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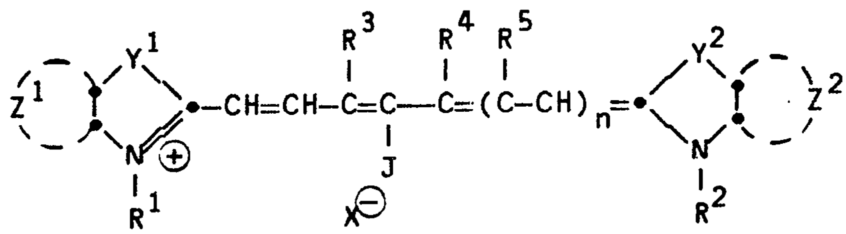
(71) Applicant: EASTMAN KODAK COMPANY (a New Jersey corporation)
343 State Street
Rochester New York 14650(US)

(72) Inventor: DeBoer, Charles David c/o
EASTMAN KODAK COMPANY
Patent Department 343 State Street
Rochester New York 14650(US)

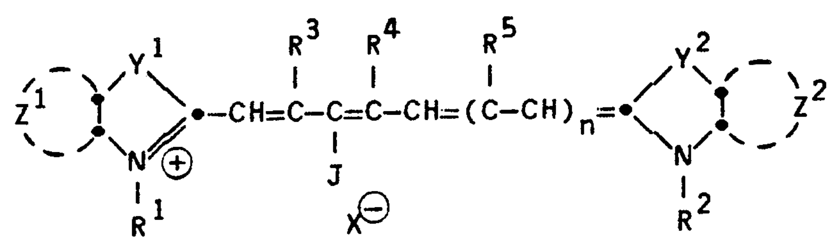
(74) Representative: Brandes, Jürgen, Dr.rer.nat.
Thierschstrasse 8
D-8000 München 22(DE)

(54) **Infrared absorbing cyanine dyes for dye-donor element used in laser-induced thermal dye transfer.**

(57) A dye-donor element for laser-induced thermal dye transfer comprising a support having thereon a dye layer and an infrared-absorbing material, characterized in that the infrared-absorbing material is a cyanine dye having the following formula:



or



wherein:
R^1 and R^2 each independently represents a substituted or unsubstituted alkyl group;
R^3, R^4, and R^5 each independently represents hydrogen or a substituted or unsubstituted alkyl group; or R^3 and R^4 may be joined together, directly or through one or more methyne or methylene groups to complete a substituted or unsubstituted cyclic ring of 5 to 9 members;
Z^1 and Z^2 each independently represents hydrogen or the atoms necessary to complete a unsubstituted or substituted benzene or naphthalene ring;

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Y^1 and Y^2 each independently represents a dialkyl substituted carbon atom, a vinylene group, an oxygen atom, a sulphur atom, a selenium atom, or a nitrogen atom with an R^1 or a substituted or unsubstituted aryl group attached;
J represents hydrogen; a substituted or unsubstituted alkyl group; a substituted or unsubstituted aryl group; a halogen atom; or a nitrogen atom substituted with an alkyl or aryl group, or the atoms necessary to complete a 5- or 6-membered heterocyclic ring;
n is 0 or 1; and
X is a monovalent anion.

INFRARED ABSORBING CYANINE DYES FOR DYE-DONOR ELEMENT USED IN LASER-INDUCED THERMAL DYE TRANSFER

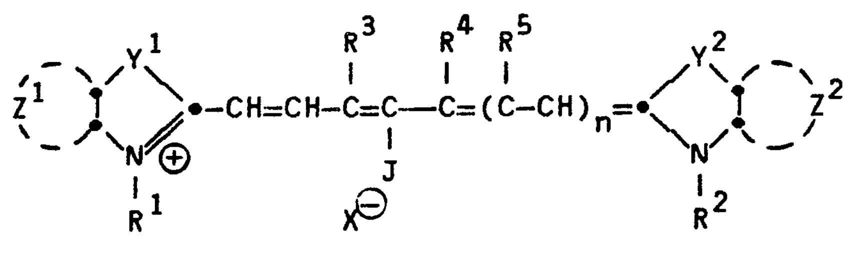
This invention relates to dye-donor elements used in laser-induced thermal dye transfer, and more particularly to the use of certain infrared absorbing cyanine dyes.

In recent years, thermal transfer systems have been developed to obtain prints from pictures which have been generated electronically from a color video camera. According to one way of obtaining such prints, an electronic picture is first subjected to color separation by color filters. The respective color-separated images are then converted into electrical signals. These signals are then operated on to produce cyan, magenta and yellow electrical signals. These signals are then transmitted to a thermal printer. To obtain the print, a cyan, magenta or yellow dye-donor element is placed face-to-face with a dye-receiving element. The two are then inserted between a thermal printing head and a platen roller. A line-type thermal printing head is used to apply heat from the back of the dye-donor sheet. The thermal printing head has many heating elements and is heated up sequentially in response to the cyan, magenta and yellow signals. The process is then repeated for the other two colors. A color hard copy is thus obtained which corresponds to the original picture viewed on a screen. Further details of this process and an apparatus for carrying it out are contained in U.S. Patent No. 4,621,271 by Brownstein entitled "Apparatus and Method For Controlling A Thermal Printer Apparatus," issued November 4, 1986.

Another way to thermally obtain a print using the electronic signals described above is to use a laser instead of a thermal printing head. In such a system, the donor sheet includes a material which strongly absorbs at the wavelength of the laser. When the donor is irradiated, this absorbing material converts light energy to thermal energy and transfers the heat to the dye in the immediate vicinity, thereby heating the dye to its vaporization temperature for transfer to the receiver. The absorbing material may be present in a layer beneath the dye and/or it may be admixed with the dye. The laser beam is modulated by electronic signals which are representative of the shape and color of the original image, so that each dye is heated to cause volatilization only in those areas in which its presence is required on the receiver to reconstruct the color of the original object. Further details of this process are found in GB 2,083,726A.

In GB 2,083,726A, the absorbing material which is disclosed for use in their laser system is carbon. There is a problem with using carbon as the absorbing material in that it is particulate and has a tendency to clump when coated which may degrade the transferred dye image. Also, carbon may transfer to the receiver by sticking or ablation causing a mottled or desaturated color image. It is an object of this invention to find an absorbing material which does not have these disadvantages.

These and other objects are achieved in accordance with this invention which relates to a dye-donor element for laser-induced thermal dye transfer comprising a support having thereon a dye layer and an infrared-absorbing material, characterized in that the infrared-absorbing material is a cyanine dye having the following formula:



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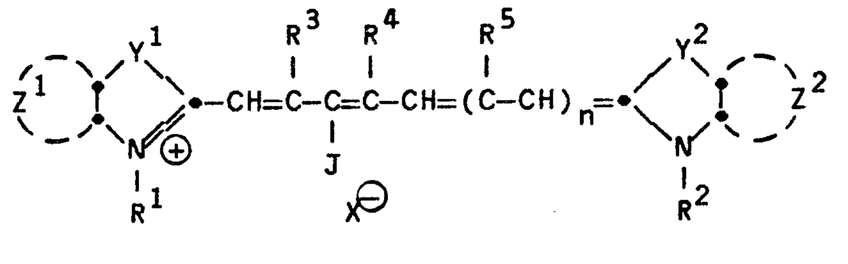
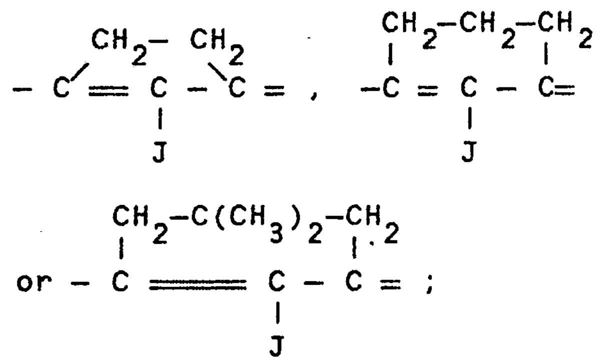


wherein: R1 and R2 each independently represents a substituted or unsubstituted alkyl group such as, CH_3,- C_2H_5 -$(CH_2)_2$-OCH_3, -$(CH_2)_3CO_2CH_3$, -C_3H_7, -C_4H_9, or -$(CH_2)_3Cl$;

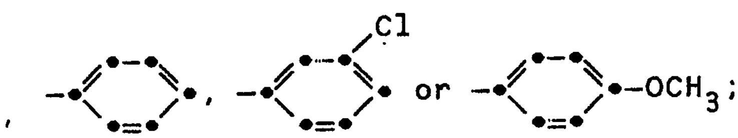
R3, R4, and R5 each independently represents hydrogen or a substituted or unsubstituted alkyl group, such as those mentioned above for R^1 and R^2; or R^3 and R^4 may be joined together, directly or through one or more methyne or methylene groups to complete a substituted or unsubstituted cyclic ring of 5 to 9 members, such as



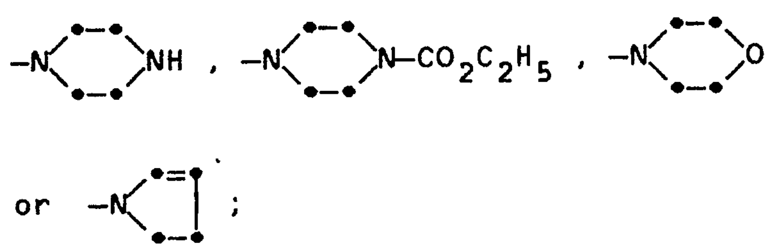
Z^1 and Z^2 each independently represents hydrogen or the atoms necessary to complete a unsubstituted or substituted benzene or naphthalene ring;

Y^1 and Y^2 each independently represents a dialkyl-substituted carbon atom, such as -$C(CH_3)2$- or -$C(C_2H_5)_2$-; a vinylene group, an oxygen atom, a sulphur atom, a selenium atom, or a nitrogen atom with an R^1 or a substituted or unsubstituted aryl group attached;

J represents hydrogen; a substituted or unsubstituted alkyl group such as those mentioned above for R^1 and R^2; a substituted or unsubstituted aryl group, such as



a halogen atom; or a nitrogen atom substituted with an alkyl or aryl group, or the atoms necessary to complete a 5- or 6-membered heterocyclic ring, such as



n is 0 or 1; and

x is a monovalent anion such as $I^{\ominus}$, BF_4, $^{\ominus}$, ClO_4 $^{\ominus}$, PF_6 $^{\ominus}$ or $Br^{\ominus}$.

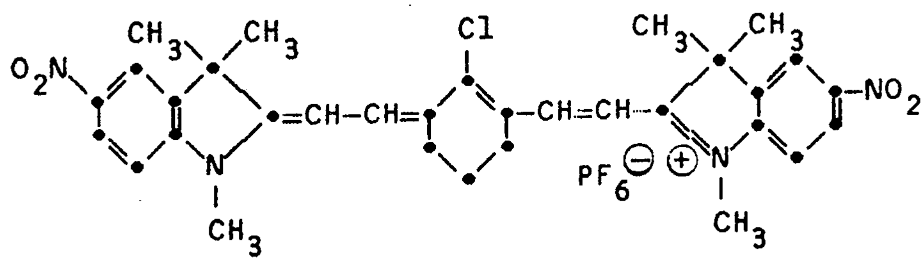
In a preferred embodiment of the invention both R^1 and R^2 are methyl and J is halogen. In another preferred embodiment, R^3 and R^4 are joined together to complete a 6-membered cyclic ring. In still another preferred embodiment, Z^1 and Z^2 both represent the atoms necessary to complete a benzene ring substituted with a nitro, halo or cyano group. In still yet another preferred embodiment, both Y^1 and Y^2 represent a dialkyl-substituted carbon atom.

The above infrared absorbing dyes may employed in any concentration which is effective for the intended purpose. In general, good results have been obtained at a concentration from 0.04 to 0.5 g/m^2 within the dye layer itself or in an adjacent layer.

Spacer beads may be employed in a separate layer over the dye layer in order to separate the dye-donor from the dye-receiver thereby increasing the uniformity and density of dye transfer. That invention is more fully described in DeBoer Application Serial No. 136,073 entitled "Spacer Bead Layer For Dye-Donor Element Used In Laser-Induced Thermal Dye Transfer", filed December 21, 1987. The spacer beads may be coated with a polymeric binder if desired.

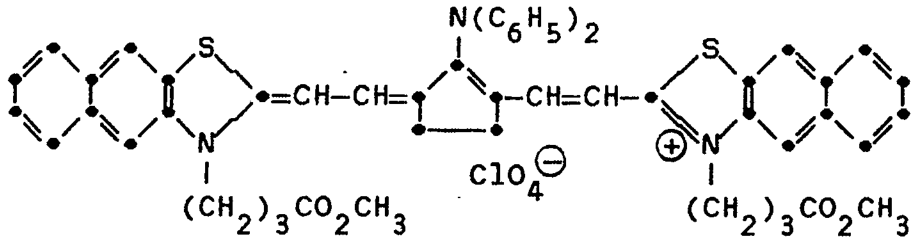
Dyes included within the scope of the invention include the following:

Compound 1



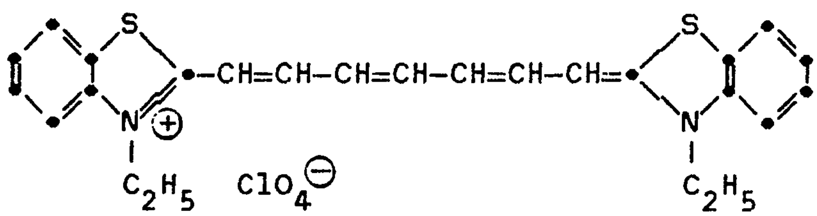
λmax = 828 nm in dimethylformamide

Compound 2



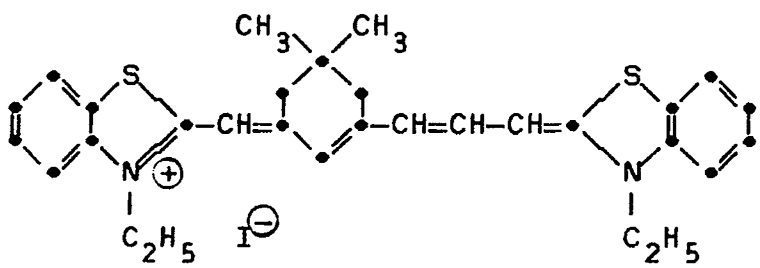
λmax = 831 nm in dimethylsulfoxide

Compound 3



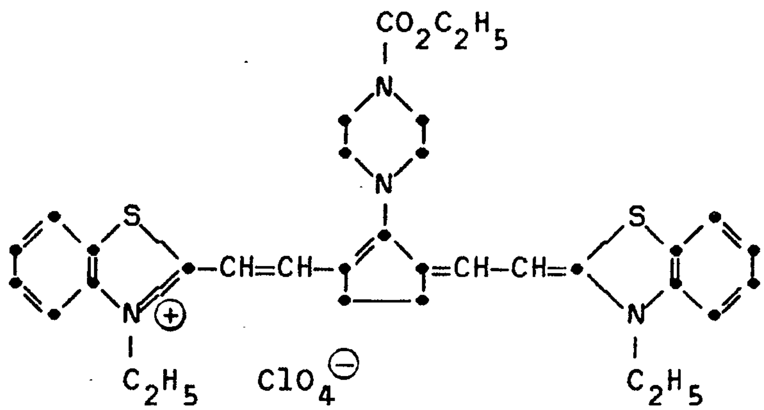
λmax = 765 nm in methanol

Compound 4



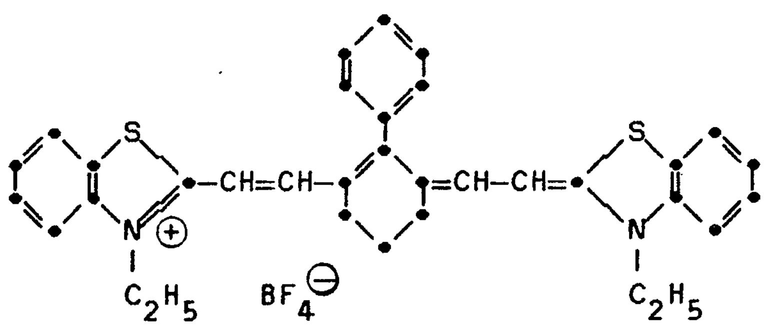
λmax = 765 nm in methanol

Compound 5



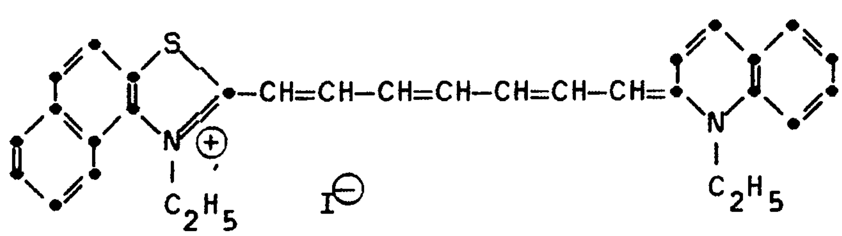
λmax = 731 nm in methanol

Compound 6



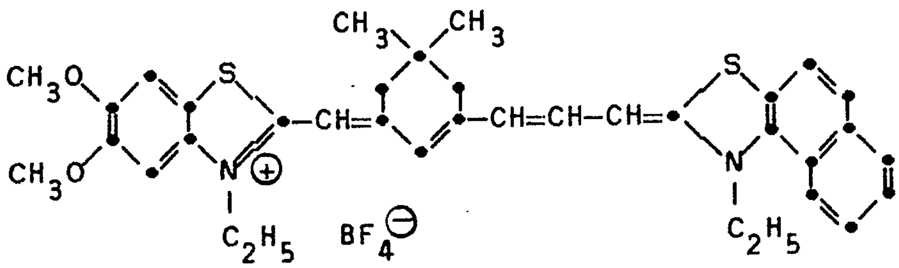
λmax = 779 nm in methanol

Compound 7



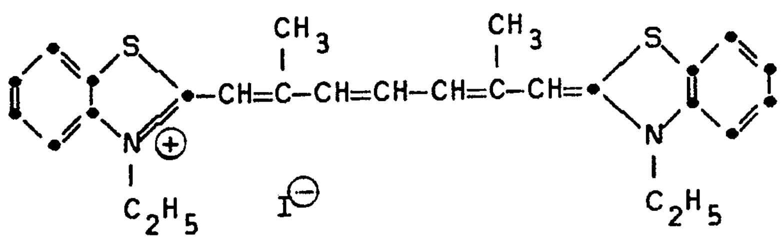
λmax = 804 nm in methanol

Compound 8



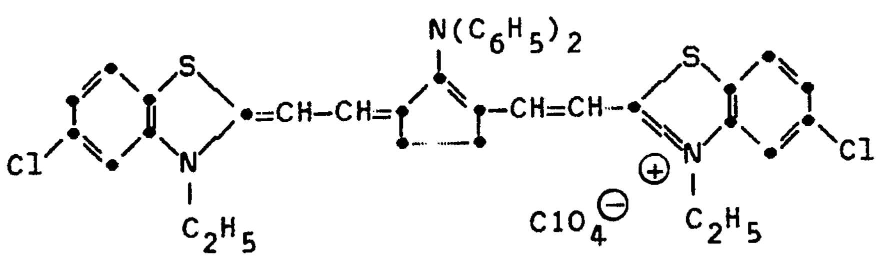
λmax = 790 nm in methanol

Compound 9

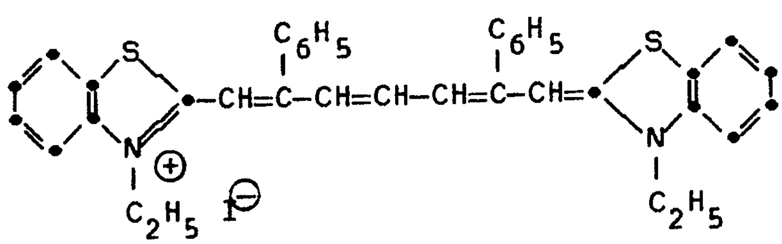


λmax = 775 nm in methanol

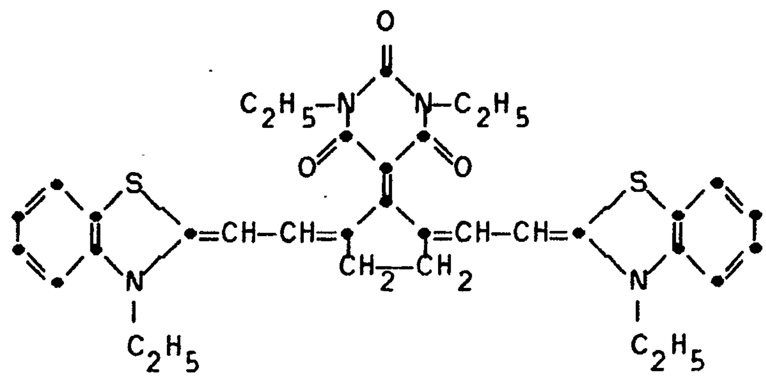
Compound 10



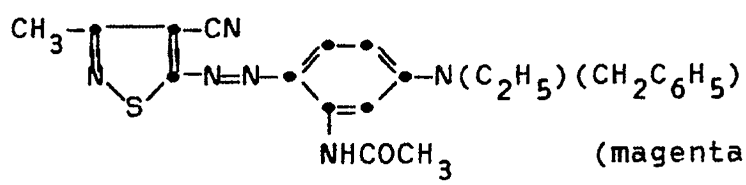
Compound 11



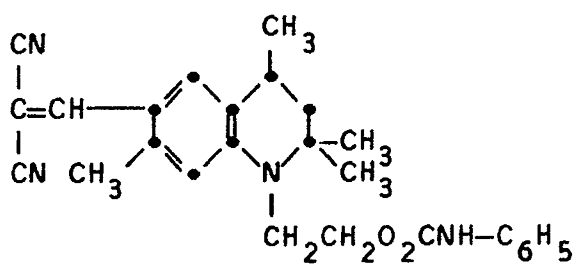
Compound 12



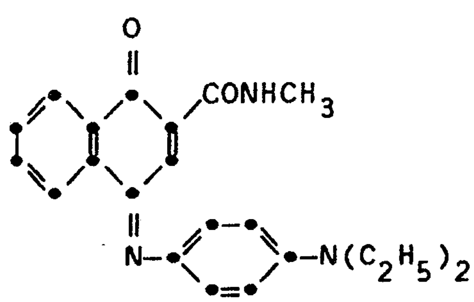
Any dye can be used in the dye layer of the dye-donor element of the invention provided it is transferable to the dye-receiving layer by the action of heat. Especially good results have been obtained with sublimable dyes such as



(magenta)



(yellow)



(cyan)

or any of the dyes disclosed in U.S. Patent 4,541,830. The above dyes may be employed singly or in combination to obtain a monochrome. The dyes may be used at a coverage of from 0.05 to l g/m^2 and are preferably hydrophobic.

The dye in the dye-donor element is dispersed in a polymeric binder such as a cellulose derivative, e.g., cellulose acetate hydrogen phthalate, cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate, cellulose triacetate; a polycarbonate; poly(styrene-co-acrylonitrile), a poly(sulfone) or a poly(phenylene oxide). The binder may be used at a coverage of from 0.1 to 5 g/m^2.

The dye layer of the dye-donor element may be coated on the support or printed thereon by a printing technique such as a gravure process.

Any material can be used as the support for the dye-donor element of the invention provided it is dimensionally stable and can withstand the heat generated by the laser beam. Such materials include polyesters such as poly(ethylene terephthalate); polyamides; polycarbonates; glassine paper; condenser paper; cellulose esters; fluorine polymers; polyethers; polyacetals; or polyolefins. The support generally has a thickness of from 2 to 250 μm. It may also be coated with a subbing layer, if desired.

The dye-receiving element that is used with the dye-donor element of the invention usually comprises a support having thereon a dye image-receiving layer. The support may be a transparent film such as poly(ethylene terephthalate) or may also be reflective such as white polyester (polyester with white pigment incorporated therein)

The dye image-receiving layer may comprise, for example, a polycarbonate, a polyurethane, a polyester, polyvinyl chloride, poly(styrene-co-acrylonitrile), poly(caprolactone) or mixtures thereof. The dye image-receiving layer may be present in any amount which is effective for the intended purpose. In general, good results have been obtained at a concentration of from l to 5 g/m^2.

As noted above, the dye-donor elements of the invention are used to form a dye transfer image. Such a process comprises imagewise-heating a dye-donor element as described above using a laser, and transferring a dye image to a dye-receiving element to form the dye transfer image.

The dye-donor element of the invention may be used in sheet form or in a continuous roll or ribbon. If a continuous roll or ribbon is employed, it may have only one dye or may have alternating areas of other different dyes, such as sublimable cyan and/or magenta and/or yellow and/or black or other dyes. Such dyes are disclosed in U. S. Patents 4,54l,830; 4,698,651; 4,695,287; and 4,701,439. Thus, one-, two-, three- or four-color elements (or higher numbers also) are included within the scope of the invention.

In a preferred embodiment of the invention, the dye-donor element comprises a poly(ethylene terephthalate) support coated with sequential repeating areas of cyan, magenta and yellow dye, and the above process steps are sequentially performed for each color to obtain a three-color dye transfer image. Of course, when the process is only performed for a single color, then a monochrome dye transfer image is obtained.

Several different kinds of lasers could conceivably be used to effect the thermal transfer of dye from a donor sheet to a receiver, such as ion gas lasers like argon and krypton; metal vapor lasers such as copper, gold, and cadmium; solid state lasers such as ruby or YAG; or diode lasers such as gallium arsenide emitting in the infrared region from 750 to 870 nm. However, in practice, the diode lasers offer substantial advantages in terms of their small size, low cost, stability, reliability, ruggedness, and ease of modulation. In practice, before any laser can be used to heat a dye-donor element, the laser radiation must be absorbed into the dye layer and converted to heat by a molecular process known as internal conversion. Thus, the construction of a useful dye layer will depend not only on the hue, sublimability and intensity of the image dye, but also on the ability of the dye layer to absorb the radiation and convert it to heat.

Lasers which can be used to transfer dye from the dye-donor elements of the invention are available commercially. There can be employed, for example, Laser Model SDL-2420-H2® from Spectrodiode Labs, or Laser Model SLD 304 V/W® from Sony Corp.

A thermal dye transfer assemblage using the invention comprises

a) a dye-donor element as described above, and

b) a dye-receiving element as described above,

the dye-receiving element being in a superposed relationship with the dye-donor element so that the dye layer of the donor element is adjacent to and overlying the image-receiving layer of the receiving element.

The above assemblage comprising these two elements may be preassembled as an integral unit when a monochrome image is to be obtained. This may be done by temporarily adhering the two elements together at their margins. After transfer, the dye-receiving element is then peeled apart to reveal the dye transfer image.

When a three-color image is to be obtained, the above assemblage is formed on three occasions during the time when heat is applied using the laser beam. After the first dye is transferred, the elements are peeled apart. A second dye-donor element (or another area of the donor element with a different dye area) is then brought in register with the dye-receiving element and the process repeated. The third color is obtained in the same manner.

The following examples are provided to illustrate the invention.

Example 1 - Magenta Dye-Donor

A dye-donor element according to the invention was prepared by coating an unsubbed 100 μm thick poly(ethylene terephthalate) support with a layer of the magenta dye illustrated above (0.38 g/m^2), infrared absorbing dye Compound 1 (0.14 g/m^2) in a cellulose acetate propionate binder (2.5% acetyl, 45%

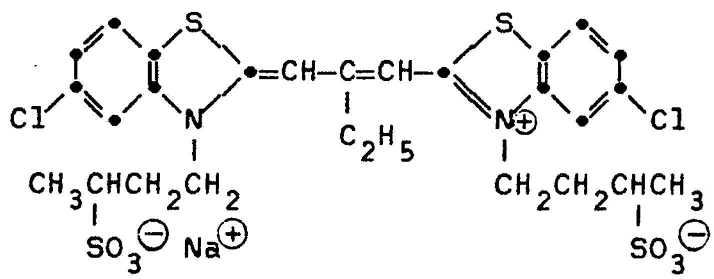
propionyl) (0.27 g/m²) coated from a cyclohexanone and butanone solvent mixture.

Over the dye layer was coated an overcoat of polystyrene beads (av. diameter 8 µm) (0.02 g/m²) from an aqueous solution as described in the DeBoer Application Serial No. 136,073 discussed above.

A control dye-donor element was made as above but omitting the magenta imaging dye.

A second control dye-donor element was prepared as described above on a 75 µm thick poly(ethylene terephthalate) support subbed with gelatin, but containing 0.32 g/m² of the following control dye (a non-infrared absorbing cyanine dye).

Control Dye:



A third control dye-donor element was prepared similar to the second control element, but the concentration of the magenta dye was increased to 0.45 g/m², the infrared absorbing dye was replaced with dispersed carbon (0.60 g/m²), and the cellulose acetate propionate binder (0.50 g/m²) was coated from a toluene and tetrahydrofuran solvent mixture.

A dye-receiving element was prepared by coating a solution of Makrolon 5705® a bisphenol A-polycarbonate resin supplied by Bayer AG (4.0 g/m²) in a methylene chloride-trichloroethylene solvent mixture on a 175 µm poly(ethyleneterephthalate) support containing titanium dioxide.

The dye-receiver was overlaid with the dye-donor placed on a drum and taped with just sufficient tension to be able to see the deformation of the surface beads. The assembly was then exposed on a 180 rpm rotating drum to a focused 830 nm laser beam from a Spectrodiode Labs Laser Model SDL-2420-H2® using a 50 µm spot diameter and an exposure time of 5 millisec. to transfer the areas of dye to the receiver. The power level was 86 milliwatts and the exposure energy was 44 microwatts/square micron.

The following observations of the image produced on each receiver were made:

The dye-donor element containing Compound 1 produced a defined magenta image in the receiver with no visible color contamination from the cyanine dye. The Status A green reflection density was 2.3.

The first control dye-donor element containing only the cyanine dye but no magenta image dye did not have any visible image in the receiver.

The second control dye-donor element also did not have any visible image, which was probably due to the fact that this dye does not absorb appreciably at 830 nm, having a λ-max of 600 nm.

The third control dye-donor element containing carbon as the absorbing material produced an image but the Status A reflection density was only 1.2. The image had a mottled appearance probably due to the clumping of the carbon dispersion during the drying process. Small specks of carbon were also observed to transfer to the receiver.

<u>Example 2 - Cyan Dye-Donor</u>

A dye-donor element according to the invention was prepared by coating an unsubbed 100 µm thick poly(ethylene terephthalate) support with a layer of the cyan dye illustrated above (0.40 g/m²), infrared absorbing dye Compound 2 (0.14 g/m²) in a cellulose acetate propionate binder (2.5% acetyl, 45% propionyl) (0.20 g/m²) coated from a cyclohexanone and butanone solvent mixture.

Over the dye layer was coated an overcoat of polystyrene beads (av. diameter 8 µm) (0.02 g/m²) from an aqueous solution as in Example 1.

A control dye-donor element was made as above but omitted the infrared absorbing dye.

A dye-receiving element was prepared and processed as in Example 1.

The following observations of the image produced on each receiver were made:

The dye-donor element containing Compound 2 produced a uniform cyan image in the receiver having a density of 0.7.

The control dye-donor element did not have any visible image in the receiver.

Example 3 - Cyan Dye-Donors - Positive Imaging

Dye-donors according to the invention were prepared by coating on an unsubbed 100 µm thick polyethylene terephthalate support a layer of the cyan dye illustrated above (0.38 g/m^2), infrared absorbing dye Compounds 1, 3, 5 and 10 (0.13 g/m^2), and CIBA-Geigy Tinuvin 770® hindered amine stabilizer (0.26 g/m^2) in a cellulose nitrate binder (0.89 g/m^2) coated from a dimethylformamide and butanone solvent mixture.

Over the dye layer was coated an overcoat of polystyrene beads (av. diameter 8 µm) (0.22 g/m^2) as described in the DeBoer Application Serial No. 136,073 discussed above.

A control donor coating was made as above but omitted the cyanine infrared absorbing dye.

A dye-receiver was prepared and processed as in Example 1 except that the drum rotation was 120 rpm.

The Status A red reflection density of the receivers were read. As shown in Table 1, except for the control which had a density of 0.2, dye-donors with added cyanine dye produced densities of 0.5 or more.

In a second variation to demonstrate positive imaging, the Status A red transmission density of the dye-donors were first read. The evaluation was done as above but no dye receiver was used; instead an air stream was blown over the donor surface to remove sublimed dye. The Status A red density of the original dye donor was compared to the residual density after the cyan image dye was sublimed away by the laser. All the densities were reduced to 1.0 or below where the cyanine dye of the invention was present, thus showing their effectiveness in positive imaging.

Table 1

Infrared Dye in Donor	Status A Red Density		
	Donor-Initial	Donor-Residual	Receiver-Transferred
None (control)	3.2	1.9	0.2
Compound 1	3.0	0.3	0.8
Compound 3	3.5	1.0	1.0
Compound 5	1.9	0.6	1.2
Compound 10	3.2	0.8	0.5

Example 4 - Magenta Dye-Donors

Dye-donors were prepared as in Example 3 but used the magenta dye illustrated above (0.38 g/m^2), omitted the stabilizer and used compounds 9, 11 and 12.

A control donor coating was made as above, but omitted the cyanine infrared absorbing dye.

A dye receiver was prepared and processed as in Example 1 and the receiver was read to Status A green reflection density as follows:

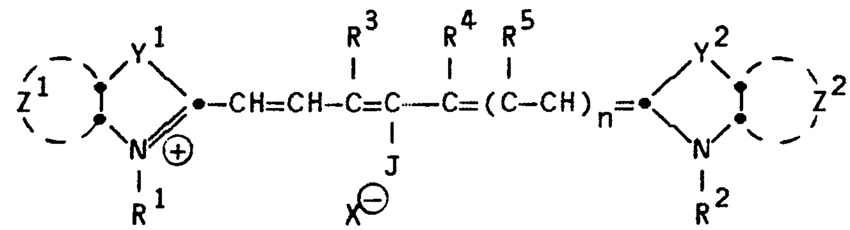
Table 2

Infrared Dye in Donor	Status A Green Density Transferred to Receiver
None (control)	0.0
Compound 9	0.1
Compound 11	0.6
Compound 12	0.4

The above results indicate that all the coatings containing an infrared absorbing cyanine dye gave substantially more density than the control.

Claims

l. A dye-donor element for laser-induced thermal dye transfer comprising a support having thereon a dye layer and an infrared-absorbing material, characterized in that said infrared-absorbing material is a cyanine dye having the following formula:



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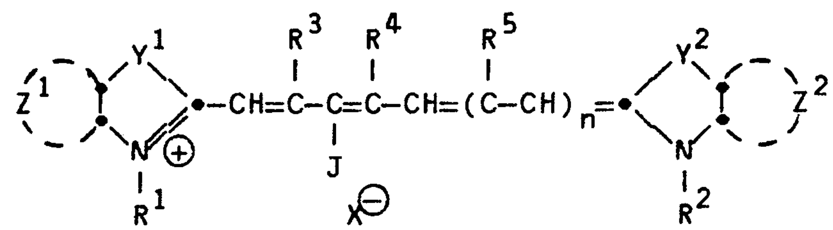

wherein:

R^1 and R^2 each independently represents a substituted or unsubstituted alkyl group;

R^3 R^4, and R^5 each independently represents hydrogen or a substituted or unsubstituted alkyl group; or R^3 and R^4 may be joined together, directly or through one or more methyne or methylene groups to complete a substituted or unsubstituted cyclic ring of 5 to 9 members;

Z^1 and Z^2 each independently represents hydrogen or the atoms necessary to complete a unsubstituted or substituted benzene or naphthalene ring;

Y^1 and Y^2 each independently represents a dialkyl-substituted carbon atom, a vinylene group, an oxygen atom, a sulphur atom, a selenium atom, or a nitrogen atom with an R^1 or a substituted or unsubstituted aryl group attached;

J represents hydrogen; a substituted or unsubstituted alkyl group; a substituted or unsubstituted aryl group; a halogen atom; or a nitrogen atom substituted with an alkyl or aryl group, or the atoms necessary to complete a 5- or 6membered heterocyclic ring;

n is 0 or 1; and

X is a monovalent anion.

2. The element of Claim 1 characterized in that both R^1 and R^2 are methyl and J is halogen.

3. The element of Claim 1 characterized in that R^3 and R^4 are joined together to complete a 6-membered cyclic ring.

4. The element of Claim 1 characterized in that Z^1 and Z^2 both represent the atoms necessary to complete a benzene ring substituted with nitro, halo or cyano group.

5. The element of Claim 1 characterized in that both Y^1 and Y^2 represent a dialkyl-substituted carbon atom.

6. The element of Claim 1 characterized in that said support comprises poly(ethylene terephthalate).

7. The element of Claim 6 characterized in that said dye layer comprises sequential repeating areas of cyan, magenta and yellow dye.