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(54) **DYE-IMAGE RECEIVING ELEMENT FOR USE ACCORDING TO THERMAL DYE SUBLIMATION TRANSFER**

FARBBIIDEMPFIANGSCHICHT ZUR ANWENDUNG IN DER THERMISCHEN
FARBSTOFFSUBLIMATIONÜBERTRAGUNG

ELEMENT RECEPTEUR D'IMAGE PRODUITE PAR COLORANTS, POUR UTILISATION DANS LE
TRANSFERT THERMIQUE DE COLORANTS PAR SUBLIMATION

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(56) References cited:
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Description

1. Field of the invention.

5 The present invention relates to dye-image receiving elements for use according to thermal dye sublimation transfer.

2. Background of the invention.

10 Thermal dye sublimation transfer also called thermal dye diffusion transfer is a recording method in which a dye-donor element provided with a dye layer containing sublimable dyes having heat transferability is brought into contact with a dye-image receiving element and selectively, in accordance with a pattern information signal, heated with a thermal printing head provided with a plurality of juxtaposed heat-generating resistors, whereby dye from the selectively heated regions of the dye-donor element is transferred to the dye-image receiving element and forms a pattern thereon, the shape and density of which is in accordance with the pattern and intensity of heat applied to the dye-donor element.

15 A dye-image receiving element for use according to thermal dye sublimation transfer usually comprises a support, e.g. paper or a transparent film, coated with a dye-image receiving layer, into which the dye can diffuse more readily. An adhesive layer may be provided between the support and the receiving layer. On top of said receiving layer a separate release layer may be provided to improve the releasability of the receiving element from the donor element after transfer is effected.

20 As resins constituting the dye-image receiving layer there are known various thermoplastic vinylcopolymers having glass transition temperatures in the range of 50°C to 100°C such as styrene-acrylonitrile acrylates as described in EP 405248.

25 Although these resins yield transferred images with improved dye density compared to resins such as polycarbonate and poly(styrene-co-acrylonitrile) having glass transition temperatures of respectively 140°C and 110°C, the densities obtained are still not high enough for some applications.

In EP 194106 mixtures of vinylchloride copolymers and aromatic polyesters for use in the receiving layer are described. The addition of aromatic polyesters increases the density a little, although not sufficiently. Further dyes transferred to such layers exhibit poor light stability.

30 In JP 02/95890 mixtures of vinyl chloride resin and polycaprolactone for use in the receiving layer are described. The use of chlorine containing resins is to be avoided for toxicological and ecological reasons.

3. Summary of the invention.

35 It is an object of the present invention to provide dye-image receiving layers yielding improved dye densities, improved light stabilities and improved gloss.

The present invention provides a dye-image receiving element for use according to thermal dye sublimation transfer comprising a support having thereon a dye-image receiving layer comprising a vinylcopolymer having a glass transition temperature in the range of 50°C to 100°C, the vinylcopolymer comprising (a) 10-80 wt% vinylaromate, (b) 5-40 wt% (meth)acrylonitrile, (c) 5-50 wt% (meth)acrylic acid ester and (d) 0-30 wt% of other vinyl monomers and a linear aliphatic polyester having a molecular weight above 1000 and/or having at least four recurring units.

40 Said dye-image receiving layers yield transferred dye images having improved dye densities together with improved light stability and improved gloss compared to the known dye-image receiving layers.

4. Detailed description of the invention.

45 The vinyl monomers are selected so that the glass transition temperature of the obtained copolymer is in the range of 50°C to 100°C, preferably in the range of 60°C to 95°C.

Suitable vinylaromates include styrene, α -methylstyrene, p-methylstyrene, m-methylstyrene, p-t-butylstyrene, p-chlorostyrene, p-chloromethylstyrene and vinylanthracene. Styrene is preferred.

50 The term (meth)acrylonitrile means methacrylonitrile as well as acrylonitrile. The term (meth)acrylic acid ester means methacrylic acid ester as well as acrylic acid ester.

The (meth)acrylic acid esters are derived from aliphatic or cycloaliphatic or aromatic or mixed aromatic aliphatic alcohols, which may be substituted. The aliphatic residue may be branched or non-branched or may be interrupted by oxygen.

55 Suitable (meth)acrylic acid esters are: methacrylate, methylmethacrylate, ethylacrylate, ethylmethacrylate, propylacrylate, propylmethacrylate, isopropylmethacrylate, n-butylacrylate, n-butylmethacrylate, iso-butylacrylate, iso-butylmethacrylate, n-hexylacrylate, n-hexylmethacrylate, ethylhexylacrylate, ethylhexylmethacrylate, n-octylacrylate, n-octylmethacrylate, decylacrylate, decylmethacrylate, stearylacrylate, stearylmethacrylate, cyclohexylacrylate, cyclohexylmethacrylate, 4-t-butylcyclohexylmethacrylate, benzylacrylate, benzylmethacrylate, phenylethylacrylate, phenylethyl-

methacrylate, phenylpropylacrylate, phenylpropylmethacrylate, phenyloctylacrylate, phenylnonylacrylate, phenylnonylmethacrylate, 3-methoxybutylmethacrylate, butoxyethylacrylate, furfurylmethacrylate and tetrahydrofurfurylacrylate.

Also suitable are mixtures of (meth)acrylates. Preferred are mixtures that contain ethylhexylacrylate, decylmethacrylate, dodecylmethacrylate or phenylethylacrylate.

As other monomers (d) are useful: vinylidenechloride, vinylchloride, vinylacetate, vinylpropionate, vinylaurate and vinyladipate.

The ratio of the components a:b is important for the dyeability of the receiving layer. This ratio is preferably between 1:1 and 4:1, more preferably between 2:1 and 4:1.

The component (c) can influence important properties of the copolymer for use in the image receiving layer. For example, use of long chain alkyl (meth)acrylates (e.g. decylmethacrylate and dodecylmethacrylate) lead to improved adhesivity of the receiving element.

The molecular weight of the vinylcopolymer is preferably between about 10000 and about 1000000.

The vinylcopolymers of the present invention can be prepared according to polymerisation methods known in the art such as bulkpolymerisation, suspensionpolymerisation and emulsionpolymerisation.

Examples of useful copolymers are given hereinafter in tables 1 and 2.

Table 1

No.	(a)	(b)	(c)	(d)
1	60% S	20% AN	20% DMA	/
2	55% S	20% AN	25% DMA	/
3	30% S	40% AN	30% DMA	/
4	56% S	19% AN	25% EHA	/
5	50% S	25% AN	25% EHA	/
6	52% S	20% AN	20% DMA	/
7	55% S	20% AN	8% FA 15% EHA 10% PEMA	/
8	50% S	20% MAN	30% DMA	/
9	50% S	20% AN	15% DMA	15% VDC
10	45% S	20% AN	15% EHA	20% VDC
11	52% S	16% AN	10% DMA 10% FA	12% VDC
S = styrene AN = acrylonitrile DMA = decylmethacrylate EHA = ethylhexylacrylate FA = furfurylacrylate PEMA = phenylethylmethacrylate MAN = methacrylonitrile VDC = vinylidenechloride				

The vinylcopolymer according to the present invention can also be crosslinked, for example, a vinylcopolymer containing reactive hydrogen radicals (e.g. OH, NH₂) can be crosslinked by polyisocyanate.

The vinylcopolymers of the present invention can also contain epoxy groups by introduction of an epoxy-containing comonomer. Crosslinking of said vinylcopolymers can be achieved by reaction with low molecular weight compounds such as polyols, polyamines, polyacids and polyisocyanates or with polymers containing a plurality of hydroxy, amino, carboxylic acid or isocyanate groups.

The linear aliphatic polyester for use according to the present invention is a polyester obtained by condensation of one or more linear aliphatic diols with one or more linear aliphatic dicarboxylic acids. Instead of linear aliphatic diols and/or dicarboxylic acids linear aliphatic hydroxy-carboxylic acids can be used.

Examples of suitable linear aliphatic diols are: ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, isobutylenediol, 1,5-pentanediol, neopentyl glycol, 1,2-hexanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol, 1,13-tridecanediol.

Examples of suitable linear aliphatic dicarboxylic acids are: oxalic acid, suberic acid, glutaric acid, adipic acid, pimelic acid, succinic acid, azelaic acid, sebacic acid, nonanedicarboxylic acid, decanedicarboxylic acid, undecanedicarboxylic acid, dodecanedicarboxylic acid, fumaric acid, maleic acid, itaconic acid, citraconic acid, mesaconic acid, malonic acid.

Examples of suitable linear aliphatic hydroxy-carboxylic acids are: 2,3-dihydroxynonanoic acid, 11-hydroxyundecanoic acid, 2-hydroxy-4,6,6-trimethylheptanoic acid, 16-hydroxyhexadecanoic acid, 12-hydroxystearic acid, 12-hydroxy-9-octadecenoic acid, hydroxyacetic acid, β -hydroxypropionic acid, γ -hydroxybutyric acid, 2,3-dihydroxybutyric acid, δ -hydroxyvaleric acid, α -hydroxy- α -methylbutyric acid, β -hydroxyisovaleric acid, 2,3-dihydroxypentanoic acid, α -hydroxycaproic acid, ε -hydroxycaproic acid, α -hydroxy- α -methylvaleric acid, β,β,β -trimethylactic acid, 2,3-dihydroxyhexanoic acid, methyl-n-butylglycolic acid, α -hydroxycaprylic acid, methyl-n-amyglycolic acid, methyl-neopentylglycolic acid.

Also suitable as linear aliphatic polyester for use according to the present invention are polyesters obtained by ring-opening polymerisation. Monomers suitable for preparing said polyesters include β -propiolactone, ε -caprolactone, dimethylpropiolactone.

Further suitable linear aliphatic polyesters are described in EP 228066.

Preferred linear aliphatic polyesters for use according to the present invention are polyethylenedipate, polybutylenedipate and polycaprolactone.

Mixed polyesters (e.g. two or more diols, hydroxyacids or diacids) can also be used in the present invention. These copolyesters can have the advantage of reducing the degree of crystallinity, resulting in a higher gloss of the receiving sheet after the drying procedure.

The molecular weight of the aliphatic polyester of the present invention is 1000 or higher and/or the aliphatic polyester has at least four recurring units. The use of lower molecular weight polyesters results in a higher degree of sticking between the donor element and the receiving element.

The molecular weight of the copolyesters can be increased by the addition of a small amount of a multi (i.e. more than two) functional comonomer.

The linear aliphatic polyester may be present in any concentration which is effective for the intended purpose. Preferably the polyester is present in an amount of from 1 to 70% by weight of the mixture vinylcopolymer/polyester, preferably 20% to 60% by weight. Higher amounts result in a higher degree of sticking between donor element and receiving element.

In addition to the vinylcopolymer and the linear aliphatic polyester according to the present invention the dye-image receiving layer may also contain a conventional receiving layer binder known in the art such as a polycarbonate, a polyurethane, a polyester, a polyamide, polyvinyl chloride, polystyrene-co-acrylonitrile or mixtures thereof.

The dye receiving element of the present invention can contain a release agent for improvement of the release property with respect to the donor element. As the release agent, solid waxes such as polyethylene wax, amide wax, and Teflon powder; fluorine based and phosphate ester based surfactants; and paraffin based, silicone based and fluorine based oils can be used. Silicone oils, preferably reactive silicone oils and silicone containing copolymers such as polysiloxane-polyether copolymers and blockcopolymers, are preferred (e.g. TEGOGLIDE supplied by Goldschmidt and SILWET supplied by Union Carbide).

For the purpose of improving the whiteness of the receiving layer to enhance sharpness of the transferred image and also imparting writability to the receiving surface as well as preventing retransfer of the transferred image, a white pigment can be added to the receiving layer. As white pigment, titanium oxide, zinc oxide, kaolin, clay, calcium carbonate, fine powdery silica, etc. can be employed, and these can be used as a mixture of two or more kinds as described above.

Also, for further enhancing the light resistance of the transferred image, one or two or more kinds of additives such as UV-ray absorbers, light stabilizers and antioxidants, can be added, if necessary. The amounts of these UV-ray absorbers and light stabilizers is preferably 0.05 to 10 parts by weight and 0.5 to 3 parts by weight, respectively, per 100 parts of the resin constituting the receiving layer.

A toplayer can be provided on top of the receiving layer to improve the release from the donor element after transfer is effected. Said toplayer generally comprises a release agent of the type described above, e.g. a polysiloxane-polyether copolymer.

As the support for the receiver sheet it is possible to use a transparent film or sheet of various plastics such as polyethylene terephthalate, polyolefin, polyvinyl chloride, polystyrene, polycarbonate, polyether sulfone, polyimide, cellulose ester or polyvinyl alcohol-co-acetal. Blue-colored polyethylene terephthalate film can also be used. The support may also be a reflective support such as paper e.g. top quality paper, art paper, cellulose fiber paper; baryta-coated

paper; polyolefin-coated paper e.g. dual polyethylene-coated paper; synthetic paper e.g. polyolefin type, polystyrene type or white polyester type i.e. white-pigmented polyester.

Also, a laminated product by any desired combination of the above can be used. Typical examples of the laminates include a laminate of cellulose fiber paper and synthetic paper and a laminate of cellulose fiber paper and a plastic film or sheet. As further examples of the laminates, a plastic film can be used with synthetic paper instead of cellulose fiber paper. Further, a laminate of cellulose fiber paper, plastic film and synthetic paper can also be used.

The support sheet serves to support the dye receiving layer, and it is desirable that the support sheet has mechanical strength sufficient enough to handle the dye receiving sheet which is heated at the time of heat transfer recording. If the dye-receiving layer alone has the necessary mechanical strength, the support sheet may be omitted.

The dye-receiving layer of the present invention preferably has an overall thickness of from 0.5 to 50 μm , more preferably from 2.5 to 10 μm , when the dye-receiving layer is provided on a support sheet, or preferably from 3 to 120 μm when it is self-supporting i.e. a support sheet is omitted.

The image receiving layer may be a single layer, or two or more such layers may be provided on the support.

Also receiving layers may be formed on both surfaces of the support. In the case of a transparent support recto-verso printing on both receiving layers as described in EP 452566 then leads to an increase in density of the transferred image.

In case a toplayer is provided the thickness of such a toplayer is preferably 0.01 to 5 μm , particularly 0.05 to 2 μm .

The image receiving element of the present invention may also have one or more intermediate layers between the support and the image receiving layer. Depending on the material from which they are formed, the intermediate layers may function as cushioning layers, porous layers or dye diffusion preventing layers, or may fulfill two or more of these functions, and they may also serve the purpose of an adhesive, depending on the particular application.

The material constituting the intermediate layer may include, for example, an urethane resin, an acrylic resin, an ethylenic resin, a butadiene rubber, or an epoxy resin. The thickness of the intermediate layer is preferably from 1 to 20 μm .

Dye diffusion preventing layers are layers which prevent the dye from diffusing into the support (particularly if the support is polyethylene-coated paper). The binders used to form these layers may be water soluble or organic solvent soluble, but the use of water soluble binders is preferred, and especially gelatin is most desirable.

Porous layers are layers which prevent the heat which is applied at the time of thermal transfer from diffusing from the image receiving layer to the support to ensure that the heat which has been applied is used efficiently.

Fine powders consisting of silica, clay, talc, diatomaceous earth, calcium carbonate, calcium sulfate, barium sulfate, aluminum silicate, synthetic zeolites, zinc oxide, lithophone, titanium oxide or alumina for example, can be included in the image receiving layers, cushioning layers, porous layers, diffusion preventing layers and adhesive layers, etc. constituting the thermal transfer image receiving element of the present invention.

Also, the image receiving element of the present invention can have antistatic treatment applied to the front or back surface thereof. Such antistatic treatment may be carried out by incorporating an antistatic agent in, for example, the image receiving layer which becomes the front surface or in an antistatic preventive layer applied to the image receiving surface. A similar treatment can also be effected to the back surface. By such treatment, mutual sliding between the image receiving sheets can be smoothly performed, and there is also the effect of preventing the attachment of dust on the image receiving sheet.

Furthermore, the image receiving sheet can have a lubricating layer provided on the back surface of the sheet support. The material for the lubricating layer may include methacrylate resins such as methyl methacrylate, etc. or corresponding acrylate resins, vinyl resins such as vinyl chloride-vinyl acetate copolymer.

The receiving element can have detection marks provided on one surface, preferably the back surface so that the receiving element can be accurately set at a desired position during transfer, whereby the image can be formed always at a correct desired position.

A dye-donor element for use according to thermal dye sublimation transfer in combination with the present receiving element usually comprises a very thin support e.g. a polyester support, one side of which is covered with a dye layer, which contains the printing dyes. Usually an adhesive or subbing layer is provided between the support and the dye layer. Normally the opposite side is covered with a slipping layer that provides a lubricated surface against which the thermal printing head can pass without suffering abrasion. An adhesive layer may be provided between the support and the slipping layer.

The dye layer can be a monochrome dye layer or it may comprise sequential repeating areas of different colored dyes like e.g. of cyan, magenta, yellow and optionally black hue. When a dye-donor element containing three or more primary color dyes is used, a multicolor image can be obtained by sequentially performing the dye transfer process steps for each color.

The dye layer of such a thermal dye sublimation transfer donor element is formed preferably by adding the dyes, the polymeric binder medium, and other optional components to a suitable solvent or solvent mixture, dissolving or dispersing the ingredients to form a coating composition that is applied to a support, which may have been provided first with an adhesive or subbing layer, and dried.

The dye layer thus formed has a thickness of about 0.2 to 5.0 μm , preferably 0.4 to 2.0 μm , and the ratio of dye to binder is between 9:1 and 1:3 by weight, preferably between 3:1 and 1:2 by weight.

As polymeric binder the following can be used: cellulose derivatives, such as ethyl cellulose, hydroxyethyl cellulose, ethylhydroxy cellulose, ethylhydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, nitrocellulose, cellulose acetate formate, cellulose acetate hydrogen phthalate, cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate, cellulose acetate pentanoate, cellulose acetate benzoate, cellulose triacetate; vinyl-type resins and derivatives, such as polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral, copolyvinyl butyral-vinyl acetal-vinyl alcohol, polyvinyl pyrrolidone, polyvinyl acetoacetal, polyacrylamide; polymers and copolymers derived from acrylates and acrylate derivatives, such as polyacrylic acid, polymethyl methacrylate and styrene-acrylate copolymers; polyester resins; polycarbonates; copolystyrene-acrylonitrile; polysulfones; polyphenylene oxide; organosilicones, such as polysiloxanes; epoxy resins and natural resins, such as gum arabic. Preferably cellulose acetate butyrate or poly(styrene-acrylonitrile(-co-butadiene)) is used as binder for the dye layer.

Any dye can be used in such a dye layer provided it is easily transferable to the dye-image-receiving layer of the receiver sheet by the action of heat.

Typical and specific examples of dyes for use in thermal dye sublimation transfer have been described in, e.g., EP 453020, EP 209990, EP 209991, EP 216483, EP 218397, EP 227095, EP 227096, EP 229374, EP 235939, EP 247737, EP 257577, EP 257580, EP 258856, EP 279330, EP 279467, EP 285665, EP 400706, US 4743582, US 4753922, US 4753923, US 4757046, US 4769360, US 4771035, JP 84/78894, JP 84/78895, JP 84/78896, JP 84/227490, JP 84/227948, JP 85/27594, JP 85/30391, JP 85/229787, JP 85/229789, JP 85/229790, JP 85/229791, JP 85/229792, JP 85/229793, JP 85/229795, JP 86/41596, JP 86/268493, JP 86/268494, JP 86/268495 and JP 86/284489.

The coating layer may also contain other additives, such as curing agents, preservatives, organic or inorganic fine particles, dispersing agents, antistatic agents, defoaming agents, viscosity controlling agents, etc., these and other ingredients being described more fully in EP 133011, EP 133012, EP 111004 and EP 279467.

Any material can be used as the support for the dye-donor element provided it is dimensionally stable and capable of withstanding the temperatures involved, up to 400°C over a period of up to 20 msec, and is yet thin enough to transmit heat applied on one side through to the dye on the other side to effect transfer to the receiver sheet within such short periods, typically from 1 to 10 msec. Such materials include polyesters such as polyethylene terephthalate, polyamides, polyacrylates, polycarbonates, cellulose esters, fluorinated polymers, polyethers, polyacetals, polyolefins, polyimides, glassine paper and condenser paper. Preference is given to a polyethylene terephthalate support. In general, the support has a thickness of 2 to 30 μm . The support may also be coated with an adhesive or subbing layer, if desired.

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

A dye-barrier layer comprising a hydrophilic polymer may also be employed in the dye-donor element between its support and the dye layer to improve the dye transfer densities by preventing wrong-way transfer of dye towards the support. The dye barrier layer may contain any hydrophilic material which is useful for the intended purpose. In general, good results have been obtained with gelatin, polyacryl amide, polyisopropyl acrylamide, butyl methacrylate grafted gelatin, ethyl methacrylate grafted gelatin, ethyl acrylate grafted gelatin, cellulose monoacetate, methyl cellulose, polyvinyl alcohol, polyethylene imine, polyacrylic acid, a mixture of polyvinyl alcohol and polyvinyl acetate, a mixture of polyvinyl alcohol and polyacrylic acid or a mixture of cellulose monoacetate and polyacrylic acid. Suitable dye barrier layers have been described in e.g. EP 227091 and EP 228065. Certain hydrophilic polymers, for example those described in EP 227091, also have an adequate adhesion to the support and the dye layer, thus eliminating the need for a separate adhesive or subbing layer. These particular hydrophilic polymers used in a single layer in the donor element thus perform a dual function, hence are referred to as dye-barrier/subbing layers.

Preferably the reverse side of the dye-donor element can be coated with a slipping layer to prevent the printing head from sticking to the dye-donor element. Such a slipping layer would comprise a lubricating material such as a surface active agent, a liquid lubricant, a solid lubricant or mixtures thereof, with or without a polymeric binder. The surface active agents may be any agents known in the art such as carboxylates, sulfonates, phosphates, aliphatic amine salts, aliphatic quaternary ammonium salts, polyoxyethylene alkyl ethers, polyethylene glycol fatty acid esters, fluoroalkyl $\text{C}_2\text{-C}_{20}$ aliphatic acids. Examples of liquid lubricants include silicone oils, synthetic oils, saturated hydrocarbons and glycols. Examples of solid lubricants include various higher alcohols such as stearyl alcohol, fatty acids and fatty acid esters. Suitable slipping layers are described in e.g. EP 138483, EP 227090, US 4567113, US 4572860, US 4717711. Preferably the slipping layer comprises as binder a styrene-acrylonitrile copolymer or a styrene-acrylonitrile-butadiene copolymer or a mixture thereof or a cellulose ester and as lubricant in an amount of 0.1 to 10 % by weight of the binder (mixture) a polysiloxane-polyether copolymer or polytetrafluoroethylene or a mixture thereof.

The dye layer of the dye-donor element may also contain a releasing agent that aids in separating the dye-donor element from the dye-receiving element after transfer. The releasing agents can also be applied in a separate layer on at least part of the dye layer. For the releasing agent solid waxes, fluorine- or phosphate-containing surfactants and silicone oils are used. Suitable releasing agents are described in e.g. EP 133012, JP 85/19138, EP 227092.

The dye-receiving elements according to the invention are used to form a dye transfer image. Such a process comprises placing the dye layer of the donor element in face-to-face relation with the dye-receiving layer of the receiver sheet and imagewise heating from the back of the donor element. The transfer of the dye is accomplished by heating for about several milliseconds at a temperature of 400°C.

When the process is performed for but one single color, a monochrome dye transfer image is obtained. A multicolor image can be obtained by using a donor element containing three or more primary color dyes and sequentially performing the process steps described above for each color. The above sandwich of donor element and receiver sheet is formed on three occasions during the time when heat is applied by the thermal printing head. After the first dye has been transferred, the elements are peeled apart. A second dye-donor element (or another area of the donor element with a different dye area) is then brought in register with the dye-receiving element and the process repeated. The third color and optionally further colors are obtained in the same manner.

In order to accomplish a perfect register when the process is performed for more than one color and in order to detect what color is existing at the printing portion of the donor element, detection marks are commonly provided on one surface of the donor element. Generally optically detectable marks are used that can be detected by a light source and a photo sensor; detection can be done by measuring the light transmitted through the detection mark or reflected from said mark. The marks being in the form of a light-absorbing or light-reflecting coating are formed in a preassigned position on the donor element by e.g. gravure printing. The detection marks can comprise an infrared absorbing compound such as carbon black. The detection mark can also comprise one of the image dyes that are used for the image formation, with the detection being in the visible range.

In addition to thermal heads, laser light, infrared flash or heated pens can be used as the heat source for supplying heat energy. Thermal printing heads that can be used to transfer dye from the dye-donor element to the receiver sheet are commercially available. In case laser light is used, the dye layer or another layer of the dye element has to contain a compound that absorbs the light emitted by the laser and converts it into heat, e.g. carbon black.

Alternatively, the support of the dye-donor element may be an electrically resistive ribbon consisting of, for example, a multi-layer structure of a carbon loaded polycarbonate coated with a thin aluminum film. Current is injected into the resistive ribbon by electrically addressing a print head electrode resulting in highly localized heating of the ribbon beneath the relevant electrode. The fact that in this case the heat is generated directly in the resistive ribbon and that it is thus the ribbon that gets hot leads to an inherent advantage in printing speed using the resistive ribbon/electrode head technology compared to the thermal head technology where the various elements of the thermal head get hot and must cool down before the head can move to the next printing position.

The following examples are provided to illustrate the invention in more detail without limiting, however, the scope thereof.

EXAMPLE 1

A receiving element was prepared as follows:

A 10% solution in methylethylketone for forming the receiving layer comprising a vinylcopolymer and a linear aliphatic polyester, the nature and amount (in g/m²) of which are indicated below in table 2 was coated (wet layer thickness 50 µm) on paper provided on both sides with a polyethylene coating and on one side thereof (the receiving layer side) supplementary with a gelatine coating. After coating the layers were dried at 90°C for 15 minutes.

The obtained dye receiving element was printed in combination with a commercially available donor element type CP100S supplied by Mitsubishi in a Mitsubishi video printer type CP 100E.

The receiver sheet was separated from the dye-donor element and the dye density of the transferred black image was measured in reflection by means of a Macbeth TD102 densitometer.

The results are indicated in table 2 below.

Table 2

vinylcopolymer	amount	polyester	amount	density
no. 3	5	/	0	1.78
no. 3	4.75	no. 1	0.25	1.85
no. 3	4.50	no. 1	0.50	1.95
no. 3	4.25	no. 1	0.75	1.94
no. 5	5	/	0	1.6
no. 5	4.75	no. 2	0.25	1.73
no. 5	4.50	no. 2	0.5	1.9
no. 5	4.25	no. 2	0.75	1.9

Vinylcopolymers nos 3 and 5 are given in table 1 above. Polyester no. 1 is a polyester having a molecular weight of 1500 derived from adipic acid and 1,3-butanediol. Polyester no. 2 is polycaprolactone with molecular weight of 2000.

The above results show that the addition of aliphatic polyesters to receiving layers containing the present vinylcopolymers with Tg between 50°C and 100°C yield improved dye densities.

Claims

1. Dye-image receiving element for use according to thermal dye sublimation transfer comprising a support having thereon a dye-image receiving layer comprising a vinylcopolymer having a glass transition temperature in the range of 50°C to 100°C and comprising (a) 10-80 wt% vinylaromate, (b) 5-40 wt% (meth)acrylonitrile, (c) 5-50 wt% (meth)acrylic acid ester and (d) 0-30 wt% of other vinyl monomers, characterized in that said dye-image receiving layer further comprises a linear aliphatic polyester having a molecular weight above 1000 and/or having at least four recurring units.
2. Dye-image receiving element according to claim 1, wherein the vinylaromate is styrene and wherein the (meth)acrylic acid ester is decylmethacrylate or ethylhexylmethacrylate or dodecylmethacrylate or phenylethylacrylate.
3. Dye-image receiving element according to claim 1 or 2, wherein the ratio of vinylaromate and (meth)acrylonitrile is between 2:1 and 4:1.
4. Dye-image receiving element according to any one of the preceding claims, wherein the linear aliphatic polyester is obtained by condensation of one or more linear aliphatic diols with one or more linear aliphatic dicarboxylic acids or by ring-opening polymerisation.
5. Dye-image receiving element according to claim 4, wherein the linear aliphatic polyester is polyethylenedipate or polybutylenedipate or polycaprolactone.
6. Dye-image receiving element according to any one of the preceding claims, wherein the linear aliphatic polyester is present in an amount of from 1 to 70% by weight of the mixture vinylcopolymer/polyester.

Patentansprüche

1. Ein Farbstoffbild-Empfangelement für den Gebrauch gemäß der Farbstoffübertragung durch Thermosublimation, das einen Träger enthält, auf dem sich eine Farbstoffbild-Empfangsschicht befindet, die ein Vinylcopolymeres enthält, welches einen Einfrierpunkt zwischen 50 °C und 100 °C hat und folgendes enthält: (a) 10 - 80 Gew.-% Vinylaromat, (b) 5 - 40 Gew.-% (Meth)acrylonitril, (c) 5 - 50 Gew.-% (Meth)acrylsäureester und (d) 0 - 30 Gew.-% anderer Vinylmonomere, dadurch gekennzeichnet, daß die Farbstoffbild-Empfangsschicht weiterhin einen linearen, aliphatischen Polyester enthält, der ein Molekulargewicht von mehr als 1000 hat und/oder wenigstens vier wiederkehrende Einheiten hat.

2. Ein Farbstoffbild-Empfangselement nach Anspruch 1, dadurch gekennzeichnet, daß das Vinylaromat Styrol ist und der (Meth)acrylsäureester Decylmethacrylat, Ethylhexylmethacrylat, Dodecylmethacrylat oder Phenylethylacrylat ist.

3. Ein Farbstoffbild-Empfangselement nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Verhältnis von Vinylaromat zu (Meth)acrylonitril zwischen 2:1 und 4:1 liegt.

4. Ein Farbstoffbild-Empfangselement nach irgendwelchem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß der lineare, aliphatische Polyester durch Kondensierung von einem oder mehreren linearen, aliphatischen Diolen mit einem oder mehreren linearen, aliphatischen Bicarbonsäuren oder durch Ringöffnung-Polymerisation erzielt wird.

5. Ein Farbstoffbild-Empfangselement nach Anspruch 4, dadurch gekennzeichnet, daß der lineare, aliphatische Polyester Poly(ethylenadipat), Poly(butylenadipat) oder Polycaprolacton ist.

6. Ein Farbstoffbild-Empfangselement nach irgendwelchem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß der lineare, aliphatische Polyester in einer Menge von 1 bis 70 Gew.-% der Mischung Vinylcopolymeres/Polyester enthalten ist.

Revendications

1. Un élément récepteur d'image de colorant pour être utilisé selon le transfert de colorant par thermosublimation, lequel élément comprend un support sur lequel se trouve une couche réceptrice d'image de colorant comprenant un copolymère de vinyle qui a une température de vitrification entre 50 °C et 100 °C et qui comprend (a) 10 - 80 % en poids d'aromate de vinyle, (b) 5 - 40 % en poids de (méth)acrylonitrile, (c) 5 - 50 % en poids d'ester d'acide (méth)acrylique et (d) 0 - 30 % en poids d'autres monomères de vinyle, caractérisé en ce que la couche réceptrice d'image de colorant comprend en plus un polyester aliphatique linéaire ayant un poids moléculaire supérieur à 1000 et/ou ayant au moins quatre unités structurales.

2. Un élément récepteur d'image de colorant selon la revendication 1, caractérisé en ce que l'aromate de vinyle est le styrène et que l'ester d'acide (méth)acrylique est le méthacrylate de décyle, le méthacrylate d'éthyle et d'hexyle, le méthacrylate de dodécyle ou l'acrylate d'éthyle et de phényle.

3. Un élément récepteur d'image de colorant selon la revendication 1 ou 2, caractérisé en ce que le rapport de l'aromate de vinyle au (méth)acrylonitrile se situe entre 2:1 et 4:1,

4. Un élément récepteur d'image de colorant selon l'une quelconque des revendications précédentes, caractérisé en ce que le polyester aliphatique linéaire est obtenu par la condensation d'un ou de plusieurs diols aliphatiques linéaires avec un ou plusieurs acides dicarboxyliques aliphatiques linéaires ou par la polymérisation à rupture du noyau.

5. Un élément récepteur d'image de colorant selon la revendication 4, caractérisé en ce que le polyester aliphatique linéaire est le poly(adipate d'éthylène), le poly(adipate de butylène) ou le polycaprolactone.

6. Un élément récepteur d'image de colorant selon l'une quelconque des revendications précédentes, caractérisé en ce que le polyester aliphatique linéaire est présent dans une quantité de 1 à 70 % en poids du mélange de copolymère de vinyle/polyester.