(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 728 073 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
**21.04.1999 Bulletin 1999/16**

(21) Application number: **94930625.2**

(22) Date of filing: **06.10.1994**

(51) Int. Cl.$^{6}$: **B41M 5/38**

(86) International application number:
**PCT/US94/11345**

(87) International publication number:
**WO 95/13195 (18.05.1995 Gazette 1995/21)**

(54) **TRANSFER PRINTING MEDIUM**
ÜBERTRAGUNGSDRUCKMATERIAL
SUPPORT D'IMPRESSION PAR TRANSFERT

(84) Designated Contracting States:
**AT DE GB IE IT**

(30) Priority: **09.11.1993 US 149285**

(43) Date of publication of application:
**28.08.1996 Bulletin 1996/35**

(73) Proprietor: **MARKEM CORPORATION**
**Keene New Hampshire 03431 (US)**

(72) Inventors:
- **MENEGHINI, Frank, A.**
  **Keene, NH 03431 (US)**
- **DEEKEN, John, S.**
  **Sullivan, NH 03445 (US)**
- **DRAKE, John, J.**
  **Keene, NH 03431 (US)**

(74) Representative:
**Hirsch, Marc-Roger et al**
**Cabinet Hirsch**
**34 rue de Bassano**
**75008 Paris (FR)**

(56) References cited:
**DE-A- 3 715 991**

- **PATENT ABSTRACTS OF JAPAN vol. 16, no. 36 (M-1205) 29 January 1992 & JP,A,03 244 588 (CANON K.K.) 31 October 1991**





Printed by Xerox (UK) Business Services
2.16.7/3.6

## Description

### Background of the Invention

**[0001]** This invention relates to laser-induced transfer printing.

**[0002]** In laser-induced transfer printing, irradiation of an ink-bearing carrier with laser light causes the ink to transfer from the carrier to a surface, e.g., the surface of a microelectronic device, audio cassette, computer diskette, or syringe body. By manipulating the scanning parameters of the laser beam, the ink can be deposited in a programmed pattern.

**[0003]** JP-A-03/244 588 describes a transfer recording material that includes an image-forming element containing a compound containing an ethylenic unsaturated double bond, a photopolyemrization initiator, and a coloring agent. The image-forming element includes a filler, such as carbon black.

### Summary of the invention.

**[0004]** The invention provides a laser-induced transfer printing method comprising the steps of

(a) providing a transfer printing medium capable of converting laser energy to heat comprising a carrier to which is applied a curable laser-transferrable ink; and
(b) irradiating said medium with laser light of a predetermined wavelength,
whereupon said laser light transfers said ink to a surface of interest and cures said ink to adhere said ink to the surface of interest.

**[0005]** Preferred embodiments correspond to claims 2 to 10.

**[0006]** The invention also provides a transfer printing medium comprising a carrier to which is applied a curable laser-transferrable ink having one or more layers, said ink comprising:

(a) at least one colorant;
(b) at least one polymerization initiator;
(c) at least one curable prepolymer; and
(d) at least one thermal convertor different from said colorant with the proviso that said thermal convertor is not carbon black,
said transfer medium being capable of converting laser energy to heat.

**[0007]** Preferred embodiments correspond to claims 12 to 23.

**[0008]** The transfer medium is capable of converting laser energy to heat. The ink includes (a) at least one colorant; (b) at least one polymerization initiator; and (c) at least one curable prepolymer. By "colorant" it is meant any additive that imparts color to the ink, including the colors white and black. Colorants include both dyes and pigments, as well as metallized coatings. By "prepolymer" it is meant any species capable of being polymerized following either thermal or photochemical initiation to form a polymer.

**[0009]** In preferred embodiments, the ink transfers to a surface of interest and cures in one step upon application of laser energy. In one preferred embodiment, at least one of the polymerization initiators is a thermal polymerization initiator and at least one of the prepolymers is thermally curable. In another preferred embodiment, at least one of the polymerization initiators is a photoinitiator and at least one of the prepolymers is photochemically curable.

**[0010]** One example of a preferred prepolymer is an epoxy-functionalized prepolymer. A second example is an epoxy-functionalized prepolymer combined with a vinyl ether-functionalized prepolymer. A third example is an epoxy-functionalized prepolymer combined with an acrylate-functionalized prepolymer. A fourth example includes the acrylate-functionalized prepolymers themselves. A fifth example is a blocked isocyanate-functionalized prepolymer and a sixth example is a blend of a vinyl ether-functionalized prepolymer and a maleate- or maleimide-functionalized prepolymer.

**[0011]** At least one of the ink layers may be a curable size coat that includes a polymerization initiator and a curable prepolymer. The size coat is used in combination with a color coat layer. In one preferred embodiment, the color coat is non-curable and includes a colorant and a thermoplastic film-forming resin. In another preferred embodiment, the color coat is curable and includes a colorant, a polymerization initiator, and a curable prepolymer. In the case of curable color coats used with curable size coats, the polymerization initiators and prepolymers found in the respective layers may be the same as, or different from, each other.

**[0012]** In a second aspect, the invention features a laser-induced transfer printing method using the above-described transfer printing medium. The method includes the steps of irradiating the particular transfer printing medium with laser light of a predetermined wavelength to transfer the ink from the carrier to a surface of interest, and curing the ink to adhere the ink to the surface of interest. The transfer and cure of the ink may be effected in a single step through irradiation with said laser light. Cure may also be effected in a separate step subsequent to transfer.

**[0013]** The invention provides transfer printing media featuring curable inks that adhere well to the surface on which they are deposited following laser irradiation. The inks transfer cleanly from the supporting carrier and cure rapidly; in some cases, transfer and cure are effected in a single step. It is not necessary to add a separate self-oxidizing material such as nitrocellulose in order to effect transfer. In addition, the ability to use non-curable layers (e.g., non-curable color coats) in combination with curable layers (e.g., curable size coats) expands the types of materials that can be used for the inks, enabling the properties of the inks to be adjusted as needed for a particular application.

**[0014]** Other features and advantages of the invention will be apparent from the following description of the preferred embodiments thereof, and from the claims.

Description of the Preferred Embodiments

**[0015]** The invention features a transfer printing medium capable of converting laser energy to heat in which a curable laser-transferrable ink having one or more layers is deposited on a carrier. The carrier must have sufficiently low surface energy to permit transfer of the ink. It also must not melt or otherwise deform upon laser irradiation. Examples of suitable carriers include flexible plastic films such as polyethylene, polypropylene, and polyester.

**[0016]** The transfer medium is capable of converting laser energy to heat to promote transfer of the ink from the carrier to the surface of interest. To this end, one or more thermal convertors different from said colorant and not carbon black are incorporated into the carrier, the ink, or both. The thermal convertors different from said colorant and not carbon black may be separate additives or may be part of the prepolymer.

**[0017]** In the case of separately added convertors included in the ink, the amount of convertor ranges from about 0.25 to about 30% by weight (based upon the total solids content of the ink). The particular convertor is selected based upon the particular laser energy used for irradiation. In the case of $CO_2$ lasers, the preferred convertors are, polyethylene glycol (e.g., PEG 3000 commercially available from Union Carbide), talc (e.g., Nytal® 400 commercially available from R.T. Vanderbilt), and PPZ, a phosphotriazine commercially available from Idemitsu Petrochemicals Co. Ltd; PPZ may also function as a prepolymer. In the case of Nd:YAG lasers, the preferred convertors are IR99, IRA 980, and IR165, all of which are proprietary dyes commercially available from Glendale Protective Technologies, IR dye 14,617 (a proprietary dye commercially available from Eastman Kodak), and Projet® 900NP (a proprietary dye commercially available from ICI). In the case of diode lasers, the preferred convertors are IR dye 14,617 and IRA 980.

**[0018]** The inks may have one or more layers, with particular ingredients (e.g., prepolymer, polymerization initiator, etc.) being present in any of the layers. One example of ink is a one layer ink (referred to here as a "one-pass" coating) having a curable color coat that includes, in a single layer, a curable prepolymer, a polymerization initiator, and a colorant. Another example is a two layer ink (referred to here as a "two-pass" coating) having a color coat (which may be curable or non-curable) in combination with an overlying curable size coat that includes a curable prepolymer and a polymerization initiator.

**[0019]** Because the inks are curable, adhesion upon transfer to a surface of interest is improved. The advantage of the size coat (which is transferred with the color coat upon laser irradiation) is that adhesion is further enhanced, thereby making it possible to use even a non-curable color coat.

**[0020]** The inks contain one or more curable prepolymers, with the total amount of curable prepolymer ranging from 25 to 95% by weight (based upon the total solids content of the ink). Curable prepolymers useful in the invention have two or more functional groups available for crosslinking (which occurs either simultaneously with transfer upon application of laser radiation or following laser irradiation in a separate thermal or photochemical cure step).

**[0021]** One class of suitable curable prepolymers includes epoxy-functionalized prepolymers such as bisphenol A diglycidyl ether (commercially available from Shell Oil under the designation Epon® 001) and epoxy-functionalized novolac resins (e.g., Epon® 164 commercially available from Shell Oil). Lower molecular epoxides such as UVR6110 (a liquid diepoxide commercially available from Union Carbide) may be added as well.

**[0022]** A second class of suitable curable prepolymers includes these epoxy-functionalized prepolymers in combination with one or more vinyl ether-functionalized prepolymers which co-cure with the epoxy-functionalized prepolymers. Examples of suitable vinyl ether-functionalized prepolymers include bisphenol A-divinyl ether adduct; 2,4-toluene diisocyanate/hydroxybutyl vinyl ether adduct; cyclohexyl divinyl ether commercially available from GAF or ISI Products; vinyl ethyl ether, vinyl isobutyl ether, vinyl octadecyl ether, polyethylene glycol divinyl ether, polytetrahydrofuran/350/divinyl ether, and trimethylol propane trivinyl ether, all of which are commercially available from BASF; Rapi/cure® divinyl ether/3, Rapi/cure® cyclohexyl vinyl ether, Rapi/cure® PEPC, and Rapi/cure® hydroxy butyl vinyl ether, all of which are commercially available from ISP; and Vectomers® 2010, 2031, 2032, 4010, 4020, and 4030, all of which are commercially available from Allied-Signal.

**[0023]** A third class of suitable curable prepolymers includes the above-described epoxy-functionalized prepolymers in combination with one or more acrylate-functionalized prepolymers. Examples of acrylate-functionalized prepolymers include RDX 29522 and Ebecryl® 639 (both of which are commercially available from Radcure); Sartomer® 351 (commercially available from Sartomer); and NR440 (commercially available from Zeneca Resins).

**[0024]** A fourth class of suitable curable prepolymers includes the acrylate-functionalized prepolymers themselves without the epoxy-functionalized prepolymers.

**[0025]** A fifth class of suitable curable prepolymers includes blocked isocyanate-functionalized prepolymers. Examples include B1299 (commercially available from Huls) and BL4165A (commercially available from Miles).

**[0026]** A sixth class of suitable curable prepolymers includes the above-described vinyl ether-functionalized prepolymers in combination with maleate- or maleimide-functionalized prepolymers. Examples of maleate-functionalized prepolymers include 89-8902 (commercially available from Cargil Products); and Astrocure® 78HV and Astrocure® 78LV (both of which are commercially available from Zircon). Examples of maleimide-functionalized prepolymers include BMI/S/M/20/TDA (commercially available from Mitsui Toatsu Chemical, Inc.

**[0027]** One or more non-curable layers may be used in combination with one or more curable layers. For example, a non-curable color coat may be combined with an overlying curable size coat. Suitable non-curable resins are thermoplastic film-forming resins. Examples include acrylic resins such as Rhoplex® B85 (an acrylic dispersion commercially available from Rohm & Haas) and Amsco® 3011 (an acrylic dispersion available from Rohm & Haas); urethane resins such as QW-16 (a urethane dispersion useful as a film-former that is commercially available from K.J. Quinn); phenoxy resins such as PKHW 35 (commercially available from Union Carbide); and combinations thereof. The amount of non-curable prepolymer in the ink ranges from about 15 to about 35% by weight (based upon the total solids content of the ink).

**[0028]** The inks also contain a polymerization initiator in an amount ranging from about 0.1 to 5% by weight (based upon the total solids content of the ink). The initiator (which typically is a free radical or cationic initiator) may be a photochemical initiator or a thermal initiator; in some cases, the same initiator can act as both a thermal and a photochemical initiator. In the case of multi-layer inks containing multiple curable layers, layers containing photochemical initiators may be combined with layers containing thermal initiators. In addition, some initiators may be used in conjunction with accelerators such as benzpinacol, copper(II)salts (e.g., copper benzoate), and hexaphenylethane.

**[0029]** In the case of thermal initiators, the initiator must exhibit good stability at ambient temperature to prevent premature curing of the prepolymer. In addition, the initiation temperature must be within the range achievable by laser irradiation. Examples of suitable thermal initiators for cationic initiation include aryl sulfonium salts (e.g., the salts described in WO90/11303, hereby incorporated by reference); aryl iodonium salts (e.g., UVE 9310 and U 479, both of which are commercially available from General Electric); and ammonium salts (e.g., FC520, commercially available from 3M). Examples of suitable thermal initiators for free radical initiation include the class of compounds leading to peroxy radicals, e.g., hydroperoxides, peroxyesters, and peroxyketals; representative compounds are commercially available from Elf-Atochem. Also suitable for free radical initiation are azo polymerization initiators commercially available from Wako.

**[0030]** In the case of photochemical initiators, the initiator must also exhibit good stability at ambient temperature to prevent premature curing of the prepolymer. In addition, it must exhibit absorption maxima in regions of the electromagnetic spectrum different from the regions in which the colorant exhibits absorption maxima. Examples of suitable photochemical initiators for cationic initiation include aryl sulfonium salts (e.g., UVI 6974 commercially available from Union Carbide) and aryl iodonium salts (e.g., UVE 9310 and U 479, both of which are commercially available from General Electric). Another example of a suitable initiator for cationic initiation is hydroxy naphthyl imide sulfonate ester. Examples of suitable photochemical initiators for free radical initiation include CPTX and ITX (both commercially available from Ciba-Geigy), each of which is combined with methyl diethanolamine (commercially available from Aldrich Chemical Co.; lucerin® TPO (commercially available from BASF) combined with methyl diethanolamine; Darcure® 4265 (commercially available from Ciba Geigy), and Irgacure® 369 combined with ITX.

**[0031]** The ink contains one or more colorants, which may be dyes, pigments, or metallized coatings (e.g., an aluminized coating). In the case of dyes and pigments, the colorant is present in an amount ranging from about 35 to 65% by weight (based upon the total solids content of the ink). The particular colorant is chosen based upon the color desired on the final printed surface. Examples of suitable colorants include pigments such as talc, $TiO_2$ (white), phthalogreen (GT-674-D), chrome green oxide (6099), ultramarine blue (RS-9), black oxide (BK-5099D), Kroma red (7097), and Novaperm yellow (HR-70), and dyes such as dynonicidine (2915) and Dianell orange, as well as the aforementioned metallized coatings.

**[0032]** In the case of inks containing photocurable prepolymers, a sensitizer may be added in an amount ranging from about 0.5 to 8% by weight (based upon the total solids content of the ink) to extend the irradiating wavelength for photoinitiation into the visible region. Such sensitizers are useful, for example, where the formulation contains large amounts of $TiO_2$ pigment which absorbs light below 400 nm and thus competes with the initiator. Examples of suitable sensitizers, all of which are commercially available from Aldrich Chemical Co., include perylene, rubrene, phenothiazine, anthracene derivatives, and thioxanthones, as well as lucerin TPO (commercially available from BASF).

**[0033]** Other ingredients which may be added to the inks to improve the coatability, printability, print performance, and durability of the inks include various surfactants, dispersing agents, and polymer dispersions. The amount of each ingredient is selected based upon the desired properties. Examples of suitable surfactants (which may be anionic, cationic, or nonionic) include Triton® X-100 (an aryl ethoxylate commercially available from Rohm & Haas) and FC 430 (a fluoroaliphatic polymeric ester available from 3M). Examples of suitable dispersing agents include polyacrylate salts such as Daxad® 30, a 30% aqueous solution of polysodiumacrylate commercially available from W.R. Grace. Examples of suitable dispersions include Shamrock® 375 and Aquacer® 355, both of which are polyethylene wax dispersions commercially available from Diamond Shamrock.

**[0034]** The transfer medium according to the invention is prepared by combining the ink ingredients in an aqueous or organic solvent (with aqueous solvents being preferred), and then applying the resulting composition to the carrier. If a size coat is used, it is applied on top of the color coat. To facilitate coating, the total solids content of the ink is adjusted to be between 10 and 50% by weight of the ink. The coated carrier is then irradiated with laser light to transfer the ink from the carrier to a desired surface, e.g., the surface of a semiconductor device. Suitable lasers include $CO_2$ lasers (irradiation wavelength equals 10.6μm), Nd:YAG lasers (irradiation wavelength equals 1.06μm), and diode lasers (irradiation wavelength equals, e.g., 0.9μm). The particular irradiation wavelength, power, and time of application parameters are selected to ensure clean transfer.

**[0035]** In the case of some inks, laser irradiation both transfers and cures the ink simultaneously. With other inks, a separate thermal or photochemical cure is effected following transfer. The cure conditions are selected based upon the particular prepolymers and initiators used in the formulation.

**[0036]** The invention will now be further described by way of the following examples.

Example 1

**[0037]** This example describes the preparation of a transfer medium having one-pass, thermally curable, cationically initiated, ink.

**[0038]** The following ingredients were combined to form a laser-transferrable ink (all amounts in weight percent):

| | |
|---|---|
| $TiO_2$ | 55.0 |
| Bisphenol A-DVE adduct | 13.0 |
| 35201[1] | 24.8 |
| PEG 3000[2] | 5.0 |
| Aryl sulfonium salt[3] | 2.0 |
| Triton® X-100[4] | 0.2 |

[1] Aqueous dispersion of bisphenol A-epichlorohydrin adduct formerly available from Rhone-Poulenc.
[2] Polyethylene glycol ($M_n$ = 3000) commercially available from Union Carbide.
[3] Aryl sulfonium salt thermal initiator of the type described in WO90/11303.
[4] Surfactant commercially available from Rohm & Haas.

**[0039]** Water was added to adjust the total solids content to 35% by weight, after which the resulting ink was coated onto 30,5 μm (1.2 mil) thick polypropylene carrier film using a #15 mayer rod. The coated surface of the film was then placed in intimate contact with the surface of a molded semiconductor device. Next, a $CO_2$ laser was directed through the uncoated side of the carrier film to transfer the ink to the surface of the semiconductor device. The laser dwelled on each addressed pixel for 16 μs. The power output of the laser at the point of contact with the coated film was 14.5 W. The device bearing the transferred image was then placed in a forced hot air oven for 30 minutes. at 175°C to cure the ink. After curing, the transferred image was found to be resistant to treatment with 1,1,1-trichloroethane (3 minutes. soak, 10 brush strokes, cycled 3 times).

Example 2

**[0040]** This example describes the preparation of a transfer medium having a two-pass, cationically initiated ink in which both the color coat and the size coat are photochemically curable.

**[0041]** The following ingredients were combined to form a photochemically curable color coat (all amounts in weight percent):

| | |
|---|---|
| $TiO_2$ | 55.0 |
| 2,4-toluene diisocyanate/HBVE adduct[1] | 35.8 |
| QW-16 (urethane dispersion)[2] | 2.0 |
| PPZ[3] | 5.0 |
| Triton® X-100[4] | 0.2 |
| UVI 6974[5] | 2.0 |

[1] Hydroxy butyl divinyl ether adduct.
[2] Pre-made urethane dispersion commercially available from K.J. Quinn.
[3] Commercially available from Idemitsu Petrochemicals Co. Ltd.
[4] Surfactant commercially available from Rohm & Haas.
[5] Triaryl sulfonium salt-based initiator commercially available from Union Carbide.

**[0042]** Water was added to adjust the total solids content to 35% by weight, after which the resulting color coat was applied to a 30,5 μm (1.2 mil) thick polypropylene carrier film using a #13 mayer rod.

**[0043]** The following ingredients were combined to form a photochemically curable size coat (all amounts in weight percent):

| | |
|---|---|
| EPON® 1001[1] | 89.1 |
| UVI 6110[2] | 5.45 |
| FC-430[3] | 2.47 |
| UVI 6974[4] | 1.68 |
| Perylene[5]® | 0.3 |
| PPZ[6] | 1.0 |

[1] Bisphenol A diglycidyl ether commercially available from Shell Qil Co.
[2] Liquid diepoxide commercially available from Union Carbide.
[3] Fluoroaliphatic polymeric ester surfactant commercially available from 3M Co.
[4] Triaryl sulfonium salt-based initiator commercially available from Union Carbide.
[5] Photosensitizer commercially available from Aldrich Chemical Co.
[6] Commercially available from Idemitsu Petrochemicals Co. Ltd.

**[0044]** Methyl ethyl ketone was added to adjust the total solids content of the size coat to 25% by weight, after which the resulting size coat was applied on top of the color coat using a #5 mayer rod.

**[0045]** The coated surface of the film was then placed in intimate contact with the surface of a molded semiconductor device. Next, a $CO_2$ laser was directed through the uncoated side of the carrier film to transfer the ink (color coat plus size coat) to the surface of the semiconductor device. The laser dwelled on each addressed pixel for 20 μs. The power output of the laser at the point of contact with the coated film was 14.5 W. The device bearing the transferred image was then cured (5 minutes. at a 150°C preheat, followed by a 3.6 sec exposure to UV radiation). The resulting cured printed image was found to be resistant to treatment with 1,1,1-trichloroethane (3 minutes. soak, 10 brush strokes, cycled 3 times).

Example 3

**[0046]** This example describes the preparation of a transfer medium having a two-pass, cationically curable ink in which the color coat is non-curable and the size coat is thermally curable.

**[0047]** The following ingredients were combined to form a non-curable color coat (all amounts in weight percent):

| | |
|---|---|
| Water | 54.0 |
| Daxad® 30[1] | 0.5 |
| $TiO_2$ | 38.4 |
| Triton® X-100[2] | 0.5 |
| Shamrock® 375[3] | 6.2 |
| Rhoplex® B85[4] | 1.4 Amsco® 3011[5] 7.7 |

[1] Polyacrylate dispersing agent commercially available from W.R. Grace.
[2] Surfactant commercially available from Rohm & Haas.
[3] Polyethylene wax dispersion commercially available from Diamond Shamrock.
[4] Acrylic dispersion commercially available from Rohm & Haas.
[5] Acrylic dispersion commercially available from Rohm & Haas.

**[0048]** Enough ammonium hydroxide was added to adjust the pH to 8.5, after which the resulting color coat was applied to a 30,5 μm (1.2 mil) thick polypropylene carrier film at a coat weight of 69 mg/m$^2$.

**[0049]** The following ingredients were combined to form a photochemically curable size coat (all amounts in weight percent):

| | |
|---|---|
| EPON® 1001[1] | 88.2 |
| UVR 6110[2] | 11.6 |
| FC-430[3] | 3.0 |
| UV 479[4] | 1.6 |
| IR 99[5] | 0.5 |
| Benzpinacole[6]® | 0.47 |

[1] Bisphenol A diglycidyl ether commercially available from Shell Oil Co.
[2] Liquid diepoxide commercially available from Union Carbide.
[3] Fluoroaliphatic polymeric ester surfactant commercially available from 3M Co.
[4] Iodonium salt thermal initiator commercially available from General Electric.
[5] Dye commercially available from Glendale Protective Technologies.
[6] Accelerator commercially available from Aldrich Chemical Co.

**[0050]** Methyl ethyl ketone was added to adjust the total solids content of the size coat to 25% by weight, after which the resulting size coat was applied on top of the color coat using a #5 mayer rod.

**[0051]** The coated surface of the film was then placed in intimate contact with the surface of a molded semiconductor device. Next, a Nd:YAG laser was directed through the uncoated side of the carrier film to transfer the ink (color coat plus size coat) to the surface of the semiconductor device. The laser dwelled on each addressed pixel for 18 μs. The power output of the laser at the point of contact with the coated film was 4.5 W. The device bearing the transferred image was then cured (4 minutes. at 175°C). The resulting cured printed image was found to be resistant to treatment with 1,1,1-trichloroethane (3 minutes. soak, 10 brush strokes, cycled 3 times).

Example 4

**[0052]** This example describes the preparation of a transfer medium having a one-pass, thermally curable, cationically initiated ink in which transfer and cure takes place in a single step upon laser irradiation.

**[0053]** The following ingredients were combined to form a laser-transferrable ink (all amounts in weight percent):

| | |
|---|---|
| Talc[1] | 30.0 |
| UVE 9310[2] | 7.0 |
| Copper benzoate[3] | 0.14 |
| EPON® 164[4] | 51.43 |
| CHVE5[4] | 11.43 |

[1] Nytal 400 commercially available from R.T. Vanderbilt.
[2] Photo and thermal initiator commercially available from General Electric.
[3] Accelerator commercially available from Aldrich Chemical Co.
[4] Epoxy novolac resin having an epoxy equivalent of 200-240 commercially available from Shell Oil.
[5] Cyclohexyl divinyl ether commercially available from GAF or ISI Products.

**[0054]** Methyl ethyl ketone was added to adjust the total solids content to 50% by weight, after which the resulting ink was coated onto a 30,5 μm (1.2 mil) thick polypropylene carrier film using a #10 mayer rod. The coated surface of the film was then placed in intimate contact with a glass slide. Next, a $CO_2$ laser was directed through the uncoated side of the carrier film to transfer the ink to the surface of the glass slide. The laser dwelled on each addressed pixel for 80 μs. After addressing, the transferred coating was removed form the glass slide and analyzed by differential scanning calorimetry. There was no evidence of residual heat of reaction, indicating that the transferred coating had cured during the transfer step.

Example 5

**[0055]** This example describes the preparation of a transfer medium having a two-pass, free radical-initiated ink in which both the color coat and the size coat are photochemically curable.

**[0056]** The following ingredients were combined to form a photochemically curable color coat (all amounts in weight percent):

| | |
|---|---|
| $TiO_2$ | 65.0 |
| Aquacer 355[1] | 11.0 |
| NR 440[2] | 18.8 |
| PPZ[3] | 3.0 |
| Triton X-100[4] | 0.2 |
| Daracure 4265[5] | 2.0 |

[1] Polyethylene wax dispersion commercially available from Diamond Shamrock.
[2] Acrylate-functionalized prepolymer commercially available from Zeneca Resins.
[3] Commercially available from Idemitsu Petrochemicals Co. Ltd.
[4] Surfactant commercially available from Rohm & Haas.
[5] Photochemical free radical initiator commercially available from Ciba Geigy.

**[0057]** Water was added to adjust the total solids content to 40% by weight, after which the resulting color coat was applied to a 30,5 μm (1.2 mil) thick polypropylene carrier film using a #13 mayer rod.

**[0058]** The following ingredients were combined to form a photochemically curable size coat (all amounts in weight percent):

| | |
|---|---|
| NR 440[1] | 78.0 |
| Ebecryl® 639[2] | 20.0 |
| Daracure® 4265[3] | 2.0 |

[1] Acrylate-functionalized prepolymer commercially available from Zeneca Resins.
[2] Acrylate-functionalized prepolymer commercially available from Radcure.
[3] Photochemical free radical initiator commercially available from Ciba Geigy.

**[0059]** Water was added to adjust the total solids content of the size coat to 40% by weight, after which the resulting size coat was applied on top of the color coat using a #5 mayer rod.

**[0060]** The coated surface of the film was then placed in intimate contact with the surface of a molded semiconductor device. Next, a $CO_2$ laser was directed through the uncoated side of the carrier film to transfer the ink (color coat plus size coat) to the surface of the semiconductor device. The laser dwelled on each addressed pixel for 20 μs. The power output of the laser at the point of contact with the coated film was 14.5 W. The device bearing the transferred image was then cured (5 minutes. at a 100°C preheat, followed by passage through a UV fusion oven equipped with an H bulb at a speed of 42,3 mm/s (100 inches per minute). The resulting cured printed image was found to be resistant to treatment with 1,1,1-trichloroethane (3 minutes. soak, 10 brush strokes, cycled 3 times).

## Claims

1. A laser-induced transfer printing method comprising the steps of

   (a) providing a transfer printing medium capable of converting laser energy to heat comprising a carrier to which is applied a curable laser-transferrable ink; and
   (b) irradiating said medium with laser light of a predetermined wavelength,
   whereupon said laser light transfers said ink to a surface of interest and cures said ink to adhere said ink to the surface of interest.

2. The laser-induced transfer printing method of claim 1 comprising the steps of:

   (a) providing a transfer printing medium capable of converting laser energy to heat comprising a carrier to which is applied a curable laser-transferrable ink having one or more layers, said ink comprising:
   (i) at least one colorant;
   (ii) at least one polymerization initiator; and
   (iii) at least one curable prepolymer;
   (b) irradiating said medium with laser light of a predetermined wavelength to transfer said ink to a surface of interest; and
   (c) curing said ink to adhere said ink to the surface of interest.

3. The method of claim 1 or 2 wherein the transfer and cure of said ink are effected in a single step through irradiation with said laser light.

4. The method of claim 1 or 2 wherein the transfer and cure of said ink are effected in separate steps.

5. The method of claim 2, 3 or 4 wherein at least one of said polymerization initiators comprises a thermal polymerization initiator and at least one of said prepolymers is thermally curable.

6. The method of claim 2, 3, or 4 wherein at least one of said polymerization initiators comprises a pho-

toinitiator and at least one of said prepolymers is photochemically curable.

7. The method of claim 2, 3, or 4 wherein at least one of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable prepolymer.

8. The method of claim 2, 3, or 4 wherein at least one of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable prepolymer and at least one of the layers of said ink is a non-curable color coat comprising a colorant and a thermoplastic film-forming resin.

9. The method of claim 2, 3, or 4 wherein at least one of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable prepolymer and at least one of the layers of said ink is a curable color coat comprising a colorant, a polymerization initiator, and a curable prepolymer.

10. The method of any one of claims 2 to 9 where the transfer printing medium comprises at least one thermal convertor that is different from said colorant.

11. A transfer printing medium comprising a carrier to which is applied a curable laser-transferrable ink having one or more layers, said ink comprising:

(a) at least one colorant;
(b) at least one polymerization initiator;
(c) at least one curable prepolymer; and
(d) at least one thermal convertor different from said colorant with the proviso that said thermal converter is not carbon black,
said transfer medium being capable of converting laser energy to heat.

12. The transfer printing medium of claim 11 wherein said ink is capable of transfer to a surface of interest and is capable of curing in one step upon application of laser energy.

13. The transfer printing medium of claim 11 or 12 wherein at least one of said polymerization initiators comprises a thermal polymerization initiator and at least one of said prepolymers is thermally curable.

14. The transfer printing medium of claim 11 or 12 wherein at least one of said polymerization initiators comprises a photoinitiator and at least one of said prepolymers is photochemically curable.

15. The transfer printing medium of any one of claims 11 to 14 wherein at least one of said prepolymers comprises an epoxy-functionalized prepolymer.

16. The transfer printing medium of claim 15 wherein said prepolymer further comprises a vinyl ether-functionalized prepolymer.

17. The transfer printing medium of claim 15 wherein said prepolymer further comprises an acrylate-functionalized prepolymer.

18. The transfer printing medium of any one of claims 11 to 14 wherein at least one of said prepolymers comprises an acrylate-functionalized prepolymer.

19. The transfer printing medium of any one of claims 11 to 14 wherein at least one of said prepolymers comprises a blocked isocyanate-functionalized prepolymer.

20. The transfer printing medium of any one of claims 11 to 14 wherein at least one of said prepolymers comprises a blend of a vinyl ether-functionalized prepolymer and a maleate- or maleimide-functionalized prepolymer.

21. The transfer printing medium of claim 11 wherein at least one of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable prepolymer.

22. The transfer printing medium of claim 11 wherein at least one of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable prepolymer and at least one of the layers of said ink is a non-curable color coat comprising a colorant and a thermoplastic film-forming resin.

23. The transfer printing medium of claim 11 wherein at least one of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable prepolymer and at least one of the layers of said ink is a curable color coat comprising a colorant, a polymerization initiator, and a curable prepolymer.

## Patentansprüche

1. Eine laserinduziertes Übertragungsdruckverfahren, umfassend die Schritte von

(a) dem Vorlegen eines Übertragungsdruckmaterials, das in der Lage ist, Laserenergie in Wärme umzuwandeln, umfassend einen Träger, auf welchen eine härtbare laserübertragbar Tinte aufgebracht ist; und
(b) dem Bestrahlen des Materials mit Laserlicht einer vorbestimmten Wellenlänge, woraufhin das Laserlicht die Tinte auf eine gewünschte

Oberfläche überträgt und die Tinte härtet, damit die Tinte auf der gewünschten Oberfläche haftet.

2. Das Verfahren gemäß Anspruch 1, umfassend die Schritte von:

(a) dem Vorlegen eines Übertragungsdruckmaterials, das in der Lage ist, Laserenergie in Wärme umzuwandeln, umfassend einen Träger, auf welchen eine härtbare laserübertragbar Tinte mit einer oder mehreren Schichten aufgebracht ist, wobei diese Tinte umfasst :
(i) mindestens einen Farbstoff ;
(ii) mindestens einen Polymerisationsinitiator ;
(iii) mindestens ein härtbares Prepolymer ;
(b) das Bestrahlen des Materials mit Laserlicht einer vorbestimmten Wellenlänge, um die Tinte auf eine gewünschte Oberfläche zu übertragen ; und
(c) das Härten der Tinte, damit die Tinte auf der gewünschten Oberfläche haftet.

3. Das Verfahren gemäß Anspruch 1 oder 2, in dem die Übertragung und das Härten der Tinte in einem einzigen Schritt durch Bestrahlung mit dem Laserlicht durchgeführt werden.

4. Das Verfahren gemäß Anspruch 1 oder 2, in dem die Übertragung und das Härten des Tinte in getrennten Schritten durchgeführt werden.

5. Das Verfahren gemäß Anspruch 2, 3 oder 4, in dem mindestens einer der Polymerisationsinitiatoren einen thermischen Polymerisationsinitiator umfasst und mindestens eines der Prepolymeren thermisch härtbar ist.

6. Das Verfahren gemäß Anspruch 2, 3 oder 4, in dem mindestens einer der Polymerisationsinitiatoren einen Photoinitiator umfasst und mindestens eines der Prepolymeren photochemisch härtbar ist.

7. Das Verfahren gemäß Anspruch 2, 3 oder 4, in dem mindestens eine der Schichten der Tinte ein härtbarer Grundüberzug ist, welcher einen Polymerisationsinitiator und ein härtbares Prepolymer umfasst.

8. Das Verfahren gemäß Anspruch 2, 3 oder 4, in dem mindestens eine der Schichten der Tinte ein härtbarer Grundüberzug ist, welcher einen Polymerisationsinitiator und ein härtbares Prepolymer umfasst und mindestens eine der Schichten der Tinte ein nicht härtbarer Farbüberzug ist, welcher einen Farbstoff und ein thermoplastisches filmbildendes Harz umfasst.

9. Das Verfahren gemäß Anspruch 2, 3 oder 4, in dem mindestens eine der Schichten der Tinte ein härtbarer Grundüberzug ist, welcher einen Polymerisationsinitiator und ein härtbares Prepolymer umfasst und mindestens eine der Schichten der Tinte ein nicht härtbarer Farbüberzug ist, welcher einen Farbstoff, einen Polymerisationsinitiator und ein härtbares Prepolymer umfasst.

10. Das Verfahren gemäß mindestens einem der Ansprüche 2 bis 9, bei dem das Übertragungsdruckmaterial mindestens einen thermischen Umwandler umfasst, der von dem Farbstoff verschieden ist.

11. Ein Übertragungsdruckmaterial, umfassend einen Träger, auf welchen eine härtbare laserübertragbare Tinte mit einer oder mehreren Schichten aufgebracht ist, wobei die Tinte umfasst :

(a) mindestens einen Farbstoff ;
(b) mindestens einen Polymerisationsinitiator ;
(c) mindestens ein härtbares Prepolymer ; und
(d) mindestens einen thermischen Umwandler, welcher vom dem Farbstoff verschieden ist, vorausgesetzt, der thermische Wandler ist nicht Rußschwarz,
wobei das Übertragungsmaterial in der Lage ist, Laserenergie in Wärme umzuwandeln.

12. Das Druckübertragungsmaterial gemäß Anspruch 11, in dem die Tinte auf eine gewünschte Oberfläche übertragen werden kann und in der Lage ist, unter Anwendung von Laserenergie in einem Schritt zu härten.

13. Das Druckübertragungsmaterial gemäß Anspruch 11 oder 12, in dem mindestens eines der Polymerisationsinitiatoren einen thermischen Polymerisationsinitiator umfasst und mindestens eines der Prepolymeren thermisch härtbar ist.

14. Das Druckübertragungsmaterial gemäß Anspruch 11 oder 12, in dem mindestens eines der Polymerisationsinitiatoren einen Photoinitiator umfasst und mindestens eines der Prepolymeren photochemisch härtbar ist.

15. Das Druckübertragungsmaterial gemäß mindestens einem der Ansprüche 11 bis 14, in dem mindestens eines der Prepolymeren ein Prepolymer mit Epoxyfunktion umfasst.

16. Das Druckübertragungsmaterial gemäß Anspruch 15, in dem das Prepolymer weiter ein Prepolymer mit Vinyletherfunktion umfasst.

17. Das Druckübertragungsmaterial gemäß Anspruch

15, in dem das Prepolymer weiter ein Prepolymer mit Acrylatfunktion umfasst.

18. Das Druckübertragungsmaterial gemaß mindestens einem der Ansprüche 11 bis 14, in dem mindestens eines der Prepolymeren ein Prepolymer mit Acrylatfunktion umfasst.

19. Das Druckübertragungsmaterial gemäß mindestens einem der Ansprüche 11 bis 14, in dem mindestens eines der Prepolymeren ein Prepolymer mit blockierter Isocyanatfunktion umfasst.

20. Das Druckübertragungsmaterial gemäß mindestens einem der Ansprüche 11 bis 14, in dem mindestens eines der Prepolymeren eine Mischung eines Prepolymers mit Vinyletherfunktion und eines Prepolymers mit Maleat- oder Maleimidfunktion umfasst.

21. Das Druckübertragungsmaterial gemäß Anspruch 11, in dem mindestens eine der Schichten der Tinte ein härtbarer Grundüberzug ist, der einen Polymerisationsinitiator und ein härtbares Prepolymer umfasst.

22. Das Druckübertragungsmaterial gemäß Anspruch 11, in dem mindestens eine der Schichten der Tinte ein härtbarer Grundüberzug ist, der einen Polymerisationsinitiator und ein härtbares Prepolymer umfasst und mindestens eine der Schichten der Tinte ein nicht härtbarer Farbüberzug ist, welcher einen Farbstoff und ein thermoplastisches filmbildendes Harz umfasst.

23. Das Druckübertragungsmaterialgemäß Anspruch 11, in dem mindestens eine der Schichten der Tinte ein härtbarer Grundüberzug ist, der einen Polymerisationsinitiator und ein härtbares Prepolymer umfasst und mindestens eine der Schichten der Tinte ein nicht härtbarer Farbüberzug ist, welcher einen Farbstoff, einen Polymerisationsinitiator und ein härtbares Prepolymer umfasst.

## Revendications

1. Une méthode d'impression par transfert au laser comprenant les étapes de:

   (a) utilisation d'un milieu d'impression par transfert capable de transformer l'énergie du laser en chaleur comprenant un support sur lequel on applique une encre durcissable transférable par laser; et
   (b) exposition dudit milieu à une lumière laser d'une longueur d'onde prédéterminée,
   de sorte qu'ainsi ladite lumière laser transfère ladite encre à une surface considérée et durcit ladite encre pour la faire adhérer à la surface considérée.

2. Le procédé d'impression par transfert au laser selon la revendication 1, comprenant les étapes de:

   (a) utilisation d'un milieu d'impression par transfert capable de transformer l'énergie laser en chaleur comprenant un support sur lequel on applique une encre durcissable, transférable par laser comportant une ou plusieurs couches, ladite encre comprenant:
   (i) au moins un colorant;
   (ii) au moins un initiateur de polymérisation et
   (iii) au moins un prépolymère durcissable;
   (b) exposition dudit milieu à une lumière laser d'une longueur d'onde prédéterminée pour transférer ladite encre sur la surface considérée et
   (c) durcissement de ladite encre pour la faire adhérer sur la surface considérée.

3. Le procédé selon la revendication 1 ou 2, dans lequel le transfert et le durcissement de ladite encre sont effectués en une seule étape par exposition à ladite lumière laser.

4. Le procédé selon la revendication 1 ou 2, dans lequel le transfert et le durcissement de ladite encre sont effectués dans des étapes séparées.

5. Le procédé selon la revendication 2, 3 ou 4, dans lequel au moins un desdits initiateurs de polymérisation comprend un initiateur de polymérisation thermique et au moins un desdits prépolymères est thermiquement durcissable.

6. Le procédé selon la revendication 2, 3 ou 4, dans lequel au moins un desdits initiateurs de polymérisation comprend un photoinitiateur et au moins un desdits prépolymères est photochimiquement durcissable.

7. Le procédé selon la revendication 2, 3 ou 4, dans lequel au moins une des couches de ladite encre est une couche d'apprêt durcissable comprenant un initiateur de polymérisation et un prépolymère durcissable.

8. Le procédé selon la revendication 2, 3 ou 4, dans lequel au moins une des couches de ladite encre est une couche d'apprêt durcissable comprenant un initiateur de polymérisation et un prépolymère durcissable et au moins une des couches desdites encres est une couche de couleur non durcissable comprenant un colorant et une résine filmogène thermoplastique.

**9.** Le procédé selon la revendication 2, 3 ou 4, dans lequel au moins une des couches de ladite encre est une couche d'apprêt durcissable comprenant un initiateur de polymérisation et un prépolymère durcissable et au moins une des couches de ladite encre est une couche colorée durcissable comprenant un colorant, un initiateur de polymérisation et un prépolymère durcissable.

**10.** Le procédé selon l'une quelconque des revendications 2 à 9, dans lequel le milieu d'impression par transfert comprend au moins un convertisseur thermique qui est différent dudit colorant.

**11.** Un milieu d'impression par transfert comprenant un support sur lequel on applique une encre durcissable transférable par laser comportant une ou plusieurs couches, ladite encre comprenant:

(a) au moins un colorant;
(b) au moins un initiateur de polymérisation;
(c) au moins un prépolymère durcissable; et
(d) au moins un convertisseur thermique différent dudit colorant avec cette condition que ledit convertisseur thermique n'est pas le noir de carbone,
ledit milieu de transfert étant capable de transformer l'énergie laser en chaleur.

**12.** Le milieu d'impression par transfert selon la revendication 11, dans lequel ladite encre est susceptible de transfert sur la surface considérée et est capable de durcissement en une seule étape après application de l'énergie laser.

**13.** Le milieu d'impression par transfert selon la revendication 11 ou 12, dans lequel au moins un desdits initiateurs de polymérisation comprend un initiateur de polymérisation thermique et au moins un desdits prépolymères est durcissable thermiquement.

**14.** Le milieu d'impression par transfert selon la revendication 11 ou 12, dans lequel au moins un desdits initiateurs de polymérisation comprend un photoinitiateur et au moins un desdits prépolymères est photochimiquement durcissable.

**15.** Le milieu d'impression par transfert selon l'une quelconque des revendications 11 à 14, dans lequel au moins un desdits prépolymères comprend un prépolymère fonctionnalisé par époxy.

**16.** Le milieu d'impression par transfert selon la revendication 15, dans lequel ledit prépolymère comprend en outre un prépolymère fonctionnalisé par un éther de vinyle.

**17.** Le milieu d'impression par transfert selon la revendication 15, dans lequel ledit prépolymère comprend en outre le prépolymère fonctionnalisé par acrylate.

**18.** Le milieu d'impression par transfert selon l'une quelconque des revendications 11 à 14, dans lequel l'un desdits prépolymères comprend un prépolymère fonctionnalisé par acrylate.

**19.** Le milieu d'impression par transfert selon l'une quelconque des revendications 11 à 14, dans lequel au moins un desdits prépolymères comprend un prépolymère séquencé fonctionnalisé à l'isocyanate.

**20.** Le milieu d'impression par transfert selon l'une quelconque des revendications 11 à 14, dans lequel au moins un desdits prépolymères comprend un mélange de prépolymère fonctionnalisé par éther vinylique et un prépolymère fonctionnalisé par maléate ou maléimide.

**21.** Le milieu d'impression par transfert selon la revendication 11, dans lequel au moins l'une des couches de ladite encre est une couche d'apprêt durcissable comprenant un initiateur de polymérisation et un prépolymère durcissable.

**22.** Le milieu d'impression par transfert selon la revendication 11, dans lequel au moins l'une des couches de ladite encre est une couche d'apprêt durcissable comprenant un initiateur de polymérisation et un prépolymère durcissable et au moins une des couches de ladite encre est une couche colorée non durcissable comprenant un colorant et une résine filmogène thermoplastique.

**23.** Le milieu d'impression par transfert selon la revendication 11, dans lequel au moins une des couches de ladite encre est une couche d'apprêt durcissable comprenant un initiateur de polymérisation et un prépolymère durcissable et au moins une des couches de ladite encre est une couche colorée durcissable comprenant un colorant, un initiateur de polymérisation et un prépolymère durcissable.