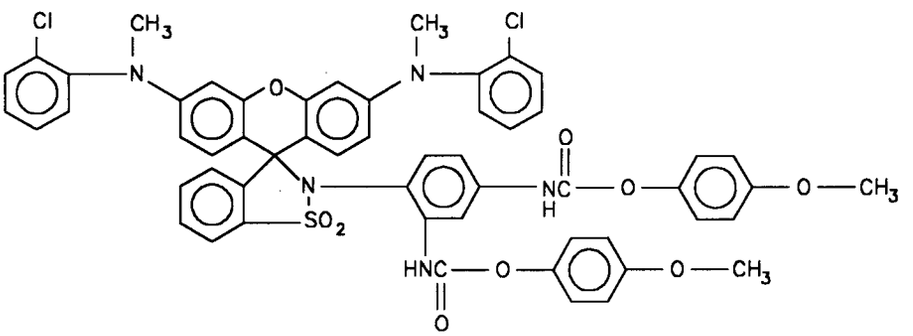
(which may be prepared by a process analogous to that described in U.S. Patent No. 4,508,811 using the 2,6-bis(1,1-dimethylethyl)-4-methylselenopyrylium salts described in the copending Application No. * (Attorney's ref. C-7660)), 3.3 parts by weight of a hindered amine stabilizer (HALS-63, sold by Fairmount Chemical Co., 117 Blanchard Street, Newark New Jersey 07105, United States of America), and 47.5 parts by weight of a poly(methyl methacrylate) binder (Elvacite 2021, sold by DuPont de Nemours, Wilmington, Delaware, United States of America; this material is stated by the manufacturer to be a methyl methacrylate/ethyl acrylate copolymer, but its glass transition temperature approximates that of poly(methyl methacrylate)). This binder has a glass transition temperature of approximately 110 °C. The color-forming layer 16 is applied by coating from a mixture of heptanes and methyl ethyl ketone.

Superposed on the yellow color-forming layer 16 is a diffusion-reducing layer 18, which, like the first diffusion-reducing layer 14, serves to prevent migration of colored material from the yellow color-forming layer 16 on storage after imaging. The diffusion-reducing layer 18, which is approximately 2 μm thick, is formed of a water-dispersible styrene acrylic polymer (Joncryl 138 sold by S.C. Johnson & Son, Inc., Racine WI 53403, United States of America), and is coated from an aqueous dispersion. This layer has a glass transition temperature of approximately 60 °C.

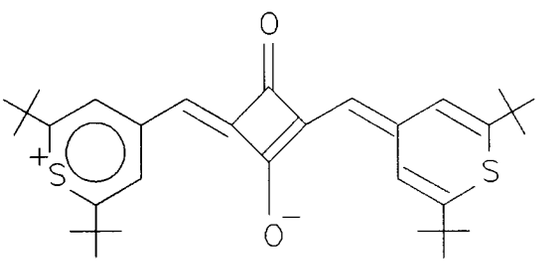
The next layer of the imaging medium 10 is a solvent-resistant interlayer 20 approximately 4.6 μm and composed of a major proportion of partially cross-linked polyurethane (NeoRez XR-9637 polyurethane sold by ICI Resins US, Wilmington, Massachusetts, United States of America) and a minor proportion of poly(vinyl alcohol) (Airvol 540, sold by Air Products and Chemicals, Inc., Allentown Pennsylvania 18195, United States of America). * corresponding to USSN 07/696 222 our file 3920-X-15.624 This solvent-resistant

interlayer 20 is coated from an aqueous dispersion. The interlayer 20 not only helps to thermally insulate the color-forming layers 14 and 22 (described below) from one another during imaging, but also prevents disruption and/or damage to the yellow color-forming layer 16 and the diffusion-reducing layer 18 during coating of the magenta color-forming layer 22. Since the yellow color-forming layer 16 and the magenta color-forming layer 22 are both coated from organic solutions, if a solvent-resistant interlayer were not provided on the layer 16 before the layer 22 was coated, the organic solvent used to coat the layer 22 may disrupt, damage or extract leuco dye or infra-red absorber from the layer 16. Provision of the solvent-resistant interlayer 20, which is not dissolved by and does not swell in the organic solvent used to coat the layer 22, serves to prevent disruption of or damage to the layer 16 as the layer 22 is coated. Furthermore, the solvent-resistant interlayer 20 serves to prevent the magenta leuco dye from the layer 22 sinking into the diffusion-reducing layer 18 and the yellow color-forming layer 16 as the layer 22 is being coated.

Superposed on the solvent-resistant interlayer 20 is the magenta color-forming layer 22, which is approximately 3 μm thick and comprises approximately 47.25 parts by weight of a leuco dye of the formula:



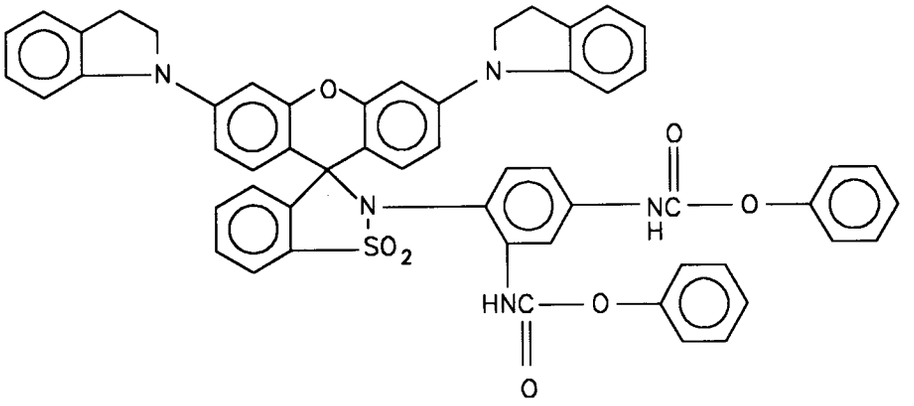
(hereinafter referred to as "Leuco Dye B"; this leuco dye may be prepared by the methods described in the aforementioned U.S. Patents Nos. 4,720,449 and 4,960,901), 1.62 parts by weight of an infra-red absorber of the formula:



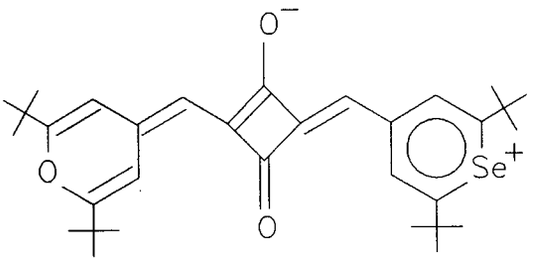
(see the aforementioned U.S. Patent No. 4,508,811), 3.6 parts by weight of a hindered amine stabilizer (HALS-63), 0.27 parts by weight of a wetting agent, and 47.25 parts by weight of a polyurethane binder (Estane 5715, supplied by The B.F. Goodrich Co., Akron Ohio 44313, United States of America). The color-forming layer 22 is applied by coating from a cyclohexanone/methyl ethyl ketone mixture.

On the color-forming layer 22 is coated a second solvent-resistant interlayer 24 which is formed from the same material, and coated in the same manner as, the solvent-resistant interlayer 20.

Superposed on the second solvent-resistant interlayer 24 is a cyan color-forming layer 26, which is approximately 3 μm thick and comprises approximately 49.5 parts by weight of a leuco dye of the formula:



(hereinafter referred to as "Leuco Dye C"; this leuco dye may be prepared by the methods described in the aforementioned U.S. Patents Nos. 4,720,449 and 4,960,901), 0.7 parts by weight of an infra-red absorber of the formula:



(which may be prepared as described in the aforementioned copending Application No. *(Attorney's reference C-7660)), 0.2 parts of a wetting agent, and 49.5 parts by weight of a polyurethane binder (Estane 5715). The color-forming layer 26 is applied by coating from methyl ethyl ketone.

As already indicated, the layers 14-26 of the imaging medium 10 are produced by coating on to the transparent support 12. However, the remaining layers of the imaging medium 10, namely the transparent bubble-suppressant layer 32, the ultraviolet filter layer 30 and the adhesive layer 28 are not coated on to the layer 26 but rather are prepared as a separate unit and then laminated to the remaining layers of the medium.

The transparent bubble-suppressant layer 32 is a 1.75 mil (44μm) PET film, a preferred film being that sold as ICI 505 film by ICI Americas, Inc., Wilmington, Delaware, United States of America. As explained in more detail in copending International Application No. PCT/US92/ , claiming priority from U.S. Application Serial No. 07/695,641, filed May 6, 1991 (Attorney's ref. C-7681), the bubble-suppressant layer 32 prevents the formation of bubbles in the imaging medium 10 during imaging, and thus helps to ensure that the colors in the imaged medium are not affected by bubble formation.

The ultraviolet filter layer 30 serves to protect the color-forming layers 16, 22 and 26 from the effects of ambient ultraviolet radiation. It has been found that the leuco dyes are susceptible to undergoing color changes when exposed to ultraviolet radiation during storage before or after imaging; such color changes are obviously undesirable since they increase the D_{min} of the image and may distort the colors therein. The ultraviolet filter layer 30 is approximately 5 μm thick and comprises approximately 83 percent by weight of a poly(methyl methacrylate) (Elvacite 2043, sold by DuPont de Nemours, Wilmington, Massachusetts, United States of America), 16.6 percent by weight of an ultraviolet filter (Tinuvin 328 sold by Ciba-Geigy, Ardsdale New York, United States of America) and 0.4 percent by weight of a wetting agent. The ultraviolet filter layer 30 is prepared by coating on to the bubble-suppressant layer 32 from a solution in methyl ethyl ketone.

The adhesive layer, which is approximately 2 μm thick, is formed of a water-dispersible styrene acrylic

* corresponding to USSN 07/696 222 our file 3920-X-15.624

polymer (Joncryl 138 sold by S.C. Johnson & Son, Inc., Racine WI 53403, United States of America) and is coated on to the ultraviolet filter layer 30 from an aqueous dispersion.

After the layers 30 and 28 have been coated on to the bubble-suppressant layer 32, the entire structure containing these three layers is laminated under heat (approximately 225 °F, 107 °C) and pressure to the structure containing the layers 12-26 to form the complete imaging medium 10.

If desired, the bubble-suppressant layer 32 may be formed by coating, rather than by lamination of a pre-formed film on to the layers 12-26. If the bubble-suppressant layer 32 is to be formed by coating, it is convenient to incorporate an ultra-violet absorber into the bubble-suppressant layer, thereby avoiding the need for a separate ultra-violet absorber layer. Thus, in this case, the layer 28 is coated on to the layer 26 using the solvent already described, and then the bubble-suppressant layer 32 containing the ultra-violet absorber may be coated on to the layer 28 from an aqueous medium.

The imaging medium 10 may be provided with additional layers, for example an anti-abrasion layer, superposed on the bubble-suppressant layer 32.

The medium 10 is imaged by exposing it simultaneously to the beams from three infra-red lasers having wavelengths of approximately 792, 822 and 869 nm. The 869 nm beam images the yellow color-forming layer 16, the 822 nm beam images the magenta color-forming layer 22 and the 792 nm beam images the cyan color-forming layer 26. Thus, a multicolor image is formed in the imaging medium 10, and this multicolor image requires no further development steps. Furthermore, the medium 10 may be handled in normal room lighting prior to exposure, and the apparatus in which the imaging is performed need not be light-tight.

It will be seen that, in the imaging medium 10, diffusion-reducing layers are present only on either side of the yellow color-forming layer 16, and only this color-forming layer comprises a polymer having a glass transition temperature of 50 °C. With the specific color-forming materials used in the imaging medium 10, post-imaging diffusion of the magenta and cyan colored materials formed in the layers 22 and 26 respectively during imaging leuco dyes is substantially less of a problem than diffusion of the yellow colored materials formed in the layer 16, and hence in this particular embodiment of the invention it is only the yellow color-forming layer which requires the use of a polymer with a high glass transition temperature, and the provision of diffusion-reducing layers, in accordance with the present invention. However, in other multicolor imaging media it may be necessary or desirable to apply the present invention to one, two or all three color-forming layers in order to prevent migration of leuco dyes therefrom.

Example 1

To demonstrate the effect of the glass transition temperatures of the color-forming layer and the diffusion-reducing subcoat and layer, a series of experimental media were prepared similar to that shown in the accompanying drawing and described above, but lacking the layers 20-26; thus, these test media produced a monochrome yellow image. The compositions of the support 12 and the color-forming layer 16 were as described above. However, in these experimental media, a coated bubble-suppressant layer was substituted for the laminated bubble-suppressant layer 32 described above. To prepare this coated bubble-suppressant layer, there was coated on to layer 18, in place of adhesive layer 28, a diffusion barrier layer approximately 2 μm thick, formed of a water-dispersible styrene acrylic polymer (Joncryl 538 sold by S. C. Johnson and San, Inc., Racine WI 53403, United States of America). On to this diffusion barrier layer was coated a bubble-suppressant layer containing an ultraviolet absorber; this bubble-suppressant layer thus served the functions of both the layers 30 and 32 described above. This bubble-suppressant layer comprised 89.5 percent by weight of a polyurethane (NeoRez R-966 sold by ICI Resins US, Wilmington, Massachusetts, United States of America), 4.7 percent by weight of a non-ionic water-soluble poly(ethylene oxide) (Polyox N-3000, sold by Union Carbide Corporation, Danbury, Connecticut, United States of America), 4 percent by weight of an ultraviolet filter (Tinuvin 1130 sold by sold by Ciba-Geigy, Ardsdale New York, United States of America) and 1.8 percent by weight of a wax lubricant (Michemlube 160 sold by Michaelman Chemical Corporation), and was coated from an aqueous dispersion. The bubble-suppressant layer was coated at a coating weights of approximately 2000 mg/ft^2 (21.5 g/m^2). The compositions of the diffusion-reducing subcoat 14 and the diffusion-reducing layer 18 were varied; the compositions of these two layers were:

Medium A: a 4:1 w/w mixture of the aforementioned Carboset 526 (T_g 70 °C) and NeoRez R-9000 (a polyurethane sold by ICI Resins US, Wilmington Massachusetts, United States of America, T_g < 40 °C)

Medium B: a 1:1 w/w mixture of NeoRez R-9000 and Nalco 1060 silica

Medium C: a 10:1 w/w mixture of the aforementioned Joncryl 538 (T_g 64 °C) and the aforementioned Carboset 526.

All three media were then imaged to maximum optical density using an infra-red laser to produce 40μm wide lines having an optical density of approximately 3, separated by non-imaged areas 60μm wide, so that the imaged medium had an overall optical density of approximately 0.4. If the yellow colored material produced during imaging diffuses into the non-imaged areas occurs upon post-imaging storage in a medium imaged in this manner, the overall optical density of the imaged medium will rise, since the optical density of the non-imaged areas increases substantially while that of the imaged areas does not change substantially. Accordingly, the overall optical transmission densities in blue light of the three imaged media were measured immediately after imaging and again after storage at 45°C for about one week; this high temperature storage can be expected to accelerate any diffusion of colored material, as compared with room temperature storage. The results are shown in Table 1 below.

Table 1

Medium	Transmission Density	
	Initial	After Storage
A	0.40	0.39
B	0.37	0.46
C	0.48	0.48

From the data in Table 1, it will be seen that media A and C, having high glass transition temperature diffusion-reducing layers, showed no evidence of diffusion after storage, whereas medium B having low glass transition temperature diffusion-reducing layers, showed significant diffusion after storage.

Example 2

To illustrate the effects of using a low glass transition temperature binder in a color-forming layer, an imaging medium was prepared similar to those used in Example 1 but with a yellow color-forming layer formed from the aforementioned Estane 5715 (T_g 16°C). The diffusion-reducing subcoat 14 and diffusion-reducing layer 18 were omitted, but a solvent-resistant interlayer 20 (formulated as described above) was provided on the color-forming layer 16.

After imaging in the same manner as in Example 1, this medium showed a overall transmission optical density in blue light of 0.45. After the post-imaging storage, this density increased to 1.10, showing the extreme diffusion of color materials experienced with a low glass transition temperature binder in a color-forming layer.

Example 3

The media used in this Example were media A and C as described in Example 1 above, and medium D, which was identical to medium B described in Example 1, except that its diffusion-reducing subcoat and diffusion-reducing layer were formed from the NeoRez XR-9637/Airvol 540 mixture used to form the solvent-resistant interlayer 20 in the preferred imaging medium described above with reference to the accompanying drawing.

All three media were then imaged to maximum optical density using an infra-red laser to produce a solid line having a transmission optical density of about 3.5 which is adjacent to a D_{min} (non-imaged) area with an optical density of about 0.07. If the yellow colored material produced during imaging diffuses into the non-imaged area, a gradient of image density will be found in the non-imaged area adjacent to the imaged line. Accordingly, the transmission optical densities in blue light of the three imaged media were measured at 40, 60 and 80 microns from the edge of the imaged line with a Joyce Loeble microdensitometer after six months' storage at room temperature. The results of these measurements are shown in Table 2 below.

Table 2

Medium	Transmission Density in D_{min} Area		
	40 microns	60 microns	80 microns
A	0.07	0.07	0.07
D	0.61	0.47	0.34
C	0.07	0.07	0.07

From the data in Table 2, it will be seen that media A and C, having high glass transition temperature diffusion-reducing layers, showed no evidence of diffusion after storage, whereas medium D having low glass transition temperature diffusion-reducing layers, showed significant diffusion after storage.

From the foregoing, it will be seen that the present invention is effective in preventing diffusion of the colored materials formed during imaging when the image is stored for substantial periods, and hence permits one to obtain sharp, well-defined images which do not suffer substantial loss of sharpness after storage.

Claims

1. An imaging medium comprising:

a color-forming layer comprising a thermal color-forming composition adapted to undergo a change of color upon increase in the temperature of the color-forming layer above a color-forming temperature for a color-forming time,

characterized in that the color-forming composition is dispersed in a first polymer having a glass transition temperature of at least 50 ° C;

and further characterized by a diffusion-reducing layer in contact with one face of the color-forming layer, the diffusion-reducing layer comprising a second polymer, having a glass transition temperature of at least 50 ° C, and being essentially free from the color-forming composition.

2. An imaging medium according to claim 1 characterized in that the color-forming composition comprises a color-forming compound which undergoes a change of color upon heating above the color-forming temperature for the color-forming time, and an absorber capable of absorbing actinic radiation and thereby generating heat in the color-forming layer.

3. An imaging medium according to either of the preceding claims characterized by two diffusion-reducing layers in contact with opposed faces of the color-forming layer.

4. An imaging medium according to any one of the preceding claims characterized in that the first polymer has a glass transition temperature of at least 75 ° C, and preferably at least 95 ° C.

5. An imaging medium according to any one of the preceding claims characterized in that the first polymer is an acrylic polymer, preferably poly(methyl methacrylate).

6. An imaging medium according to any one of the preceding claims characterized in that the or each diffusion-reducing layer has a glass transition temperature of at least 55 ° C.

7. An imaging medium according to any one of the preceding claims characterized in that the or each diffusion-reducing layer comprises an acrylic polymer, preferably a styrene-acrylic polymer.

8. An imaging medium according to any one of the preceding claims characterized in that at least one diffusion-reducing layer has a thickness of at least 1μm.

9. An imaging medium according to any one of the preceding claims characterized by:

a support;

a first color-forming layer superposed on the support;

a diffusion-reducing layer superposed on the first color-forming layer;

a second color-forming layer superposed on the second diffusion-reducing layer, the second color-

forming layer comprising a second color-forming composition adapted to undergo a change of color upon increase in the temperature of the color-forming layer above a second color-forming temperature for a second color-forming time, the color change undergone by the second color-forming layer being different from that undergone by the other color-forming layer; and

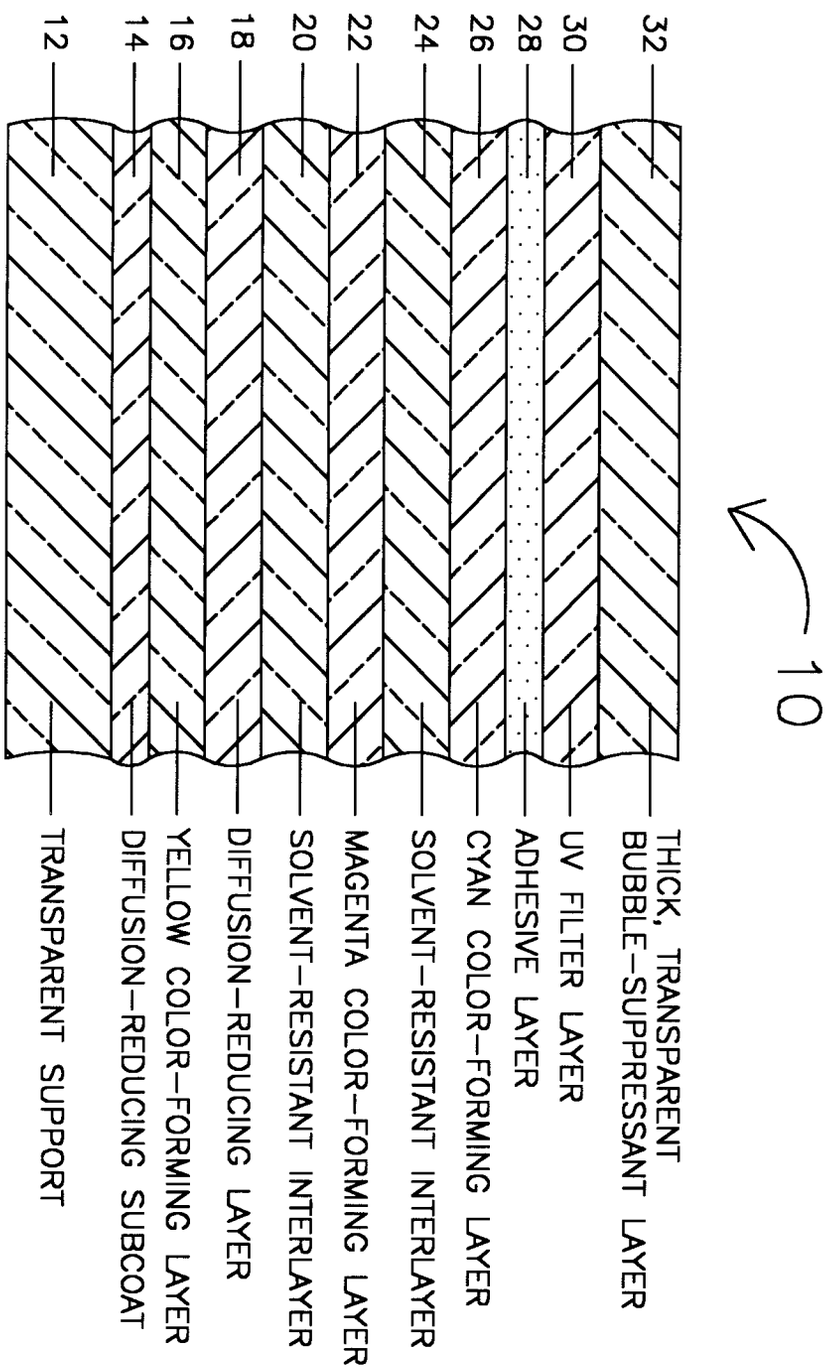
an interlayer interposed between the diffusion-reducing layer and the second color-forming layer, the interlayer having a glass transition temperature less than 50 ° C.

10. A process for forming and storing an image, the process comprising:

providing an imaging medium according to any one of the preceding claims;

imagewise heating the color-forming layer above the color-forming temperature for the color-forming time, thereby causing the color-forming composition to undergo the change of color in heated regions, produce a colored material in these heated regions, and thereby form an image;

storing the image for a period of at least about one week without substantial movement of the colored material outwith the color-forming layer and the diffusion-reducing layer.


10
32
30
28
26
24
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18
16
14
12
THICK, TRANSPARENT BUBBLE-SUPPRESSANT LAYER
UV FILTER LAYER
ADHESIVE LAYER
CYAN COLOR-FORMING LAYER
SOLVENT-RESISTANT INTERLAYER
MAGENTA COLOR-FORMING LAYER
SOLVENT-RESISTANT INTERLAYER
DIFFUSION-REDUCING LAYER
YELLOW COLOR-FORMING LAYER
DIFFUSION-REDUCING SUBCOAT
TRANSPARENT SUPPORT

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 7576

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.5)
X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 21 (M-661)(2868) 22 January 1988 & JP-A-62 179 985 (OJI PAPER K.K.) 7 August 1987 * abstract *	1-10	B41M5/40 B41M5/28
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 123 (M-581)(2570) 17 April 1987 & JP-A-61 263 795 (CANON K.K.) 21 November 1986 * abstract *	1-10	
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 249 (M-338)(1686) 15 November 1984 & JP-A-59 124 890 (KONISHIROKU SHASHIN KOGYO K.K.) 19 July 1984 * abstract *	1-10	
A	PATENT ABSTRACTS OF JAPAN vol. 6, no. 210 (M-166)(1088) 22 October 1982 & JP-A-57 116 692 (RICOH K.K.) 20 July 1982 * abstract *	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

B41M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07 JULY 1992	BACON A.J.

CATEGORY OF CITED DOCUMENTS

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