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(71) Applicant: **E.I. DU PONT DE NEMOURS AND COMPANY**
Wilmington Delaware 19898 (US)

(72) Inventors:
- **Blanchet-Fincher, Graciela Beatriz**
  Greenville, Delaware 19807 (US)
- **Moore, Michael F.**
  Wilmington, Delaware 19808 (US)

(74) Representative: **Towler, Philip Dean**
Frank B. Dehn & Co.,
European Patent Attorneys,
179 Queen Victoria Street
London EC4V 4EL (GB)

(54) Thermal imaging process providing color versatility

(57) A processes for laser thermal imaging and imaged laserable assemblages A method for forming an image comprising the steps of:

(1) forming a first coating solution of a first colorant and a second coating solution of a second colorant;
(2) providing a first base element having a first coatable surface;
(3) forming a first imageable element by applying an amount of the first coating solution to the coatable surface to form a first thermally imageable layer thereon, the first thermally imageable layer having a first thermal sensitivity;
(4) forming a first laserable assemblage including the first imageable element and a receiver element having an image receiving layer which is in contact with the first imageable element;
(5) first imagewise exposing to laser radiation the first laserable assemblage, whereby the exposed areas of the first thermally imageable layer are transferred to the receiver element to form a first imaged receiver element;
(6) providing a second base element having a second coatable surface;
(7) forming a second imageable element by applying an amount of the second coating solution to the coatable surface to form a second thermally imageable layer thereon, the second thermally imageable layer having a second thermal sensitivity;
(8) forming a second laserable assemblage including the second imageable element and the first imaged receiver element, the first image of which is adjacent to the second imageable element;
(9) imagewise exposing to laser radiation, at substantially the same laser fluence as the first imagewise exposing, the second laserable assemblage, whereby the exposed areas of the second thermally imageable layer are transferred to the first imaged receiver element to form a second imaged receiver; and
(10) separating at least the second imageable element from the second imaged receiver to produce an imaged receiver having a revealed image.

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Description

FIELD OF THE INVENTION

[0001] This invention relates to improved processes for effecting laser-induced thermal transfer imaging. More particularly, it relates to improved processes providing color versatility which operate effectively at high speeds and which afford high image densities and good durability of images present on receiver elements upon thermal imaging.

BACKGROUND OF THE INVENTION

[0002] Laser-induced thermal transfer processes are well-known in applications such as color proofing and lithography. Such laser-induced processes include, for example, dye sublimation, dye transfer, melt transfer, and ablative material transfer. These processes have been described in, for example, Baldock, U.K. Patent 2,083,726; DeBoer, U. S. Patent 4,942,141; Kellogg, U.S. Patent 5,019,549; Evans, U.S. Patent 4,948,776; Foley et al., U.S. Patent 5,156,938; Ellis et al., U.S. Patent 5,171,650; and Koshizuka et al., U.S. Patent 4,643,917.

[0003] Laser-induced processes use a laserable assemblage comprising (a) a imageable element that contains a thermally imageable layer, i.e., the material to be transferred, and (b) a receiver element that are in contact. The laserable assemblage is imagewise exposed by a laser, usually an infrared laser, resulting in transfer of material from the imageable element to the receiver element. The (imagewise) exposure takes place only in a small, selected region of the laserable assemblage at one time, so that transfer of material from the imageable element to the receiver element can be built up one pixel at a time. Computer control produces transfer with high resolution and at high speed. The laserable assemblage, upon imagewise exposure to a laser as described supra, is henceforth termed an imaged laserable assemblage.

[0004] For the preparation of images for proofing applications and in photomask fabrication, the thermally imageable layer, the exposed areas of which are transferred upon exposure, comprises a colorant Laser-induced processes are fast and result in transfer of material with high resolution. However, in many cases, the available processes do not provide the color versatility need for proofing applications.

[0005] US 5,681,681 describes one way of obtaining this color flexibility. Instead of using the 'precolored' foils they apply a toner image to form a laser radiation-ablative discontinuous film topcoat. An electrostatic station is provided for applying the toner image. Electrostatic development has disadvantages in that it is humidity sensitive and can result in the topcoat layer being non-uniform. This non-uniformity will limit the resolution achievable on the final image.

[0006] A need still exists for a process for providing color versatility, which operates effectively at high speeds, and which affords high image densities and good durability of images present on receiver elements upon thermal imaging.

[0007] Thermally imageable coatings use solvent based systems on production scale equipment that can safely accommodate flammable solvents. Flammable solvents are used with polyester substrates in thermally imageable coatings because of the ease of coating. The problem encountered with coating the solvent based coatings using coaters that are not equipped to accommodate flammable solvents is that sparks and static discharge may ignite the flammable solvents under the conditions of use.

[0008] The solution to the problem is to use aqueous based formulations as opposed to solvent based formulations in coaters not equipped to accommodate flammable solvents.

SUMMARY OF THE INVENTION

[0009] Processes and products for laser induced thermal imaging with color flexibility are disclosed herein.

[0010] The invention relates to a method for forming an image comprising the steps of: (1) forming a first coating solution of a first colorant and a second coating solution of a second colorant; (2) providing a first base element having a first coatable surface; (3) forming a first imageable element by applying an amount of the first coating solution to the coatable surface to form a first thermally imageable layer thereon, the first thermally imageable layer having a first thermal sensitivity; (4) forming a first laserable assemblage including the first imageable element and a receiver element having an image receiving layer which is in contact with the first imageable element; (5) first imagewise exposing to laser radiation the first laserable assemblage, whereby the exposed areas of the first thermally imageable layer are transferred to the receiver element to form a first imaged receiver element; (6) providing a second base element having a second coatable surface; (7) forming a second imageable element by applying an amount of the second coating solution to the coatable surface to form a second thermally imageable layer thereon, the second thermally imageable layer having a second thermal sensitivity; (8) forming a second laserable assemblage including the second imageable element and the first imaged receiver element, the first image of which is adjacent to the second imageable element; (9) imagewise exposing to laser radiation, at substantially the same laser fluence as the first imagewise exposing, the second laserable assemblage, whereby the exposed areas of the second thermally imageable layer are transferred to the first imaged receiver element to form a second imaged receiver; and (10) separating at least the second imageable element from the second imaged receiver to produce an imaged receiver having a revealed image.

[0011] In one embodiment, the invention further relates to the step of applying the second imaged receiver to a permanent substrate.

[0012] Typically, the selection of base colors is at most fifty base colors, each of the at most fifty base colors comprising a colorant, typically, an aqueous colorant. The base color is formed into a coating solution which typically has a viscosity of between about 1 to about 10 centipoise. In one embodiment of the invention, the coating solution further including a component selected from an near infrared absorber, a gas former component, and a combination thereof.

[0013] Typically, the thermally imageable layer has a thickness of between about 1 and about 1.5 microns, the layer having a dimension of at most 80 inches (203.2 cm) in length and at most 60 inches (152.4 cm) in width.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Figure 1 illustrates an imageable element (10) useful in the invention having a support (11); a base element having a coatable surface comprising a flexible ejection layer or subbing layer (12) and a heating layer (13); and a thermally imageable layer (14).

[0015] Figure 2 illustrates a receiver element (20) useful in the invention having a receiver support (21) and an image receiving layer (22).

[0016] Figure 3 illustrates an image rigidification element (30) useful the invention having a support having a release surface (31) and a thermoplastic polymer layer (34).

[0017] Figure 4 illustrates the imageable element (10) in contact with the receiver element (20) forming a sandwich with the thermally imageable layer (14) adjacent the image receiving layer (22).

[0018] Figure 5 illustrates the receiver element (20) having an image (14a) present on the image receiving layer (22) resulting from exposure of the sandwich in Figure 4, followed by separation of the imageable element and the receiver element.

[0019] Figure 5a illustrates the sandwich formed by contacting the permanent substrate (40) with the sandwich shown in Figure 5 with the color image (14a) in contact with the permanent substrate (40).

[0020] Figure 5b illustrates the final element, e.g. a printed proof, formed when the support (21) is separated from the image receiving layer(22).

[0021] Figure 6 illustrates the image rigidification element (30) in contact with the image receiving layer (22) having thereon the image (14a), with the image (14a) encased between the thermoplastic polymer layer (34) and the image receiving layer (22).

[0022] Figure 6a illustrates the sandwich in Figure 6 following removal of the rigidification support having a release surface (31).

[0023] Figure 7 illustrates the sandwich resulting from the lamination of the sandwich shown in Figure 6a to the permanent substrate (40), e.g., paper, with the thermoplastic polymer layer (34) adjacent the paper.

[0024] Figure 8 illustrates the final element, e.g., a printed proof, formed when the support (21) is separated from the image receiving layer(22).

[0025] Figure 9 illustrates the imaging region associated with thermal sensitivity and show transfer efficiency.

DETAILED DESCRIPTION OF THE INVENTION

[0026] Processes and products for laser induced thermal transfer imaging with improved color versatility are disclosed.

[0027] The target color of the first thermally imageable layer and the second thermally imageable layer (collectively, "the thermally imageable layers") can be obtained by mixing pre-determined amounts following a recipe, usually the recipe is precisely followed to achieve the target color. The formulations that form the basic color set cover a range of colors using various pigment systems. A multiplicity of colors from a pre-specified recipe can be obtained by mixing pre-determined amounts of two or more solutions selected from a basic set of formulations. The water borne color solution is then coated on a first base element or a second base element (collectively, "the base elements") which each have a coatable surface to form the thermally imageable layers. The imageable element having a thermally imageable layer obtained in this fashion allows the end user to fabricate a variety of colors and allow Pantone® color guide matching.

[0028] The first laserable assemblage which is formed comprises (a) a first imageable element that contains a first thermally imageable layer, i.e., the material to be transferred, and (b) a receiver element, wherein (a) and (b) are in contact The first laserable assemblage is imagewise exposed by a laser, usually an infrared laser, resulting in transfer of material imagewise (e.g., one pixel at a time) from the first imageable element to the receiver element. Upon exposure and imagewise transfer of material, the resulting laserable assemblage is termed a first imaged laserable assemblage.

The first imaged laserable assemblage in many instances following imaging is separated into two portions - the exposed thermally imageable layer and the imaged receiver element. Either the exposed thermally imageable layer and/or the imaged receiver element can represent imaged products made in accordance with this invention.

[0029] Before the improved processes of this invention are described in further detail, several exemplary laserable assemblages will be described. The processes of this invention are fast and are preferably conducted using one of these laserable assemblages to afford with high sensitivity upon laser imaging an image having higher durability characteristics and higher optical density values in comparison to those for comparative processes (prior art).

Imageable element

[0030] As shown in Figure 1, an exemplary imageable element useful for thermal imaging in accordance with the processes of this invention comprises a thermally imageable layer (14) and a base element having a coatable surface which comprises an optional ejection layer or subbing layer (12) and a heating layer (13). Each of these layers has separate and distinct functions as described, infra. Optionally, a support (11) of the imageable element may also be present. In one embodiment, the heating layer (13) may be present directly on the support (11).

Thermally Imageable Layer:

[0031] The thermally imageable layer (14) which is formed by applying a coating solution to a base element having a coatable surface, comprises (i) a polymeric binder which is different from the polymer in the ejection layer, and (ii) a colorant.

[0032] The polymer (binder) for the thermally imageable layer is a polymeric material having a decomposition temperature that is greater than 300°C and preferably greater than 350°C. The binder should be film forming and coatable from solution or from a dispersion. Binders having melting points less than about 250°C or plasticized to such an extent that the glass transition temperature is < 70°C are preferred. However, heat-fusible binders, such as waxes should be avoided as the sole binder since such binders may not be as durable, although they are useful as cobinders in decreasing the melting point of the top layer.

[0033] It is preferred that the binder (polymer) does not self-oxidize, decompose or degrade at the temperature achieved during the laser exposure so that the exposed areas of the thermally imageable layer are transferred intact for improved durability. Examples of suitable binders include copolymers of styrene and (meth)acrylate esters, such as styrene/methyl-methacrylate; copolymers of styrene and olefin monomers, such as styrene/ethylene/butylene; copolymers of styrene and acrylonitrile; fluoropolymers; copolymers of (meth)acrylate esters with ethylene and carbon monoxide; polycarbonates having higher decomposition temperatures; (meth)acrylate homopolymers and copolymers; polysulfones; polyurethanes; polyesters. The monomers for the above polymers can be substituted or unsubstituted. Mixtures of polymers can also be used.

[0034] Preferred polymers for the thermally imageable layer include, but are not limited to, acrylate homopolymers and copolymers, methacrylate homopolymers and copolymers, (meth)acrylate block copolymers, and (meth)acrylate copolymers containing other comonomer types, such as styrene.

[0035] The binder (polymer) generally has a concentration of about 15-50% by weight, based on the total weight of the thermally imageable layer, preferably 30-40% by weight.

[0036] The thermally imageable layer also comprises a colorant. The colorant may comprise a blend of at least two colors from a selection of base colors. The colorant may be a pigment or a dye, preferably a non-sublimable dye. It is preferred to use a pigment as the colorant for stability and for color density, and also for the high decomposition temperature. Examples of suitable inorganic pigments include carbon black and graphite. Examples of suitable organic pigments include Rubine F6B (C.I. No. Pigment 184); Cromophthal® Yellow 3G (C.I. No. Pigment Yellow 93); Hostaperm® Yellow 3G (C.I. No. Pigment Yellow 154); Monastral® Violet R (C.I. No. Pigment Violet 19); 2,9-dimethylquinacridone (C.I. No. Pigment Red 122); Indofast® Brilliant Scarlet R6300 (C.I. No. Pigment Red 123); Quindo Magenta RV 6803; Monastral® Blue G (C.I. No. Pigment Blue 15); Monastral® Blue BT 383D (C.I. No. Pigment Blue 15); Monastral® Blue G BT 284D (C.I. No. Pigment Blue 15); and Monastral® Green GT 751D (C.I. No. Pigment Green 7). Combinations of pigments and/or dyes can also be used. For color filter array applications, high transparency pigments (that is at least about 80 % of light transmits through the pigment) are preferred, having small particle size (that is about 100 nanometers).

[0037] In accordance with principles well known to those skilled in the art, the concentration of colorant will be chosen to achieve the optical density desired in the final image. The amount of colorant will depend on the thickness of the active coating and the absorption of the colorant. Optical densities greater than 1.3 at the wavelength of maximum absorption are typically required. Even higher densities are preferred. Optical densities in the 2-3 range or higher are achievable with application of this invention.

[0038] A dispersant is usually present when a pigment is to be transferred, in order to achieve maximum color strength, transparency and gloss. The dispersant is generally an organic polymeric compound and is used to separate the fine pigment particles and avoid flocculation and agglomeration. A wide range of dispersants is commercially available. A dispersant will be selected according to the characteristics of the pigment surface and other components in the composition as practiced by those skilled in the art. However, one class of dispersant suitable for practicing the invention is that of the AB dispersants. The A segment of the dispersant adsorbs onto the surface of the pigment. The B segment extends into the solvent into which the pigment is dispersed. The B segment provides a barrier between pigment particles to counteract the attractive forces of the particles, and thus to prevent agglomeration. The B segment should have good compatibility with the solvent used. The AB dispersants of choice are generally described in Assignees, US 5,085,698 issued February 4, 1992. Conventional pigment dispersing techniques, such as ball milling, sand milling, etc., can be employed.

[0039] The colorant may be present in an amount of from about 25 to 95% by weight, preferably 35-65% by weight, based on the total weight of the thermally imageable layer composition. Although the above discussion was directed to color proofing, the element and process of the invention apply equally to the transfer of other types of materials in different applications. In general, the scope of the invention is intended to include any application in which solid material is to be applied to a receptor in a pattern.

[0040] The thermally imageable layer may be applied by coating onto the base element from a solution in a suitable solvent, however, it is preferred to coat the layer(s) from a dispersion. Any suitable solvent can be used as a coating solvent, as long as it does not deleteriously affect the properties of the assemblage, using conventional coating techniques or printing techniques, for example, gravure printing. A preferred solvent is water. The coating of the thermally imageable layer may also be accomplished using the WaterProof® Color Versatility Coater sold by DuPont, Wilmington, DE. Coating of the thermally imageable layer can thus be achieved shortly before the exposure step. This also allows for the mixing of various basic colors together to fabricate a wide variety of colors to match the Pantone® color guide currently used as one of the standards in the proofing industry.

[0041] The first thermally imageable layer has a first thermal sensitivity. The second thermally imageable layer has a second thermal sensitivity. The thermal sensitivities of the thermally imageable layers are such that the same laser fluence can be used in the both the first imagewise exposing step and the second imagewise exposing step. This feature of the invention may be accomplished by matching the color of the coating solutions so that each have the same thermal absorbance or by adding an amount of thermal absorber to one or both of the coating solutions.

Additives

[0042] Other materials can be present as additives in the thermally imageable layer as long as they do not interfere with the essential function of the layer. Examples of such additives include coating aids, plasticizers, flow additives, slip agents, antihalation agents, antistatic agents, surfactants, and others which are known to be used in the formulation of coatings. However, it is preferred to minimize the amount of additional materials in this layer, as they may deleteriously affect the final product after transfer. Additives may add unwanted color for color proofing applications, or they may decrease durability and print life in lithographic printing applications.

Base Element Having A Coatable Surface

[0043] In the process of this invention, there is a first base element and a second base element. The first base element has a first coatable surface. The second base element has a second coatable surface. The imageable elements are formed by applying an amount of the coating solution to the coatable surface.

[0044] One preferred base element comprises an ejection or subbing layer (12), optionally on a support (11), and a heating layer (13). The surface of the heating layer provides the coatable surface on which the thermally imageable layer is applied.

Support:

[0045] Preferably, the support is a thick (400 gauge) co-extruded polyethylene terephthalate film. Alternately, the support may be a polyester, specifically polyethylene terephthalate that has been plasma treated to accept the heating layer. When the support is plasma treated, a subbing layer or ejection layer is usually not provided on the support. Backing layers may optionally be provided on the support. These backing layers may contain fillers to provide a roughened surface on the back side of the support. Alternately, the support itself may contain fillers, such as silica, to provide a roughened surface on the back surface of the support.

Ejection or Subbing Layer:

[0046] The flexible ejection layer or subbing layer (12), as shown in Figure 1, is the layer that provides the force to effect transfer of the thermally imageable layer to the receiver element in the exposed areas. When heated, this layer decomposes into gaseous molecules providing the necessary pressure to propel or eject the exposed areas of the thermally imageable layer onto the receiver element. This is accomplished by using a polymer having a relatively low decomposition temperature (less than about 350°C, preferably less than about 325°C, and more preferably less than about 280°C). In the case of polymers having more than one decomposition temperature, the first decomposition temperature should be lower than 350°C. Furthermore, in order for the ejection layer to have suitably high flexibility and conformability, it should have a tensile modulus that is less than or equal to 2.5 Gigapascals (GPa), preferably less than 1.5 GPa, and more preferably less than 1 Gigapascal (GPa). The polymer chosen should also be one that is dimensionally stable. If the laserable assemblage is imaged through the ejection layer of the imageable element, the ejection layer should be capable of transmitting the laser radiation, and not be adversely affected by this radiation.

[0047] Examples of suitable polymers include (a) polycarbonates having low decomposition temperatures (Td), such as polypropylene carbonate; (b) substituted styrene polymers having low decomposition temperatures, such as poly (alphamethylstyrene); (c) polyacrylate and polymethacrylate esters, such as polymethylmethacrylate and polybutylmethacrylate; (d) cellulosic materials having low decomposition temperatures (Td), such as cellulose acetate butyrate and nitrocellulose; and (e) other polymers such as polyvinyl chloride; poly(chlorovinyl chloride) polyacetals; polyvinylidene chloride; polyurethanes with low Td; polyesters; polyorthoesters; acrylonitrile and substituted acrylonitrile polymers; maleic acid resins; and copolymers of the above. Mixtures of polymers can also be used. Additional examples of polymers having low decomposition temperatures can be found in Foley et al., U.S. Patent 5,156,938. These include polymers which undergo acid-catalyzed decomposition. For these polymers, it is frequently desirable to include one or more hydrogen donors with the polymer.

[0048] Preferred polymers for the ejection layer are polyacrylate and polymethacrylate esters, low Td polycarbonates, nitrocellulose, poly(vinyl chloride) (PVC), and chlorinated poly(vinyl chloride) (CPVC). Most preferred are poly(vinyl chloride) and chlorinated poly(vinyl chloride).

[0049] Other materials can be present as additives in the ejection layer as long as they do not interfere with the essential function of the layer. Examples of such additives include coating aids, flow additives, slip agents, antihalation agents, plasticizers, antistatic agents, surfactants, and others which are known to be used in the formulation of coatings.

[0050] Alternately, a subbing layer (12) maybe provided in place of the ejection layer resulting in a imageable element having in order at least one subbing layer (12), at least one heating layer (13), and at least one thermally imageable layer (14), Some suitable subbing layers include polyurethanes, polyvinyl chloride, cellulosic materials, acrylate or methacrylate homopolymers and copolymers, and mixtures thereof. Other custom made decomposable polymers may also be useful in the subbing layer. Preferably useful as subbing layers for polyester, specifically polyethylene terephthalate, are acrylic subbing layers. Preferably, the subbing layer has a thickness of 100 to 1000 A.

Thermal Amplification Additive

[0051] A thermal amplification additive is optionally, and preferably, present in the ejection layer(s), subbing layer or the thermally imageable layer. It can also be present in both of these layers. Usually, when the thermal amplification additive is employed in the thermally imageable layer it is added in an amount sufficient to allow the thermally imageable layers to have thermal sensitivities which are matched so that the imagewise exposing steps is conducted at the same laser fluence.

[0052] The function of the thermal amplification additive is to amplify the effect of the heat generated in the heating layer and thus to further increase sensitivity. The additive should be stable at room temperature. The additive can be (1) a compound which, when heated, decomposes to form gaseous byproducts(s), (2) a dye which absorbs the incident laser radiation, or (3) a compound which undergoes a thermally induced unimolecular rearrangement which is exothermic. Combinations of these types of additives may also be used.

[0053] Thermal amplification additives which decompose upon heating include those which decompose to form nitrogen, such as diazo alkyls, diazonium salts, and azido (-N3) compounds; ammonium salts; oxides which decompose to form oxygen; carbonates; peroxides. Mixtures of additives can also be used. Preferred thermal amplification additives of this type are diazo compounds such as 4-diazo-N,N' diethyl-aniline fluoroborate (DAFB).

[0054] When the absorbing dye is incorporated in the ejection or subbing layer, its function is to absorb the incident radiation and convert this into heat, leading to more efficient heating. It is preferred that the dye absorb in the infrared region. For imaging applications, it is also preferred that the dye have very low absorption in the visible region. Examples of suitable NIR (near infrared absorbing) dyes which can be used alone or in combination include poly(substituted) phthalocyanine compounds and metal-containing phthalocyanine compounds; cyanine dyes; squarylium dyes; chalcogenopyryioacrylidene dyes; croconium dyes; metal thiolate dyes; bis(chalcogenopyrylo) polymethine dyes; oxyindolizine dyes; bis(aminoaryl) polymethine dyes; merocyanine dyes; and quinoid dyes.

[0055] Infrared absorbing materials disclosed in U.S. Patent Nos. 4,778,128; 4,942,141; 4,948,778; 4,950,639; 5,019,549; 4,948,776; 4,948,777 and 4,952,552 may also be suitable herein. The weight percentage of the thermal amplification additive, versus, for example, the total solid weight composition of the ejection or subbing layer may range from 0-20%. When present in the thermally imageable layer, the thermal amplification weight percentage is generally at a level of 0.95-11.5%. The percentage can range up to 25% of the total weight percentage in the thermally imageable layer. These percentages are non-limiting and one of ordinary skill in the art can vary them depending upon the particular composition of the ejection layer or thermally imageable layer.

[0056] The thermally imageable layer generally has a thickness in the range of about 0.1 to 5 micrometers, preferably in the range of about 0.1 to 1.5 micrometers. Thicknesses greater than about 5 micrometers are generally not preferred as they require excessive energy in order to be effectively transferred to the receiver.

[0057] It is possible to have more than two thermally imageable layers. That is, a third thermally imageable layer. The third thermally imageable layer may have the same or different composition from the first and the second thermally imageable layers, as long as they all function as described above. The total thickness of the combined thermally imageable layers should be in the range given above.

Heating-Layer

[0058] The heating layer (13), as shown in Figure 1, is deposited on the flexible ejection or subbing layer. The function of the heating layer is to absorb the laser radiation and convert the radiation into heat. Materials suitable for the layer can be inorganic or organic and can inherently absorb the laser radiation or include additional laser-radiation absorbing compounds.

[0059] Examples of suitable inorganic materials are transition metal elements and metallic elements of Groups IIIB, IVB, VB, VIB, VIII, IIB, IIIA, and VA, their alloys with each other, and their alloys with the elements of Groups IA and IIA of the Periodic Table of the Elements (CAS Version). Tungsten (W) is an example of a Group VIB metal that is suitable and which can be utilized. Carbon (a Group IVA nonmetallic element) can also be used. Preferred metals include Al, Cr, Sb, Ti, Bi, Zr, Ni, In, Zn, and their alloys; carbon is a preferred nonmetal. More preferred metals and nonmetals include Al, Ni, Cr, Zr and C. Most preferred metals are Al, Ni, Cr, and Zr. A useful inorganic material is TiO_2.

[0060] The thickness of the heating layer is generally about 20 Angstroms to 0.1 micrometer, preferably about 40 to 100 Angstroms.

[0061] Although it is preferred to have a single heating layer, it is also possible to have more than one heating layer, and the different layers can have the same or different compositions, as long as they all function as described above. The total thickness of all the heating layers should be in the range given above, i.e., 20 Angstroms to 0.1 micrometer.

[0062] The heating layer(s) can be applied using any of the well-known techniques for providing thin metal layers, such as sputtering, chemical vapor deposition, and electron beam.

Additional layers:

[0063] The imageable element may have additional layers (not shown) as well. For example, an antihalation layer may be used on the side of the flexible ejection layer opposite the thermally imageable layer. Materials which can be used as antihalation agents are well known in the art. Other anchoring or subbing layers can be present on either side of the flexible ejection layer and are also well known in the art.

[0064] In some embodiments of this invention, a pigment, such as carbon black, is present in a single layer, termed the top layer. This type of pigment functions as both a heat absorber and a colorant, and thus the top layer has a dual function of being both a heating layer and a thermally imageable layer. A preferred colorant/heat absorber is carbon black.

Further Embodiments of the Imageable element:

[0065] Other imageable elements may comprise alternate thermally imageable layer or layers on a support. Additional layers may be present depending of the specific process used for imagewise exposure and transfer of the formed images. Some suitable imageable elements are disclosed in US 5,773,188, US 5,622,795, US 5,593,808, US 5,334,573, US 5,156,938, US 5,256,506, US 5,427,847, US 5,171,650 and US 5,681,681.

[0066] Figure 9 is a plot which shows the imaging region and the decomposition region. Within the imaging region transfer efficiency would be high and transfer efficiency would be low in the decomposition region. This underscores the value of the process of this invention. The ability to match the coating solution's thermal sensitivities facilitates imaging with coating solutions having different decomposition and imaging regions.

Receiver Element

[0067] The receiver element (20), shown in Figure 2, is the second part of the laserable assemblage, to which the exposed areas of the thermally imageable layer, comprising non-degraded polymer (polymeric binder) and colorant, are transferred. In most cases, the exposed areas of the thermally imageable layer will not be removed from the imageable element in the absence of a receiver element. That is, exposure of the imageable element alone to laser radiation does not cause material to be removed, or transferred. The exposed areas of the thermally imageable layer, are removed from the imageable element only when it is exposed to laser radiation and the imageable element is in contact with or adjacent to the receiver element. In the preferred embodiment, the imageable element actually touches the receiver element.

[0068] The receiver element (20) may be non-photosensitive or photosensitive. The non-photosensitive receiver element preferably comprises a receiver support (21) and an image receiving layer (22). The receiver support (21) comprises a dimensionally stable sheet material. The assemblage can be imaged through the receiver support if that support is transparent. Examples of transparent films for receiver supports include, for example polyethylene terephthalate, polyether sulfone, a polyimide, a poly(vinyl alcohol-co-acetal), polyethylene, or a cellulose ester, such as cellulose acetate. Examples of opaque support materials include, for example, polyethylene terephthalate filled with a white pigment such as titanium dioxide, ivory paper, or synthetic paper, such as Tyvek® spunbonded polyolefin. Paper supports are typical and are preferred for proofing applications, while a polyester support, such as poly(ethylene terephthalate) is typical and is preferred for a medical hardcopy and color filter array applications. Roughened supports may also be used in the receiver element

[0069] The image-receiving layer (22) may be a coating of, for example, a polycarbonate; a polyurethane; a polyester; polyvinyl chloride; styrene/acrylonitrile copolymer; poly(caprolactone); vinylacetate copolymers with ethylene and/or vinyl chloride; (meth)acrylate homopolymers (such as butylmethacrylate) and copolymers, polycaprolactone; and mixtures thereof. Preferably the image receiving layer is a crystalline polymer layer. The image receiving layer polymers preferably have melting points in the range of 50 to 64°C, more preferably 56 to 64°C, and most preferably 58 to 62°C. Blends made from 5-40% Capa® 650 (melt range 58-60°C) and Tone® P-300 (melt range 58-62°C), both polycaprolactones, are useful in this invention. Preferably, 100% Tone P-300 is used. Useful receiver elements are also disclosed in US Patent 5,534,387 issued on July 9, 1996. One preferred example is the WaterProof® Transfer Sheet sold by DuPont. Preferably, it has an ethylene/vinyl acetate copolymer in the surface layer comprising more ethylene than the vinyl acetate.

[0070] This image-receiving layer can be present in any amount effective for the intended purpose. In general, good results have been obtained at coating weights of range of 10 to 150 mg/dm^2, preferably 40 to 60 mg/m^2.

[0071] In addition to the image-receiving layer, the receiver element may optionally include one or more other layers (not shown) between the receiver support and the image receiving layer. An additional layer between the image-receiving layer and the support is a release layer. The receiver support alone or the combination of receiver support and release layer may also be referred to as a first temporary carrier. The release layer can provide the desired adhesion balance to the receiver support so that the image-receiving layer adheres to the receiver support during exposure and separation from the imageable element, but promotes the separation of the image receiving layer from the receiver support upon transfer, for example by lamination, of the image receiving layer to a permanent substrate or support. Examples of materials suitable for use as the release layer include polyamides, silicones, Vinyl chloride polymers and copolymers, vinyl acetate polymers and copolymers and plasticized polyvinyl alcohols. The release layer can have a thickness in the range of 1 to 50 microns. A cushion layer which is a deformable layer may also be present in the receiver element, typically between the release layer and the receiver support. The cushion layer may be present to increase the contact between the receiver element and the imageable element when assembled. Examples of suitable materials for use as the cushion layer include copolymers of styrene and olefin monomers such as styrene/ethylene/butylene/styrene, styrene/butylene/styrene block copolymers, and other elastomers useful as binders in flexographic plate applications.

[0072] The receiver element is an intermediate element in the process of the invention because the laser imaging step is normally followed by one or more transfer steps by which the exposed areas of the thermally imageable layer are transferred to the permanent substrate.

IMAGE RIGIDIFICATION ELEMENT

[0073] Optionally, an image rigidification element (30), shown in Figure 3, comprising a support having a release surface (31), also referred to as a second temporary carrier, and a thermoplastic polymer layer (34) may be used.

Support Having a Release Surface or Second Temporary Carrier:

[0074] The support having a release surface or second temporary carrier (31) may comprise a support (32) and a surface layer (33) which may be a release layer. If the material used as the support, has a release surface, e.g., polyethylene or a fluoropolymer, no additional surface layer is needed. The surface or release layer (33) should have sufficient adhesion to the support (32) to remain affixed to the support throughout the processing steps of the invention. Almost any material that has reasonable stiffness and dimensional stability is useful as the support. Some examples of useful supports include polymeric films such as polyesters, including polyethylene terephthalate and polyethylene naphthanate; polyamides; polycarbonates; fluoropolymers; polyacetals; polyolefins, etc. The support may also be a thin metal sheet or a natural of synthetic paper substrate. The support may be transparent, translucent or opaque. It may be colored and may have incorporated therein additives such as fillers to aid in the movement of the image rigidification element through the lamination device during its lamination to the color image containing receiver element.

[0075] The support may have antistatic layers coated on one or both sides. This may be useful in reducing static when the support is removed from the thermoplastic polymer layer during the process of the invention. It is generally preferred to have antistatic layers coated on the back side of the support, i.e., the side of the support away from the thermoplastic polymer layer. Materials which can be used as antistatic materials are well known in the art. Optionally, the support may also have a matte texture to aid in transport and handling of the image rigidification element.

[0076] The support typically has a thickness of about 20 μ to about 250 μ. A preferred thickness is about 55 to 200 μ.

[0077] The release surface of the support may be provided by a surface layer (33). Release layers are generally very thin layers which promote the separation of layers. Materials useful as release layers are well known in the art and include, for example, silicones; melamine acrylic resins; vinyl chloride polymers and copolymers; vinyl acetate polymers and copolymers; plasticized polyvinyl alcohols; ethylene and propylene polymers and copolymers; etc. When a separate release layer is coated onto the support, the layer generally has a thickness in the range of 0.5 to 10 micrometers.

[0078] The release layer (33) may also include materials such as antistats, colorants, antihalation dyes, optical brighteners, surfactants, plasticizers, coating aids, matting agents, and the like.

Thermoplastic Polymer Layer:

[0079] Thermoplastic polymers useful in this layer are preferably amorphous, i.e., non-crystalline, in character, have high softening points, moderate to high molecular weight and compatibility with the components of the image receiving polymer layer, e.g., polycaprolactone. Additionally, flexibility without cracking and possessing the capability to be attached to many different permanent substrates is advantageous. The polymer is preferably solvent soluble, has good solvent and light stability and is a good film former.

[0080] There are many useful thermoplastic polymer materials. Preferred for use in this invention are thermoplastic polymers having Tgs (glass transition temperatures) in the range of about 27 to 150°C, preferably 40 to 70°C, and more preferably 45 to 55°C, a relatively high softening points, e.g., Tg of 47°C, melt flow of 142°C), low elongations at break as determined by ASTM D822A of e.g., 3, and moderate weight average molecular weight (Mw), e.g., in the area of 67,000. Polyester polymers, e.g., having a Tg of about 47°C, are preferred because good compatibility is achieved between the image receiving polymer, e.g., crystalline polycaprolactone and the polyester polymer in the image rigidification layer. However, other suitable polymers have been shown to give acceptable results. Some suitable materials include methacrylate/acrylate, polyvinylacetate, polyvinylbutyral, polyvinylformal, styrene-isoprene-styrene and styrene-ethylenebutylene-styrene polymers, etc.

[0081] The thermoplastic polymer is present in the amount of about 60 to 90%, preferably about 70 to 85%, based on the total weight of the thermoplastic polymer layer components.

[0082] The thermoplastic polymer layer and image receiving layer relate to each other in that the image is encased between them so that it does not move significantly during lamination to the permanent substrate, e.g., paper, and cooling. This significantly reduces halftone dot movement, swath boundary cracking and banding compared to similar processes not employing a thermoplastic polymer layer in this manner, i.e., an image rigidification element, and renders them barely perceptible or substantially eliminated.

[0083] The use of the thermoplastic polymer layer in the processes and products of this invention results in an increase in lamination throughput speeds from 200 mm/min to approximately 600-800 mm/min (3-4 fold increase) without the introduction of defects, and provides lamination process latitude to allow image transfer to many different types of permanent substrates.

[0084] The thermoplastic polymer layer also provides a vehicle or mechanism for the introduction of bleaching chemistry to reduce the impact on final color associated with the NIR dye in the transferred color image to the permanent substrate.

Additives:

[0085] The thermoplastic polymer layer may also contain additives as long as they do not interfere with the functioning of this layer. For example, additives such as plasticizers, other modifying polymers, coating aids, surfactants can be used. Some useful plasticizers include polyethylene glycols, polypropylene glycols, phthalate esters, dibutyl phthalate and glycerine derivatives such triacetin. Preferably, the plasticizer is present in the amount of about 1 to 20%, most preferably 5 to 15%, based on the total weight of the thermoplastic polymer layer components.

[0086] As noted above, the thermoplastic polymer layer also preferably contains dye bleaching agents for bleaching the thermal amplification additive, such as an NIR dye, which may be present in the thermally imageable or imageable element and/or the receiver element Some useful bleaching agents include amines, azo compounds, carbonyl compounds, organometallic compounds, and carbanions. Useful oxidants include peroxides, diacyl peroxides, peroxy acids, hydroperoxides, persulfates, and halogen compounds. Particularly preferred dye bleaching agents with polymethine type NIR dyes are those selected from the group consisting of hydrogen peroxide, organic peroxides, hexaaryl biimidazoles, halogenated organic compounds, persulfates, perborates, perphosphates, hypochlorites and azo compounds.

[0087] Dye bleaching agents are present in the amount of about 1 to 20%, preferably 5 to 15%, based on the total weight of the thermoplastic polymer layer components.

PERMANENT SUBSTRATE

[0088] One advantage of the process of this invention is that the permanent substrate, also known as a permanent support or final receptor, for receiving the image can be chosen from almost any sheet material desired. For most proofing applications a paper support is used, preferably the same paper on which the image will ultimately be printed. Most any paper stock can be used. Other materials which can be used as the permanent substrate include cloth, wood, glass, china, most polymeric films, synthetic papers, thin metal sheets or foils, etc. Almost any material which will adhere to the thermoplastic polymer layer (34), can be used as the permanent substrate.

PROCESS STEPS

Blending of Colorants and Coating Method:

[0089] The target color of the coating solution on the thermally imageable layer can be obtained by mixing predetermined amounts following a precise recipe. The formulations that form the basic set of colors cover a range of colors using various pigment/dispersant systems. A multiplicity of colors from a pre-specified recipe or calculated by an appropriate color matching algorithm are formed by mixing a pre-determined amounts of two or more solutions selected from a basic set of at most 50 of these formulations. Preferably, the coating solution further including an infrared absorber. Typically, the coating solution has a viscosity of between about 1 to about 10 centipoise.

[0090] The thermally imageable layer may be coated on the base element from a solution or a dispersion in a suitable solvent, however, it is preferred to coat the layer(s) from a dispersion. Any suitable solvent can be used as a coating solvent, as long as it does not deleteriously affect the properties of the assemblage, using conventional coating techniques or printing techniques, for example, gravure printing. Preferably, the solvent is water. Preferably, the coating is accomplished using the WaterProof® Color Versatility Coater sold by DuPont, Wilmington, DE.

[0091] The imageable element obtained in this fashion allows the end user to fabricate a wide variety of colors and allows him to match the Pantone® color guide currently used as one of the standards in the proofing industry. The imageable element fabricated in this fashion can be imaged using commercial infrared laser apparatus allowing the generation of digital proofs.

Exposure:

[0092] The next step in the process of the invention is imagewise exposing the laserable assemblage, e.g., as shown in Figure 4, to laser radiation. The exposure step is preferably effected at a laser fluence of about 600 mJ/cm^2 or less, most preferably about 250 to 440 mJ/cm^2. The laserable assemblage comprises the imageable element and the receiver element, described above.

[0093] The assemblage is normally prepared following removal of coversheet(s), if present, by placing the imageable element in contact with the receiver element such that thermally imageable layer actually touches the image-receiving layer on the receiver element. This is represented in Figure 4. Vacuum and/or pressure can be used to hold the two elements together. Alternately, the imageable element and receiver elements may be spaced slightly apart using spacer particles in the thermally imageable layer or the image receiving layer. As one alternative, the imageable element and receiver element can be held together by fusion of layers at the periphery. As another alternative, the imageable element and the receiver element can be taped together and taped to the imaging apparatus, or a pin/clamping system can be used. As yet another alternative, the imageable element can be laminated to the receiver element to afford a laserable assemblage. The laserable assemblage can be conveniently mounted on a drum to facilitate laser imaging.

[0094] Various types of lasers can be used to expose the laserable assemblage. The laser is preferably one emitting in the infrared, near-infrared or visible region. Particularly advantageous are diode lasers emitting in the region of 750 to 870 nm which offer a substantial advantage in terms of their small size, low cost, stability, reliability, ruggedness and ease of modulation. Diode lasers emitting in the range of 780 to 850 nm are most preferred. Such lasers are available from, for example, Spectra Diode Laboratories (San Jose, CA).

[0095] The exposure can take place through the flexible ejection layer or subbing layer of the imageable element or through the receiver element, provided that these are substantially transparent to the laser radiation. In most cases, the ejection layer or subbing layer of the imageable element will be a film which is transparent to infrared radiation and the exposure is conveniently carried out through the flexible ejection or subbing layer. However, if the receiver element is substantially transparent to infrared radiation, the process of the invention can also be carried out by imagewise exposing the receiver element to infrared laser radiation.

[0096] The laserable assemblage is exposed imagewise so that the exposed areas of the thermally imageable layer are transferred to the receiver element in a pattern. The pattern itself can be, for example, in the form of dots or line work generated by a computer, in a form obtained by scanning artwork to be copied, in the form of a digitized image taken from original artwork, or a combination of any of these forms which can be electronically combined on a computer prior to laser exposure. The laser beam and the laserable assemblage are in constant motion with respect to each other, such that each minute area of the assemblage, i.e., "pixel" is individually addressed by the laser. This is generally accomplished by mounting the laserable assemblage on a rotatable drum. A flat bed recorder can also be used.

Separation:

[0097] The next step in the process of the invention is separating the imageable element from the receiver element. Usually this is done by simply peeling the two elements apart. This generally requires very little peel force, and is accomplished by simply separating the support of the imageable element from the receiver element. This can be done using any conventional separation technique and can be manual or automatic without operator intervention.

[0098] As shown in Figure 5, separation results in a laser generated color image, also known as the image, preferably a halftone dot image, comprising the transferred exposed areas of the thermally imageable layer, being revealed on the image receiving layer of the receiver element. Preferably the image formed by the exposure and separation steps is a laser generated halftone dot color image formed on a crystalline polymer layer, the crystalline polymer layer being located on a first temporary carrier.

Transfer of the Image to the Permanent Substrate:

[0099] The color image on the receiver element is then transferred to the permanent substrate by contacting the permanent substrate with, preferably laminating it to, the color image on the image receiving layer shown in Figure 5. A WaterProof® Laminator, manufactured by DuPont, is preferably used to accomplish the lamination. However, other conventional means may be used to accomplish this contact which results in the sandwich shown in Figure 5a.

[0100] Another embodiment includes the additional step of removing, preferably by peeling off, the receiver support (21) (also known as the first temporary carrier), resulting in the assemblage shown in Figure 5b. In a preferred embodiment, the assemblages illustrated in Figures 5a and 5b represent a printing proof comprising a laser generated halftone dot color thermal image formed between the image receiving layer, which is preferably a crystalline polymer layer, and the permanent substrate.

ALTERNATE PROCESS:

Lamination of the Image Rigidification Element:

[0101] In an alternate embodiment, the image rigidification element is brought into contact with, preferably laminated to, the receiver element with the image in contact with the thermoplastic polymer layer of the image rigidification element resulting in the thermoplastic polymer layer of the rigidification element and the image receiving layer of the receiver element encasing the color image. This is best seen in Figure 6. A WaterProof® Laminator, manufactured by DuPont is preferably used to accomplish the lamination. However, other conventional means may be used to accomplish contact of the image carrying receiver element with the thermoplastic polymer layer of the rigidification element. It is important that the adhesion of the rigidfication element support having a release surface (31), also known as the second temporary carrier, to the thermoplastic polymer layer (34) be less than the adhesion between any other layers in the sandwich. The novel assemblage or sandwich, e.g., as illustrated by Figure 6, is highly useful, e.g., as an improved image proofing system.

Transfer of the Image to the Permanent Substrate:

[0102] The support (32) having a release surface (33) (or second temporary carrier) is then removed, preferably by peeling off, to reveal the thermoplastic film as seen in Figure 6a. The image on the receiver element is then transferred to the permanent substrate by contacting the permanent substrate with, preferably laminating it to, the revealed thermoplastic polymer layer of the sandwich shown in Figure 6a. Again a WaterProof® Laminator, manufactured by DuPont, is preferably used to accomplish the lamination. However, other conventional means may be used to accomplish this contact which results in the sandwich shown in Figure 7.

[0103] Another embodiment includes the additional step of removing, preferably by peeling off, the receiver support (21) (also known as the first temporary carrier), resulting in the assemblage or sandwich shown in Figure 8. In a preferred embodiment, the assemblages illustrated in Figures 7 and 8 represent a printing proof comprising a laser generated halftone dot color thermal image formed on a crystalline polymer layer, and a thermoplastic polymer layer laminated on one surface to said crystalline polymer layer and laminated on the other surface to the permanent substrate, whereby the color image is encased between the crystalline polymer layer and the thermoplastic polymer layer..

Formation of multicolor images:

[0104] In proofing applications, the receiver element can be an intermediate element onto which a multicolor image is built up. A imageable element having a thermally imageable layer comprising a first colorant is prepared and exposed and separated as described above. The receiver element has a image formed with the first colorant, which is preferably a laser generated halftone dot color thermal image, Thereafter, a second imageable element having a thermally imageable layer different than that of the first thermally imageable element forms a laserable assemblage with the receiver element having the image of the first colorant and is imagewise exposed and separated as described above. The steps of (a) forming the laserable assemblage with a imageable element having a different colorant than that used before and the previously imaged receiver element, (b) exposing, and (c) separating are sequentially repeated as often as necessary in order to build the multiimage of a color proof on the receiver element.

[0105] In one embodiment of the invention, in the formation of these multicolor images, at least two base colors are in separate compositions and the color compositions are of substantially similar thermal sensitivity. A technique for accomplishing this similarity in thermal sensitivity is with an NIR dye. Typically, both color compositions have a thermal sensitivity in the range of 100 to 600 mJ/cm^2, more typically less than or equal to 350 mJ/cm^2, and even more typically in the range of 200 to 350 mJ/cm^2.

[0106] The permanent substrate is then brought into contact with, preferably laminated to, the multiple images on the image receiving element with the last image in contact with the permanent substrate.

[0107] In the alternate process, the rigidification element is then brought into contact with, preferably laminated to, the multiple images on the image receiving element with the last image in contact with the thermoplastic polymer layer. The process is then completed as described above.

EXAMPLES

[0108] These non-limiting examples demonstrate the processes and imaged laserable assemblages claimed and described herein wherein pigmented images of a wide variety of colors are obtained. All temperatures throughout the specification are in °C (degrees Centigrade) and all percentages are weight percentages unless indicated otherwise.

L*a*b*.

[0109] Color consists of complex wavelength information that the human eye converts into a three-value system of primary colors in order to simplify processing. Hue, its basic color (pink, orange, red), saturation (vividness or dullness) and lightness (brightness or darkness). These attributes provide three coordinates that can be use to map the colors in the three dimensional color spaces. In the color space, lightness is the center of the vertical axis, saturation is horizontal axis and hue is the angle at which the saturation axis extends from the lightness axis. This three dimensional format is a convenient way to compare the relationship between any two colors by their distance in color space. In 1931, the Commision Intemationale d'Eclairage (CIE) established standards for a series of color spaces that represent the visible spectrum. In the data presented here we refer to the color scale called CIE L*a*b*. The well balance structure of this color spaces based on the theory that a color can not be red and green at the same time nor blue and yellow at the same time. As a result, single values can be used to describe the red/green and yellow/blue attributes. In the examples below the colors will be express in CIE L*a* and b*, L* defines lightness, a* denotes red/green value and b* denotes yellow/blue value. One of the more common instruments used to measure color are calorimeters. It measures light and breaks the light down into the RGB components. A color's numeric value is then determined using the L*a*b* color space. In each example the color coordinates of the pigmented coating is matched to the corresponding color in the Pantone® color formula guide. A X-Rite color head (Grandville, Michigan) was used to measure the color coordinates. The illumination source most commonly used for proofing applications for color matching evaluation is D50. The measured color can then be matched to a standard color matching systems such as a Pantone® Matching System.

[0110] The following procedures were used to prepare the pigmented or thermally imageable layer solutions and illustrate the ability of varying color by combining two colors from a basic set; green as defined below and white or green and black.

[0111] • E is the L*,a*,b* difference between Pantone® color and measured color, typically less than about 6, more typically less than about 4.

[0112] In the following procedures it was demonstrated that by adding another color selected from a basic set of colors a separate Pantone color can be matched very closely; i.e., within a • E less than 6.

Procedure 1:

[0113] The following ingredients were mixed and stirred.

Table 1

Control	Solution (grs)	Solids (%)
GJD3007	9.08	21
YJD3174	3.0	8
RJD3022	0.6	1
Polymer 1	34.9	51.2
Polymer 2	8.75	12.8
PEG300	1.35	6
Zonyl® FSA	.3	
H2O	92.00	
Total solution	149.75	
Total solids	21.26	
%solids	14.17	

In the Table above GJD3007, YJD3174 and RJD3022 are a green, yellow and red dispersions dispersions by Sun Chemicals, Polymers 1 and 2 are ter-polymers of MMA/BA/MAA and GMA in the following ratios: 87/0/3/10 and 7/80/3/10 respectively. PEG300 is polyethylene glycol with 300 molecular weight, Zonyl FSA(DuPont) is a fluoro-surfactant. Grs in this and all the following Tables stands for grams.

[0114] After stirring for 30 minutes, the control solution was coated using a Meyer rod #6 onto LOE paper to a nominal thickness of about 1 micron. The coated paper was placed into an oven at 60°C and dried for 1 minute prior to the measurement of the color coordinates using an X-Rite color head. Results are shown in Table 2 below.

Table 2

Color	Control Sample C1	Pantone® Color
L*	52, 34	
A*	-68.36	
B*	29.65	
Pantone® #		355
ΔE		4.0

[0115] It has been found that with certain pigments enough absorption can be achieved without the need for an NIR dye. Some examples of such a pigment include green and black.

Procedure 2:

[0116] Procedure 2 demonstrates that by adding a second color from a basic set of colors additional colors can be generated. For preparing Samples 1 through 5 a white solution was added to the control sample formulation listed above. The white solution was 27.7 gr. of WND-DC06 white dispersion by Sun Chemicals and 72.2 gr. of water. This corresponded to a white solution at 15 % solids. The formulations obtained from the mixing of the control and white solutions are listed below. The coating and measuring procedure followed were identical to that stated for the control.

Table 3

	CI (grs)	Sample 1 (grs)	Sample 2 (grs)	Sample 3 (grs)	Sample 4 (grs)	Sample 5 (grs)
Control solution	10	10	10	9.23	4.16	10
White solution		1.28	3.0	5.77	5.83	0.45
L*		45.91	52.71	51.39	87.63	28
A*	52.43	-51.14	-66.37	-58.1	-20.09	-20.5
B*	-68.34	23.64	28.65	20.52	9.37	14.3
% Control/W	29.65	4.76	50	64.7	83.4	15
Pantone® match	355	356	347	348	351	350
∆E	4	4.2	5.3	3.8	2.1	5.3

Procedure 3:

[0117] Procedure 3 also demonstrates that by adding a second color from a basic set of colors additional colors can be generated. For preparing Samples 6 and 7 a black solution was added to the control sample formulation listed above, The black solution was comprised of 31.38 gr, of LHD-9303 black dispersion by Sun Chemicals and 68.61 gr. of water. This corresponded to a black solution at 15% solids. The formulations obtained from the mixing of the control and black solutions are listed below. The coating and measuring procedure followed were identical to that stated for the control, Results are shown in Table 4.

Table 4

	C1 (grs)	Sample 6 (grs)	Sample 7 (grs)
Control solution	10	10	10
Black solution		0.15	0.33
L*	52.43	45.91	27.08
A*	-68.34	-51.14	-25.47
B*	29.65	23.64	10.25
% Contr/W or K	0	4.76	10
Pantone® match	355	356	349
∆E	4	4.2	3.7

Procedure 3a:

[0118] This Procedure 3a demonstrates that by adding a second color from a basic set of colors and infrared dye, additional colors that can be imaged at comparable exposures. For preparing Samples 1 a through 5a, shown in Table 3a, a white solution was added to the control sample (C1 of Procedure 1). The white solution was 27.7 gr. of WND-

DC06 white dispersion by Sun Chemicals and 72.2 gr. of water. This corresponded to a white solution at 15 % solids. The formulations obtained from the mixing of the control and white solutions as indicated in Table 3a. The coating and measuring procedure followed were identical to that described in Procedure 1.

Table 3a

	C1 (grs)	Sample 1a (grs)	Sample 2a (grs)	Sample 3a a(grs)	Sample 4a (grs)	Sample 5a (grs)	Sample 6a (grs)
Control solution	10	10	10	10	10	10	10
White solution		1.28	3.0	6.25	14.01	0.45	
Black Solution							0.15 grs
SDA4927		0.008	0.01	0.012	0.018	0.008	
H2O		0.045	0.06	0.068	0.102	0.042	
L*		51.09	53.33	55.97	62.2	50.96	39.93
A*	52.43	-62,47	-63.72	-62.63	-57.86	-64.79	-50.33
B*	-68.34	31.32	29.97	27.39	22.64	31.26	25.57
Pantone® match	355	356	347	348	3395	347	349
Exposure (Watts)	15	15	15	15	15	15	15
Resolution (12-RPM/16 Watts)	1 pixel	1 pixel	1 pixel	1 pixel	1 pixel	1 pixel	1 pixel

Procedure 4:

[0119] Procedure 1 was repeated with the following exceptions: a basic red dispersion was prepared by mixing and stirring the ingredients shown in Table 5.

Table 5

Control	Solution (grs)	Solids (%)
Frazer red	16.5	11
Castle Magenta	9.96	12
Polymer 1	49.8	74
SDA 4927	0.45	2
PEG300	0.45	2
Zonyl® FSA	0.3	
H20	72.25	
Total solution	149.71	
Total solids	21.73	
%solids	14.51	

In the Table above Frazer red is a red ink jet dispersion (DuPont) and Castle Magenta is an ink jet magenta dispersion (DuPont). Polymer 1 is a ter-polymers of MMA/BA/MAA and GMA in the following ratios ; 87/0/3/10. SDA4927 is an infrared dye absorbing at 850 nm as the laser wavelength PEG300 is polyethylene glycol with 300 molecular weight, Zonyl® FSA(DuPont) is a fluoro-surfactant.

[0120] After stirring for 30 minutes, the control solution was coated using a Meyer rod #6 onto LOE paper to a nominal thickness of about 1 micron. The coated paper was placed into an oven at 60°C and dried for 1 minute prior to the measurement of the color coordinates using an X-Rite color head. Results are shown in Table 6 below.

Table 6

Color	Control sample C2	Matching
L*	53.36	
A*	72.86	
B*	42.41	
Pantone® #		185
ΔE		3.9

Procedure 5:

[0121] Procedure 5 demonstrates that by adding another color from a basic set of colors additional colors can be generated. For preparing Samples 8 through 13 (S8 through S13), a white solution was added to the control sample formulation from Procedure 4. The white solution was 27.7 gr. of WND-DC06 white dispersion by Sun Chemicals and 72.2 gr. of water. This corresponded to a white solution at 15 % solids. The formulations obtained from the mixing of the control and white solutions are listed below. The coating and measuring procedure followed were identical to that stated for Procedure 4. Results are shown in Table 7.

Table 7

	C2 (grs)	S8 (grs)	S9 (grs)	S10 (grs)	S11 (grs)	S12 (grs)	S13 (grs)
Control solution	10	10	10	10	10	9.23	4.16
White solution		0.33	0.75	1.28	3.0	5.77	5.83
L*	53.36	55.66	43.56	53.86	54.67	59.25	70.17

Table 7 (continued)

	C2 (grs)	S8 (grs)	S9 (grs)	S10 (grs)	S11 (grs)	S12 (grs)	S13 (grs)
A*	72.86	68.45	68.45	74.87	68.86	61.87	45.25
B*	42.41	45.32	45.32	59.18	43.92	33.42	20.20
% Control/White	0	10	20	30	50	64.7	83.4
Pantone® match	185	1795	485-2x	1788	032	1785	177
ΔE	4.1	5.3	2.3	2.7	3.7	5.1	4.2

Procedure 6:

[0122] Procedure 6 also demonstrates that by adding another color from a basic set of colors additional colors can be generated. For preparing Samples 14 and 18 (S14 through S18), a black solution was added to the control sample formulation from Procedure 4. The black solution was comprised of 31.38 gr. of LHD-9303 black dispersion by Sun Chemicals and 68.61 grs. of water. This corresponded to a black solution at 15 % solids. The formulations obtained from the mixing of the control and black solutions are listed below. The coating and measuring procedure followed were identical to that stated for the control. Results are shown in Table 8.

Table 8

	C2 (grs)	S14 (grs)	S15 (grs)	S16 (grs)	S17 (grs)	S18 (grs)
Control solution	10	10	10	10	10	9.23
Black solution		0.33	0.15	0.09	0.04	0.02
L*	53.36	30.92	36.12	45.31	47.85	50.11
A*	72.86	41.78	49.88	56.39	59.6	64.58
B*	42.41	29.71	35.6	38.34	40.36	44.36
% Control/Black	0	10	4.76	2.9	1.3	0.6
Pantone® match	185	1795	485-2x	1788	032	1785
ΔE	4.1	5.3	2.3	2.7	3.7	5.1

Procedure 6a:

[0123] An NIR dye was added to Samples 8-11 (S8 to S11) from Table 7 and Samples 3-4 (S3 and S4) of Table 3a to increase the thermal sensitivity of the samples to be substantially similar to the thermal sensitivity of samples containing the black solution,

Table 7a

	C2 (grs)	S8a (grs)	S9a (grs)	S10a (grs)	S11a (grs)	S12a (grs)	S13a (grs)	S14a (grs)
Control solution	10	10	10	10	10	10	10	10
White solution		0.33	0.75	1.28	3.0	6.25	14.01	
Black solution								0.15
L*	53.36	49.68	49.63	49.27	50.02	52.85	56.37	40.94
A*	72.86	66.79	67.08	66.79	65.15	63.7	5936	52.47
B*	42.41	41.49	41.62	41.77	39.65	37.49	32.1	32.96

Table 7a (continued)

	C2 (grs)	S8a (grs)	S9a (grs)	S10a (grs)	S11a (grs)	S12a (grs)	S13a (grs)	S14a (grs)
Pantone® match	185	1795	485-2x	1788	032	1785	177	
CIE at (watts)	15	15	15	15	15	15	15	15
Resolution	1 pixel	1pixel	1 pixel	1 pixel	1 pixel	1 pixel	1 pixel	1 pixel

[0124] In the examples below the films comprised the following structure. The substrate is a 4 mil Mylar® backing is coated during extrusion with a thin subbing layer. A thin metal Cr layer sputtered onto the ejection layer and a 1 micron pigmented coating of the formulation listed in each specific example coated on top of the sputtered metal layer.

Example 1

[0125] A base element having the following structure was prepared: a subbed Mylar® substrate, an ejection layer and a heating layer. The base, 4 mil (10.16 microns)Mylar® 200D was coated with a 1 micron PVC (Aldrich, MW: 78,000) ejection layer by reverse gravure to 54" wide at a line speed of 100 FPM. The film thickness was about 1 micron (10^{-4} cm.) which corresponds to coating weights of 15 mgr./dm^2. In order to avoid the cracking of ejection layer during film handling 10 % by weight di-phenyl phalate was added to the formulation. The solids in the PVC solution were adjusted to 11.5% leading to a viscosity of about 300 centipoisse. The solvent comprised Methyl Ethyl Ketone (MEK) 80% and Cyclohexanone (Cy) 20%. The latter was used to aid in the dilution and slow the film drying. The solutions were filtered in line using a 10 micron filter. After the coating of the ejection layer was completed, the film was submitted to Vacuum Deposit Inc. (Louisville, KY) for sputtering of the Cr heating layer to 40% transmissions (80 Å). The metal thickness was monitored *in situ* using a quartz crystal and after deposition by measuring reflection and transmission of the films.

[0126] The 3 layer imageable element was then placed on a piece of paper taped onto a WaterProof® carrier plate for solution coating of the pigmented coating using the solution shown in Table 9

Table 9

Example 1	Solution (grs)	Solids (%)
Frazer red	2.3	11.5
Castle Magenta	1.27	11.5
MMA//nBMA	5.94	74
ADS-830	0.03	1
PEG300	0.06	2
Zonyl® FSA	0.04	
H2O	10.36	
Total solution	20	
Total solids	3	
%solids	15	

In the Table above Frazer red is a red ink jet dispersion (DuPont) and Castle Magenta is an ink jet magenta dispersion (DuPont). ADS-830 is an NIR dye absorbing at 850 nm, PEG300 is polyethylene glycol with 300 molecular weight, Zonyl® FSA(DuPont) is a fluoro-surfactant.

[0127] The sheet of paper helps avoid color contamination. The paper taped to the carrier was discarded after the coating was completed. The imageable element comprising the substrate, subbing and metal layers were cut to the desired size and placed on top of the paper with the metal layer away from the surface of the carrier. A number 6 Meyer rod was placed in the corresponding coater slots with the leading edge of the imageable element positioned directly under the Meyer rod. A syringe was used to apply the solution onto the base element prepared above. After 9 ml of the solution were measured and drawn into a 10 ml plastic syringe, a 2 micron filter was attached at the mouth of the syringe to filter the solution during delivery. The solution was then delivered uniformly across the 23" Meyer rod, and the coating solution was coated by mechanically transporting the carrier through the nip area into the drier area using drive rollers mounted to the side frames of the apparatus. The drying time and temperature at the drier were set at 60°C for 4 minutes using the dial indicators in the machine. After drying was completed the imageable element was pulled out and trimmed to 23 1/4" x 31 1/4".

[0128] The receiver element (P300) used in this example was comprised of a 4 mil Mylar® 400D base coated with a 2 micron layer of polycaprolactone.

[0129] The imageable element and receiver element were then loaded onto the 4-up cassette of the Creo 3244 Spectrum Trendsetter (Creo, Vancouver, BC) for imaging. A Tyvex® sheet was used to separate the imageable element and the receiver element for automatic loading. The receiver element was loaded onto the imaging drum and held by vacuum. Once its loading was completed the imageable element, slightly larger than the receiver element was loaded on top of the receiver, and held by vacuum, with the thermally imageable layer directly in contact with the polycarpolactone surface of the receiver. This laserable assemblage was exposed using an array of overlapping 240 5 x 2 micron spots that resulted from the splitting through a light valve of a 20 watt infrared diode lasers beam emitting at 830 nm and at a 1 microsecond pulse width. The drum speed was varied to achieve sensitivities in the 200 to 350 mJ/cm^2 range. Results are shown in Table 10.

Table 10

mj	L*,a*,b*	Pantone match/ΔE
375	51.2,60.3,36	711/4.4
350	51,60.6.37.3	711/3.7
325	50.8,60,36.2	711/3.8
300	51.5,61.4,38	711/3.8
275	51.6,59.6,36.4	711/4.7
250	52.1,59.8,36.9	711/4.9
225	52.5,59.2,36.7	711/5.6
200	53.0,58.2,35.9	711/6.7

[0130] The image on the receiver element was laminated onto paper using a Waterproof® laminator. The temperature of the upper and lower roller was set to 115 and 120°C, respectively and the transfer speed was 600 mm/minute. After lamination was completed and the image cooled for 2 minutes the backing of the receiver element was removed. The l*, a* and b* of the transferred image at 250 mJ/cm^2 were 53, 53,64.63 and 38.19, respectively. The color match and •E are 711 and 5.0, respectively. This in fact shows that lamination does not affect the color coordinates of the transferred image in any significant manner.

Example 2:

[0131] Example 1 was repeated with the following exception: the coated layer had the following composition:

Table 11

Example 2	Solution (grs)	Solids (%)
GJD3007	1.21	21
YJD3174	0.40	8
RJD3022	0.08	1
MMA/nBMA	4.97	62
PEG300	0.24	8
Zonyl® FSA	0.04	
H20	13.06	
Total solution	10	

Table 11 (continued)

Example 2	Solution (grs)	Solids (%)
Total solids	3	
%solids	15	

[0132] In the Table above GJD3007, YJD3174 and RJD3022 are a green, yellow and red dispersions by Sun Chemicals, PEG300 is polyethylene glycol with 300 molecular weight, Zonyl® FSA(DuPont) is a fluoro-surfactant.

[0133] The color coordinates of the image digitally transferred from the green imageable element onto the receiver element as a function of the laser fluence used in transfer are shown in the table below.

Mj	L*,a*,b*	Pantone match/ΔE
375	56.44,-63.1,32.35	355/5.5
350	54.21,-63.5,32.27	355/5.8
325	54.59,-62.73,32.9	355/4.7
300	54.9,-63.07,31.69	355/4.4
275	52.74,-64.48,32.1	355/4.6
250	55.14,-64.33,34.9	355/4.4
225	54.69,-64.8,32,31	355/3.5
200	52.4,-70.75,35.3	355/2.2

EXAMPLE 3:

[0134] This example illustrates colors obtained by mixing two base colors, in this case process magenta and Pantone red 185. The latter obtained from the recipe below:

Magenta		
Magenta	0.44	11.5
MMA/nBMA	5.94	74
PEG300	0.06	2

Pantone® Red 185		
Frazer red	2.3	11.5
Castle Magenta	1.27	11.5
MMA//nBMA	5.94	74
ADS-830	0.03	1
PEG300	0.06	2
Zonyl® FSA	0.04	
H2O	10.36	
Total solution	20	
Total solids	3	
%solids	15	

[0135] After stirring for 30 minutes, the control solution was coated using a Meyer rod #6 onto LOE paper to a nominal thickness of about 1 micron. The coated paper was placed into an oven at 60°C and dried for 1 minute prior to the measurement of the color coordinates using an X-Rite color head. The Pantone® colors and ΔE results are shown in

Table 13.

Table 13

Pantone® Red 185	11.16	8.41	8.57	8.72
Magenta	0,54	0.43	0.32	0.21
Pcolor/ΔE	199/4.8	192/2.9	192/5.3	032/2.9

Example 4:

[0136] This example illustrates the use of specialty colors for proofing applications. The six color imageable element had the structure indicated in Example 1 with the pigmented coating being the process colors: cyan, yellow, magenta and black. The two specialty color imageable elements with the formulation listed in Tables 1 and 5 were coated following the procedure described above. The six imageable elements and one receiver element were loaded onto the 4-up cassette of the Creo 3244 Spectrum Trendsetter for imaging. A Tyvex® sheet was used to separate the imageable element and receiver element for automatic loading. The receiver element was loaded onto the imaging drum and held by vacuum. Once its loading was completed the imageable element, slightly larger than the receiver element was loaded on top of the receiver, and held by vacuum, with the black thermally imageable layer directly in contact with the surface of the receiver. This laserable assemblage was exposed using an array of overlapping 240 5 x 2 micron spots that resulted from the splitting through a light valve of a 20 watt infrared diode lasers beam emitting at 830 nm and at a 1 microsecond pulse width. The resulting image on the exposed imageable element corresponded to the RIPed images of the color separation negatives. The order in which the laserable assemblages were loaded, digitally exposed and unloaded was: K, C, M ,Y, G and R imageable elements. The corresponding drum speeds, sensitivities laser power for the different colors are listed below.

[0137] Results are shown in Table 14.

Table 14

	Laser Power (Watts)	Drum Speed (RPM)	Sensitivity (mJ/cm2)
Black	12.5	170	200
Cyan	14	160	250

[0138] Results are shown in Table 14.

Table 14

	Laser Power (Watts)	Drum Speed (RPM)	Sensitivity (mJ/cm2)
Black	12.5	170	200
Cyan	14	160	250
Magenta	14.5	140	275
Yellow	12	130	275
Green	14	160	250
Red	14	160	250

Claims

1. A method for forming an image comprising the steps of:

(1) forming a first coating solution of a first colorant and a second coating solution of a second colorant;
(2) providing a first base element having a first coatable surface;
(3) forming a first imageable element by applying an amount of the first coating solution to the coatable surface to form a first thermally imageable layer thereon, the first thermally imageable layer having a first thermal sensitivity;
(4) forming a first laserable assemblage including the first imageable element and a receiver element having

an image receiving layer which is in contact with the first imageable element;
(5) first imagewise exposing to laser radiation the first laserable assemblage, whereby the exposed areas of the first thermally imageable layer are transferred to the receiver element to form a first imaged receiver element;
(6) providing a second base element having a second coatable surface;
(7) forming a second imageable element by applying an amount of the second coating solution to the coatable surface to form a second thermally imageable layer thereon, the second thermally imageable layer having a second thermal sensitivity;
(8) forming a second laserable assemblage including the second imageable element and the first imaged receiver element, the first image of which is adjacent to the second imageable element;
(9) imagewise exposing to laser radiation, at substantially the same laser fluence as the first imagewise exposing, the second laserable assemblage, whereby the exposed areas of the second thermally imageable layer are transferred to the first imaged receiver element to form a second imaged receiver; and
(10) separating at least the second imageable element from the second imaged receiver to produce an imaged receiver having a revealed image.

2. The method of Claim 1 further comprising the step of applying the second imaged receiver to a permanent substrate.

3. The method of Claim 2 in which the in which the receiver element further comprises a support, the support being removed to effectuate transfer of the revealed image and the image receiving layer to the permanent substrate the revealed image being sandwiched between the image receiving layer and the permanent substrate.

4. The method of Claim 3 wherein the permanent substrate is paper,

5. The method of Claim 1 wherein the imagewise exposing steps are repeated to form a multi-image comprising four colors.

6. The method of Claim 3 further comprising contacting the second imageable element with an image rigidification element comprising:

(a) a support having a release surface, and
(b) a thermoplastic polymer layer,

the image being adjacent to the thermoplastic polymer layer whereby the image is encased between the thermoplastic polymer layer and the image receiving layer;
removing the support thereby revealing the thermoplastic polymer layer; and
contacting the revealed thermoplastic polymer layer with a permanent substrate.

7. The method of Claim 1 wherein the exposure step is effected at a laser fluence of 600 mJ/cm^2 or less.

8. The method of Claim 1 wherein the first base element and the second base element comprise:

(a) an ejection or subbing layer; and
(b) a heating layer.

9. The method of Claim 1 wherein the first base element and the second base element comprise:

(a) a heating layer, and
(b) a base element support.

10. The method of Claim 1 wherein the first imageable element and the second imageable element further comprise a polymeric binder.

11. The method of Claim 10 wherein the polymeric binder is a low decomposition temperature polymer having a decomposition temperature greater than about 350°C.

12. The method of Claim 1 wherein the first colorant and the second colorant comprise a pigment dispersion.

13. The method of Claim 1 wherein the first colorant and the second colorant comprise a dye.

14. The method of Claim 1 wherein the first thermally imageable layer or the second thermally imageable layer or both comprise a near infrared absorbing dye.

15. The method of Claim 14 wherein the NIR dye is selected from the group consisting of poly(substituted) phthalocyanine compounds, metal-containing phthalocyanine compounds; cyanine dyes; squarylium dyes; chalcogenopyryioacrylidene dyes; croconium dyes; metal thiolate dyes; bis(chalcogenopyrylo) polymethine dyes; oxyindolizine dyes; bis(aminoaryl) polymethine dyes; merocyanine dyes; quinoid dyes and mixtures thereof.

16. The method of Claim lwherein the image receiving layer of the receiver element comprises a crystalline polymer.

17. The method of Claim 16 wherein the crystalline polymer is polycaprolactone.

18. The method of Claim 6 wherein the thermoplastic polymer is selected from the group consisting essentially of polyester, methacrylate, acrylate, polyvinylacetate, polyvinylbutyral, polyvinylformal, styrene-isoprene-styrene and styrene-ethylene-butylene-styrene polymers.

19. The method of Claim 18 wherein the thermoplastic polymer is polyester.

20. The method of Claim 6 wherein the thermoplastic polymer layer comprises an NIR dye bleaching agent.

21. The method of Claim 20 wherein the NIR dye bleaching agent is selected from the group consisting of amines, azo compounds, carbonyl compounds, organometallic compounds, carbanions, peroxides, diacylperoxides, peroxy acids, hydroperoxides, persulfates, and halogen compounds.

FIG. 1

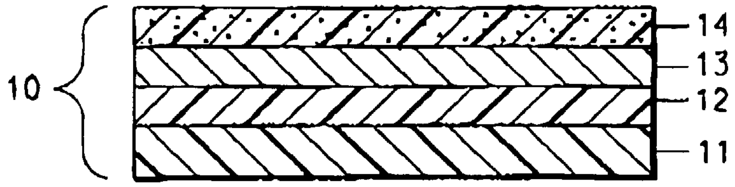


FIG. 2

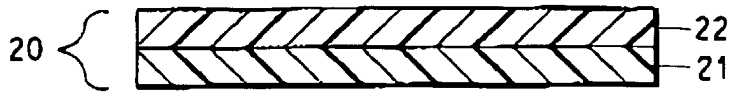


FIG. 3

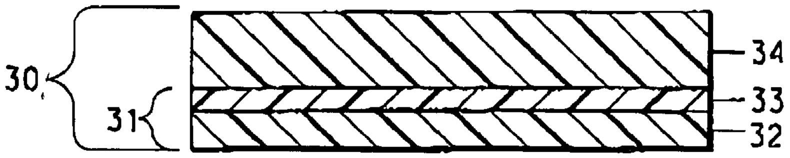


FIG. 4

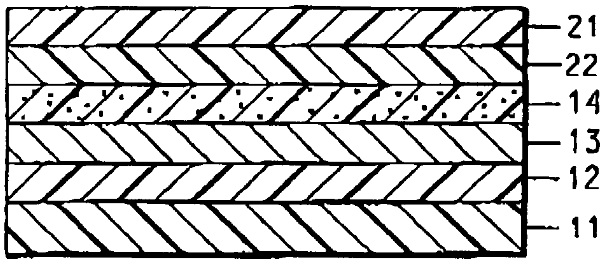


FIG. 5

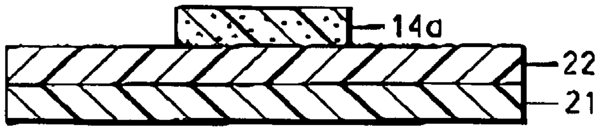


FIG. 5A

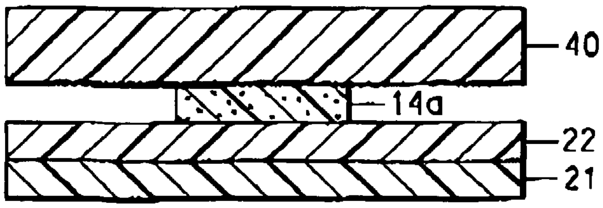


FIG. 5B

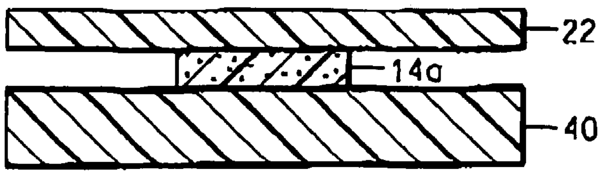


FIG. 6

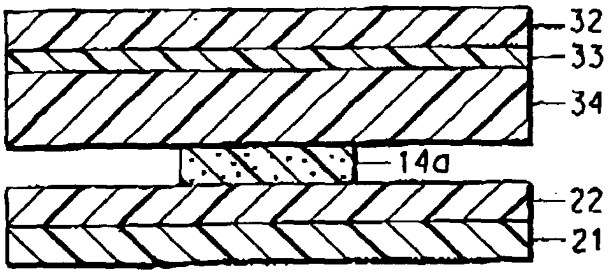


FIG. 6A

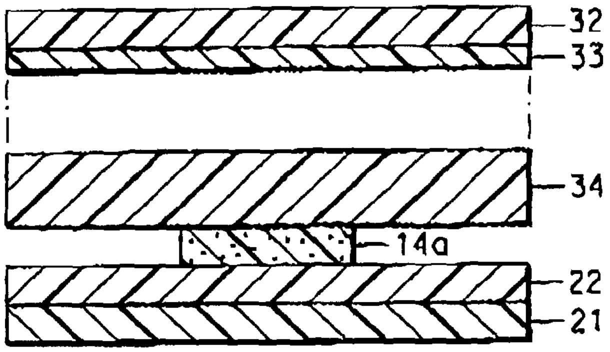


FIG. 7

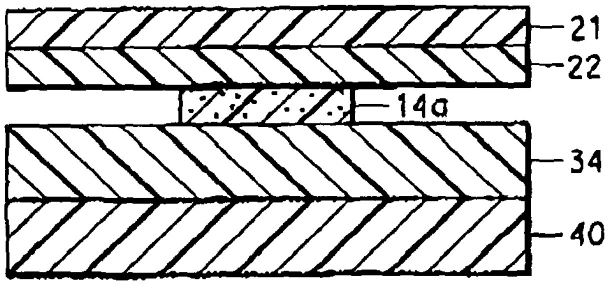
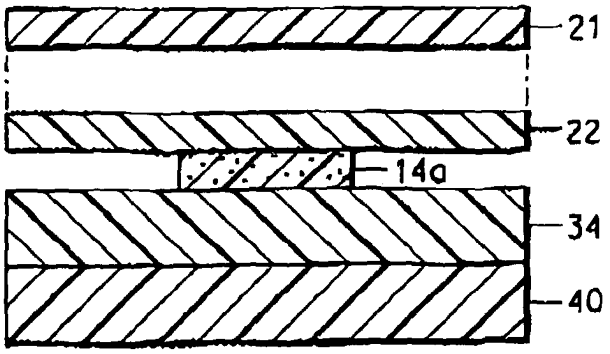


FIG. 8



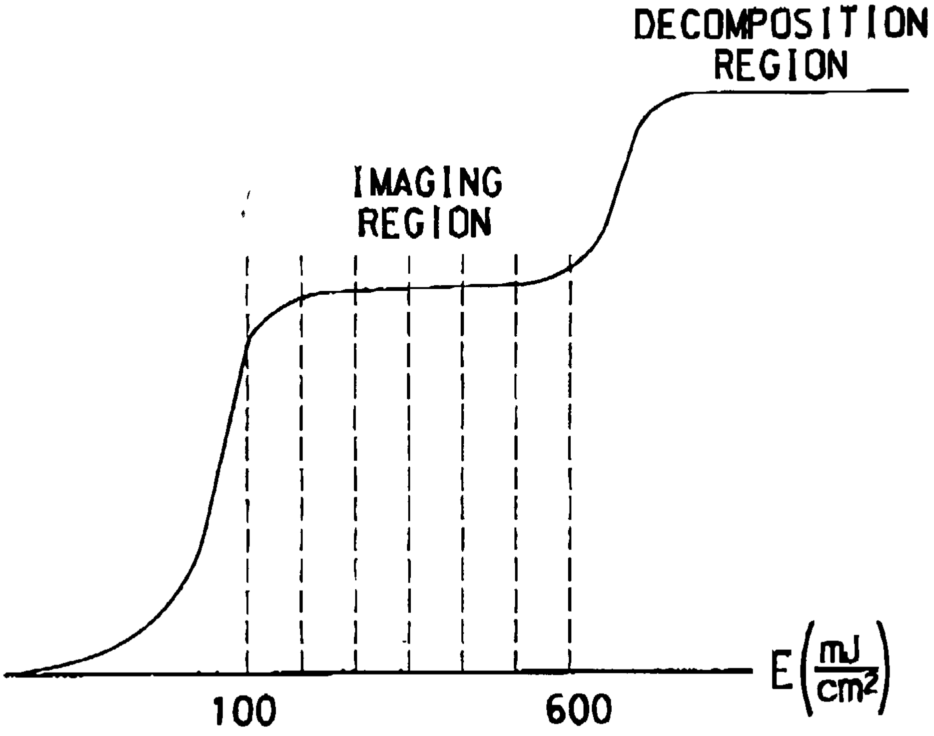

DECOMPOSITION
REGION
IMAGING
REGION
100
600
$E\left(\frac{mJ}{cm^2}\right)$

FIG. 9