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54 **Thermal transfer printing process using a mixture of reducing agents for image-wise reducing a silver source.**

57 The present invention provides a donor for use in thermal transfer printing. The donor element comprises on a support a donor layer comprising a binder and a mixture of at least two thermotransferable reducing agents capable of reducing a silver source to metallic silver upon heating. The donor element is image-wise heated while being in contact with an image receiving material comprising a thermoreducible silver source. By using a mixture of reducing agents crystallization is reduced and the obtained images exhibit an increased density and a more neutral grey hue.

EP 0 677 776 A1

1. Field of the invention.

The present invention relates to a thermal imaging process, more particularly to a process wherein a thermotransferable reducing agent of a donor element is transferred image-wise to a receiving layer on a support of an image receiving element.

2. Background of the invention

Thermal imaging or thermography is a recording process wherein images are generated by the use of imagewise modulated thermal energy.

In thermography two approaches are known :

1. Direct thermal formation of a visible image pattern by imagewise heating of a recording material containing matter that by chemical or physical process changes colour or optical density.
2. Formation of a visible image pattern by transfer of a coloured species from an imagewise heated donor element onto a receptor element.

A survey of "direct thermal" imaging methods is given in the book "Imaging Systems" by Kurt I. Jacobson-Ralph E. Jacobson. The Focal Press - London and New York (1976), Chapter VII under the heading "7.1 Thermography". Thermography is concerned with materials which are not photosensitive, but are heat sensitive. Imagewise applied heat is sufficient to bring about a visible change in a thermosensitive imaging material.

According to a direct thermal embodiment operating by physical change, a recording material is used which contains a coloured support or support coated with a coloured layer which itself is overcoated with an opaque white light reflecting layer that can fuse to a clear, transparent state wherein the coloured support is no longer masked. Physical thermographic systems operating with such kind of recording material are described on pages 136 and 137 of the above mentioned book of Kurt I. Jacobson et al.

Yet most of the "direct" thermographic recording materials are of the chemical type. On heating to a certain conversion temperature, an irreversible chemical reaction takes place and a coloured image is produced.

It has been suggested to use a thermoreducible silver source in combination with a reducing agent in a direct thermal film in order to increase the optical density in transmission of a printed image (see EP-A-537.795). Although continuous tones can be obtained by said printing method, the gradation produced by said printing method is too high resulting in only a few intermediate density levels. Fluctuations in the heat transfer from the heat source to the printing material result in a density difference of the final image. Thus, it is extremely difficult to obtain images having a uniform density profile. A direct thermal printing method moreover has the disadvantage that in the non-image places the co-reactants always remains unchanged, impairing the shelf-life and preservability.

Thermal dye transfer printing is a recording method wherein a dye-donor element is used that is provided with a dye layer wherefrom dyed portions or incorporated dye is transferred onto a contacting receiving element by the application of heat in a pattern normally controlled by electronic information signals.

In European Patent Application No. 94200612.3, a thermal imaging process is provided using

(i) a donor element comprising on a support a donor layer containing a binder and a thermotransferable reducing agent capable of reducing a silver source to metallic silver upon heating and (ii) a receiving element comprising on a support a receiving layer comprising a silver source capable of being reduced by means of heat in the presence of a reducing agent, said thermal imaging process comprising the steps of

- bringing said donor layer of said donor element into face to face relationship with said receiving layer of said receiving element,
- image-wise heating a thus obtained assemblage by means of a thermal head, thereby causing image-wise transfer of an amount of said thermotransferable reducing agent to said receiving element in accordance with the amount of heat supplied by said thermal head and
- separating said donor element from said receiving element.

This printing method is further referred to as 'reducing agent transfer printing' or 'RTP'.

However, the stability of the donor element in said European Patent Application has been found to be poor. More particularly, the reducing agent tends to crystallize in the donor layer. As a result of this crystallization during storage, transfer of reducing agent is seen during printing, even on places where no heat has been applied by the thermal head. This leads to a printing fog in the final image. This problem is especially seen when a high amount of reducing agent is used in the donor layer. This high concentration is

necessary to obtain high optical densities of the final printed image (above 2.0 - 2.5).

Moreover, the neutral hue of the grey scale of the printed image is dependent on the choice of a specific reducing agent. It is extremely difficult to find reducing agents that yield a neutral grey-tone (e.g. for medical diagnostics). It has also been found that the reducing agent shows the disadvantage after transfer that the oxidation product of the reducing agent tends to crystallize in the receiving element, giving rise to 'white dust' at the surface of the print after storage.

3. Object of the present invention

It is an object of the present invention to provide a donor element for use in thermal transfer printing, yielding images with high optical densities and a neutral grey hue and a good stability of the donor element and the printed image.

It is another object of the invention to provide a printing method using a donor element with increased stability.

Further objects will become apparent from the description hereinafter.

According to the present invention there is provided a donor element for use in thermal transfer printing wherein said donor element comprises on a support (a) a donor layer comprising a binder and a mixture of at least two thermotransferable reducing agents capable of reducing a silver source to metallic silver upon heating and (b) on the side of the support opposite to the side comprising said donor layer, a heat-resistant backing layer.

According to the present invention, there is further provided a thermal imaging process using (i) a donor element comprising on a support (a) a donor layer comprising a binder and a mixture of at least two thermotransferable reducing agents capable of reducing a silver source to metallic silver upon heating and (b) on the side of the support opposite to the side comprising said donor layer, a heat-resistant backing layer and (ii) a receiving element comprising on a support a receiving layer comprising a silver source capable of being reduced by means of heat in the presence of a reducing agent, said thermal imaging process comprising the steps of

- bringing said donor layer of said donor element into face to face relationship with said receiving layer of said receiving element,
- image-wise heating a thus obtained assemblage preferably by means of a thermal head, thereby causing image-wise transfer of an amount of said thermotransferable reducing agents to said receiving element in accordance with the amount of heat supplied and
- separating said donor element from said receiving element.

According to the present invention there is further provided a thermal imaging system consisting of a donor element and a receiving element for use in combination with said donor element, said donor element comprising on a support (a) a donor layer comprising a binder and a mixture of at least two thermotransferable reducing agents capable of reducing a silver source to metallic silver upon heating and (b) on the side of the support opposite to the side comprising said donor layer, a heat-resistant backing layer and

said receiving element comprising on a support a receiving layer comprising a silver source capable of being reduced by means of heat in the presence of a reducing agent.

4. Detailed description of the invention

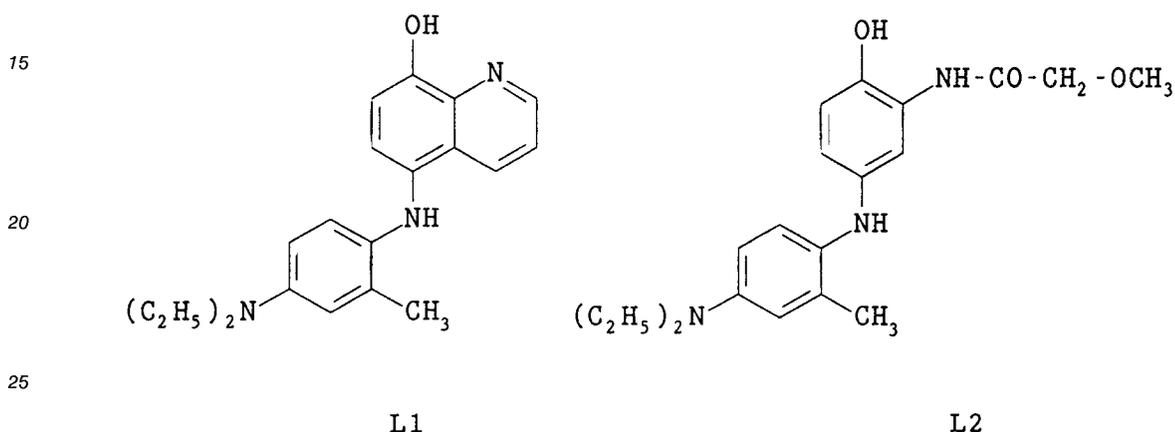
The donor element of the present invention comprises on one side of the support a donor layer, comprising at least two reducing agents capable of reducing a silver source to metallic silver upon heating, and a binder.

The reducing agents for the silver source may be any of the conventional photographic developers known in the art, such as phenidones hydroquinones and catechol provided that the reducing agents are thermotransferable,

Examples of suitable reducing agents are aminohydroxycycloalkenone compounds, esters of amino reductones, N-hydroxyurea derivatives, hydrazones of aldehydes and ketones, phosphoramidophenols, phosphoramidoanilines, polyhydroxybenzenes, e.g. hydroquinone, t-butylhydroquinone, isopropylhydroquinone, and (2,5-dihydroxyphenyl)methylsulfone, dihydroxybenzene derivatives such as pyrocatechol, and pyrogallol derivatives such as 4-phenylpyrocatechol, t-butylcatechol, pyrogallol or pyrogallol derivatives such as pyrogallol ethers or esters, dihydroxybenzoic acid, dihydroxybenzoic acid esters such as dihydroxybenzoic acid, methyl ester, ethyl ester, propyl ester, butyl ester and the like, dihydroxy benzaldehyde and keton derivatives, gallic acid, gallic acid esters such as methyl gallate, ethyl

gallate propyl gallate and the like, gallic acid amides, sulfhydroxamic acids, sulfonamidoanilines, 2-tetrazolylthiohydroquinones, e.g., 2-methyl-5-(1-phenyl-5-tetrazolylthio)hydroquinone, tetrahydroquinoxalines, e.g. 1,2,3,4-tetrahydroquinoxaline, amidoximes, azines, hydroxamic acids, 5-pyrazolones sulfonamidophenol reducing agents, 2-phenylindan-1,3-dione and the like, 1,4-dihydropyridines, such as 2,6-dimethoxy-3,5-dicarbethoxy-1,4-dihydropyridine, bisphenols, e.g., bis(2-hydroxy-3-butyl-5-methylphenyl) methane, bis(6-hydroxy-m-tolyl)mesitol 2,2-bis (4-hydroxy-3-methylphenyl)propane, 4,4-ethylidene-bis(2-t-butyl-6-methylphenol) and 2,2-bis(3,5-dimethyl-4-hydroxyphenyl) propane, ascorbic acid derivatives and 3-pyrazolidones.

Reducing agents being coloured in an oxidized form or capable of forming colour in an oxidized form (further referred to as color forming reducing agents) can also be used. Specific examples are 4-methoxynaphthol and leucoazomethines in particular leucoindoanilines such as for example:



30 The mixture of reducing agents comprises at least two, and more preferably at least three reducing agents. Preferably, two or more reducing agents derived from 1,2-dihydroxybenzene (pyrocatechol) or 1,2,3-trihydrobenzene (pyrogallol) are used in the donor layer.

35 The mixture of reducing agents may consist of strong reducing agents, weak reducing agents or a mixture thereof, preferably at least one strong reducing agent is used. By the terms strong and weak reducing agent is meant the following: A strong reducing agent is an agent that is capable of reducing a silver ion to metallic silver by the application of heat while a weak reducing is only capable of doing so when nuclei of metallic silver are present. A simple method to determine whether a reducing agent is weak or strong, is to coat a layer having the following composition:

40

compound I (see below)	0.34g/m ²
polyvinylbutyral (Butvar B79)	4.5g/m ²
silver behenate	4.5g/m ²
reducing agent to test	2g/m ²

45 on a 175 μm thick clear polyethylene terephthalate support. The obtained element is then heated from the back side on an aluminium hot plate at a temperature of 118°C for 10 seconds. A strong reducing agent will yield a visual density in transmission (measured on a Macbeth TR 924) of 0.15 or more while a weak reducing agent will show a visual density of less than 0.15.

50 structure of compound I:



As a binder for the donor layer, hydrophilic or hydrophobic binders can be used, although the use of hydrophobic binders is preferred.

Hydrophilic binders which can be used are polyvinylalcohol gelatine, polyacrylamide and hydrophilic cellulosic binders such as hydroxyethyl cellulose, hydroxypropyl cellulose and the like.

5 The hydrophobic binders may be used as a dispersion in e.g. water or as a solution in an organic solvent.

Suitable binders for the donor layer are cellulose derivatives, such as ethyl cellulose, methyl cellulose, cellulose nitrate, cellulose acetate formate, cellulose acetate hydrogen phthalate, cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate, cellulose acetate pentanoate, cellulose acetate benzoate, 10 cellulose triacetate; vinyl-type resins and derivatives, such as 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 polymethyl methacrylate and styrene-acrylate copolymers; polyester resins; polycarbonates; copoly(styrene-co-acrylonitrile); polysulfones; polyphenylene oxide; organosilicones, such as polysiloxanes; epoxy resins and 15 natural resins, such as gum arabic. Preferably, the binder for the donor layer of the present invention comprises poly(styrene-co-acrylonitrile) or a mixture of poly(styrene-co-acrylonitrile) and a toluenesulphonamide condensation product.

The binder for the donor layer preferably comprises a copolymer comprising styrene units and acrylonitrile units, preferentially at least 60% by weight of styrene units and at least 25% by weight of 20 acrylonitrile units binder. The binder copolymer may comprise other comonomers than styrene units and acrylonitrile units. Suitable other comonomers are e.g. butadiene, butyl acrylate, and methyl methacrylate. The binder copolymer preferably has a glass transition temperature of at least 50 °C.

It is also possible to use a mixture of the copolymer comprising styrene units and at least 15% by weight of acrylonitrile units with another binder known in the art, but preferably the acrylonitrile copolymer is 25 present in an amount of at least 50% by weight of the total amount of binder.

The donor layer generally has a thickness of about 0.2 to 5.0 μm , preferably 0.4 to 2.0 μm , and the amount ratio of reducing agent to binder generally ranges from 9:1 to 1:3 by weight, preferably from 3:1 to 1:2 by weight. The total amount of reducing agent is preferably between 40 and 80 % by weight of the total weight of the donor layer.

30 The donor layer may also contain other additives such as i.a. thermal solvents, stabilizers, curing agents, preservatives, dispersing agents, antistatic agents, defoaming agents, and viscosity-controlling agents.

The donor layer of the donor element in connection with the present invention may consist of multiple layers. In the latter case the different thermotransferable reducing agents may be present in different layers. 35 However, to avoid the problem of crystallization it is preferred to have at least two thermotransferable reducing agents present in a layer.

Any material can be used as the support for the 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 reducing agent on the other side to effect 40 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 support comprising polyethylene terephthalate. In general, suitable supports can have a thickness of 2 to 30 μm , preferably a thickness of 4 to 10 μm is used. The support may also be 45 coated with an adhesive or subbing layer, if desired.

Subbing layers comprising aromatic copolyesters, vinylidene chloride copolymers, organic titanate, zirconates and silanes, polyester urethanes and the like can be used.

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

50 A barrier layer comprising a hydrophilic polymer may also be employed between the support and the donor layer of the donor element to enhance the transfer of reducing agent by preventing wrong-way transfer thereof backwards to the support. The barrier layer may contain any hydrophilic material that is useful for the intended purpose. In general, good results can be obtained with gelatin, polyacrylamide, polyisopropyl acrylamide, butyl methacrylate-grafted gelatin, ethyl methacrylate-grafted gelatin, ethyl acrylate-grafted gelatin, cellulose monoacetate, methylcellulose, polyvinyl alcohol, polyethyleneimine, 55 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.

Certain hydrophilic polymers e.g. those described in EP 227,091 also have an adequate adhesion to the support and the donor layer, so that the need for a separate adhesive or subbing layer is avoided. The particular hydrophilic polymers used in a single layer in the donor element thus perform a dual function, hence are referred to as barrier/subbing layers.

5 The donor element of the present invention can be used in combination with a thermal head, a laser or a resistive ribbon heating system. A thermal head is especially preferred.

Owing to the fact that the thin support softens when heated during the printing operation and then sticks to the thermal printing head, thereby causing malfunction of the printing apparatus and reduction in image quality, the back of the support (the side opposite to that carrying the donor layer) is typically provided with a heat-resistant layer to facilitate passage of the donor element past the thermal printing head. An adhesive layer may be provided between the support and the heat-resistant layer.

10 Any heat-resistant layer known in the field of thermal sublimation printing or wax printing can be used in the present invention.

The heat-resistant layer generally comprises a lubricant and a binder. In the conventional heat-resistant layers the binder is either a cured binder as described in e.g. EP 153,880, EP 194,106, EP 314,348, EP 329,117, JP 60/151,096, JP 60/229,787, JP 60/229,792, JP 60/229,795, JP 62/48,589, JP 62/212,192, JP 62/259,889, JP 01/5884, JP 01/56,587, and JP 92/128,899 or a polymeric thermoplast as described in e.g. EP 267,469, JP 58/187,396, JP 63/191,678, JP 63/191,679, JP 01/234,292, and JP 02/70,485.

20 During printing, a smooth transport of the donor ribbon and the receiving element is required in order to obtain a good density uniformity all over the print.

It is preferred to use different types of lubricants to allow continuous transport of the donor ribbon relative to the thermal head.

Well known lubricants are polysiloxanes such as those mentioned in EP 267,469, US 4,738,950, US 4,866,028, US 4,753,920 and US 4,782,041. Especially useful slipping agents are polysiloxane-polyether block or graft polymers.

Other lubricants for the heat-resistant slipping layer of the donor element are phosphoric acid derivatives such as those mentioned in EP 153,880 and EP 194,106, metal salts of long fatty acids (such as mentioned in EP 458,538, EP 458,522, EP 314,348, JP 01/241,491 and JP 01/222,993), wax compounds such as polyolefin waxes such as e.g. polyethylene or polypropylene wax, carnauba wax, candelilla wax, bees wax, glycerine monostearate, amid wax such as ethylene bisstearamide and the like.

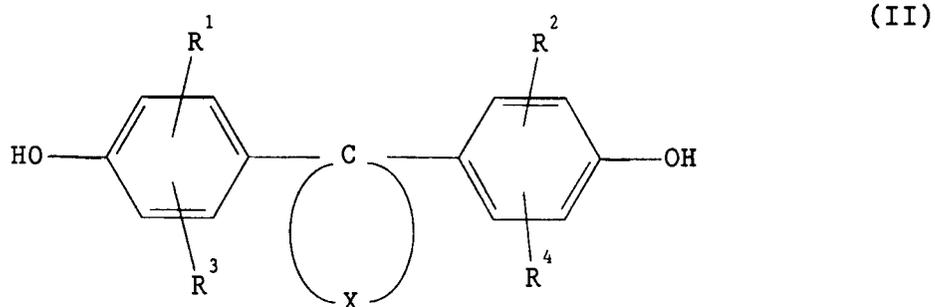
30 A heat-resistant layer such as mentioned in European Patent Application no. 93 202 050.6 is especially preferred.

Inorganic particles such as salts derived from silica such as e.g. talc, clay, china clay, mica, chlorite, silica, or carbonates such as calcium carbonate, magnesium carbonate or calcium magnesium carbonate (dolomite) can be further added to the heat-resistant layer.

35 It is highly preferred to add mixtures of particles to the heat resistant layer having a Mohs hardness below 2.7 and particles having a Mohs hardness above 2.7 such as mentioned in EP-A-93201642.1.

A mixture of talc and dolomite particles is highly preferred.

40 A particular heat-resistant layer for the present invention comprises as a binder a polycarbonate derived from a bis(hydroxyphenyl)-cycloalkane, corresponding to general formula (II):



wherein :

55 R¹, R², R³, and R⁴ each independently represents hydrogen, halogen, a C₁-C₈ alkyl group, a substituted C₁-C₈ alkyl group, a C₅-C₆ cycloalkyl group, a substituted C₅-C₆ cycloalkyl group, a C₆-C₁₀ aryl group, a substituted C₆-C₁₀ aryl group, a C₇-C₁₂ aralkyl group, or a substituted C₇-C₁₂ aralkyl group; and

X represents the atoms necessary to complete a 5- to 8-membered alicyclic ring, optionally substituted

with a C₁-C₆ alkyl group, a 5- or 6-membered cycloalkyl group or a fused-on 5- or 6-membered cycloalkyl group,
 as lubricants polyether modified polysiloxane block copolymer and zinc stearate and as particles talc particles with a weight average particle size of 4.5 μm.

5 Lubricants and binder can be coated in a single layer, or can be casted in a separate layer. It is highly preferred to cast the salt of a fatty acid in the heat resistant layer (e.g. as a dispersion) and the polysiloxane based lubricant in a separate topcoat. This separate topcoat is preferably coated from a non-solvent for the heat-resistant layer.

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

The heat-resistant layer thus formed has a thickness of about 0.1 to 3 μm, preferably 0.3 to 1.5 μm.

15 Preferably a subbing layer is provided between the support and the heat-resistant layer to promote the adhesion between the support and the heat-resistant layer. As subbing layer any of the subbing layers known in the art for dye-donor elements can be used. Suitable binders that can be used for the subbing layer can be chosen from the classes of polyester resins, polyurethane resins, polyester urethane resins, modified dextrans, modified cellulose, and copolymers comprising recurring units such as i.a. vinyl chloride, vinylidene chloride, vinyl acetate, acrylonitrile, methacrylate, acrylate, butadiene, and styrene (e.g. poly-(vinylidene chloride-co-acrylonitrile). Suitable subbing layers have been described in e.g. EP 138,483, EP 227,090, European Patent Application No. 92200907.1, US 4,567,113, US 4,572,860, US 4,717,711, US 20 4,559,273, US 4,695,288, US 4,727,057, US 4,737,486, US 4,965,239, US 4,753,921, US 4,895,830, US 4,929,592, US 4,748,150, US 4,965,238, and US 4,965,241.

The receiving element for use according to the printing method of the present invention comprises a receiving layer provided on a support, said receiving layer comprising a silver source capable of being reduced by means of heat in the presence of a reducing agent.

25 The reducible silver source may comprise any material which contains a reducible source of silver ions. Silver salts of organic and hetero-organic acids, particularly long chain fatty carboxylic acids (comprising from 10 to 30, preferably 15 to 25 carbon atoms) are preferred. Complexes of organic or inorganic silver salts in which the ligand has a gross stability constant for silver ion of between 4.0 and 10.0 are also useful. Examples of suitable silver salts are disclosed in Research Disclosure Nos. 17029 and 29963 and include :
 30 salts of organic acids, e.g., gallic acid, oxalic acid, behenic acid, stearic acid, palmitic acid, lauric acid and the like; silver carboxyalkylthiourea salts, e.g., 1-(3-carboxypropyl)thiourea, 1-(3-carboxypropyl)-3,3-dimethylthiourea and the like; complexes of silver with the polymeric reaction product of an aldehyde with a hydroxy-substituted aromatic carboxylic acid, e.g., aldehydes, such as formaldehyde, acetaldehyde and butyraldehyde, and hydroxy-substituted acids, such as
 35 salicylic acid, benzilic acid, 3,5-dihydroxybenzilic acid and 5,5-thiodisalicic acid; silver salts or complexes of thiones, e.g., 3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione and 3-carboxymethyl-4-methyl-4-thiazoline-2-thione; complexes of salts of silver with nitrogen acids selected from imidazole, pyrazole, urazole, 1,2,4-triazole and 1H-tetrazole, 3-amino-5-benzylthio-1,2,4-triazole and benzotriazole; silver salts of saccharin, 5-chlorosalicylaloxime and the like; and silver salts of mercaptides. The preferred silver source
 40 is silver behenate.

The silver source is preferably added as a dispersion to the coating liquid of the receiving layer.

45 As binding agent for the receiving layer preferably thermoplastic water insoluble resins are used wherein the ingredients can be dispersed homogeneously or form therewith a solid-state solution. For that purpose all kinds of natural, modified natural or synthetic resins may be used, e.g. cellulose derivatives such as ethylcellulose, cellulose esters, carboxymethylcellulose, starch ethers, polymers derived from α,β-ethylenically unsaturated compounds such as polyvinyl chloride, after chlorinated polyvinyl chloride, copolymers of vinyl chloride and vinylidene chloride, copolymers of vinyl chloride and vinyl acetate, polyvinyl acetate and partially hydrolysed polyvinyl acetate, polyvinyl alcohol, polyvinyl acetals, e.g. polyvinyl butyral, copolymers of acrylonitrile and acrylamide, polyacrylic acid esters, polymethacrylic acid
 50 esters and polyethylene or mixtures thereof. A particularly suitable ecologically interesting (halogen-free) binder is polyvinyl butyral. A polyvinyl butyral containing some vinyl alcohol units is marketed under the trade name BUTVAR B79 of Monsanto USA.

The binder to organic silver salt weight ratio is preferably in the range of 0.2 to 6, and the thickness of the receiving layer is preferably in the range of 5 to 16 μm.

55 It is preferred to use a so-called toning agent in the receiving layer or in a layer adjacent to said receiving layer. This toning agent serves to change the tone of the silver image from brown to black or grey. Suitable toning agents are e.g. phthalazinone, phthalazine, phthalimide, succinimide, phthalic acid, benzimidazole and compound (I) mentioned above. The use of phthalazinone or compound (I) is highly

preferred.

It is highly preferred to use a release agent in the receiving element on the side of the receiving layer. This release agent may be added to the coating solution of the receiving layer or may be applied, optionally in a mixture with other ingredients, as a separate layer called the release layer on top of said receiving
5 layer. The use of a release layer is preferred, since the release agent is in that case on top of the receiving element.

The use of a release agent is preferred in the printing method of the present invention since the reducing agents useful in the present invention can give rise to a sticky contact between donor element and receiving element.

10 As release agents, inorganic and organic release agents can be used. Among them, the organic release agents are preferred.

Solid waxes, fluorine- or phosphate-containing surfactants and silicone oils can be used as releasing agent. Suitable releasing agents have been described in e.g. EP 133012, JP 85/19138, and EP 227092.

When, as mentioned above, a separate release layer, incorporating the release agent, is provided on
15 top of the receiving layer, other ingredients such as binders, plasticizers, or particulate fillers such as talc, silica or colloidal particles can be added to said release layer, provided that the transfer of the reducing agent to the receiving layer comprising the reducible silver source can take place.

Examples of binders for the release layer are polyvinylbutyral, ethylcellulose, cellulose acetate propionate, cellulose acetate butyrate, polyvinylchloride, copolymers of vinylchloride vinylacetate and vinylalcohol, aromatic or aliphatic copolyesters, polymethylmethacrylate, polycarbonates derived from bisphenol
20 A, polycarbonates comprising bisphenols according to formula (I) and the like. The release layer can also act as a protective layer for the images.

A subbing layer is usually provided between the support and the receiving layer, such as those mentioned in e.g. US 4,748,150, US 4,954,241, US 4,965,239 and US 4,965,238 and European Patent
25 Application no. 92 201 620.9.

The subbing layer can further comprise other polymers, particles, or low molecular weight additives. Addition of inorganic particles such as silica, colloidal silica, water soluble polymers such as gelatin, polymeric latices, polystyrene sulfonic acid and polystyrene sulfonic acid sodium salt, surfactants such as cationic, anionic, amphoteric and non-ionic surfactants, and polymeric dispersants is preferred.

Especially preferred additives are colloidal silica, the above mentioned surfactants, butadiene containing
30 latices such as poly(butadiene-co-methylmethacrylate-co-itaconic acid), polystyrene sulfonic acid and polystyrene sulfonic acid sodium salt. The addition of silica to the subbing layer decreases sticking on the coating roll after coating of the subbing layer. The addition of polystyrene sulfonic acid or polystyrene sulfonic acid sodium salt to the subbing layer accelerates the recycling process.

The subbing layer of the present invention is applied directly to the support of the receiving element. The subbing layer can be applied by coextrusion or can be coated on the support. Coating from an aqueous solution is preferred due to its simplicity and the possibility of adding other ingredients.

The receiving layer is usually hydrophobic in order to enhance the absorption of reducing agent into the receiving element. The polyester recycling procedure, however, uses a cleaning step whereby the film
40 waste is immersed in an alkaline or acid soap solution in water. It is an object of this cleaning process to remove all layers coated on the polymeric substrate.

In order to remove the hydrophobic receiving layer, it is highly preferred to cast an intermediate layer of an hydrophilic polymer between the subbing layer and the receiving layer. This intermediate layer accelerates the cleaning step in the recycling procedure. Typical examples of hydrophilic polymers which
45 can be used in such intermediate layers are polyvinyl alcohol, polyacrylamide, hydroxyethylcellulose, gelatin, polystyrene sulfonic acid, polyethylene glycol, poly(meth)acrylic acid, poly(meth)acrylic acid, alkali metal salts of polyacrylic acid, crosslinked copolymers containing (meth)acrylic acid or alkali metal salts of (meth)acrylic acid, alkali metal salts of polystyrene sulfonic acid, dextran, carrageenin and the like. Alkali metal salts of polystyrene sulfonic acid such as the sodium salt of polystyrene sulfonic acid is highly
50 preferred, since the use of this polymer in the intermediate layer results in better anti-static properties of the receiving element. Anti-static coatings such as those described in EP 440,957 can be incorporated in the intermediate layer or in the subbing layer. This results both in a higher hydrophilicity and in better anti-static properties.

The intermediate layer may further comprise polymeric dispersions or latices, surfactants, inorganic
55 particles such as silica and colloidal silica and the like. Addition of surfactants, colloidal silica and/or latices is preferred. Addition of silica to the intermediate layer decreases sticking to the coating roll after coating. Addition of latices to the intermediate layer improves the addition and improves the removing step in the recycling process in case of acrylic acid or methacrylic acid type latices.

The intermediate layer may also have a cushioning property, such as mentioned in US 4,734,397.

The support for the receiver sheet may be a transparent film of e.g. polyethylene terephthalate, a polyether sulfone, a polyimide, a cellulose ester, or a polyvinyl alcohol-co-acetal. The support may also be a reflective one such as baryta-coated paper, polyethylene-coated paper, or white polyester i.e. white-pigmented polyester. Blue-coloured polyethylene terephthalate film can also be used as a support.

Although the subbing layer is useful for application on polyethylene-coated paper, substrates based on polyester, transparent or reflective, are preferred. In this case, the subbing layer can be applied before, during or after the biaxial stretching procedure.

At the opposite side of the receiving element (opposite to the receiving layer), a backcoat can be provided, optionally in combination, with an appropriate subbing layer to improve the adhesion between the backcoat and the support.

Hydrophilic as well as hydrophobic backcoats can be used. Hydrophilic backcoats can be applied easily from water, while hydrophobic backcoats have the advantage that the backcoat performs well at all humidity levels (no curl).

Examples of hydrophilic backcoat layers are layers comprising polyvinylalcohol, polyethylene glycol, polyacrylamide, hydroxyethylcellulose, dextran and gelatin. The use of gelatin is highly preferred.

These hydrophilic backcoat layers may further comprise dispersions or latices of hydrophobic polymers, inorganic particles, surfactant and the like. The addition of these particles can be used in order to obtain a specific surface gloss, such as mentioned in European patent application no. 91 203 008.7. Especially preferred particles are silica and polymethylmethacrylate beads of 0.5 to 10 μm . Antistatic treatment can be provided on one or both sides of the support of the receiving element.

Examples of hydrophobic backcoat layers are backcoat layers comprising addition polymers such as polymethylmethacrylate, polyvinylchloride and polycondensates such as polyesters, polycarbonates in combination with the above mentioned particles for the hydrophilic backcoat layers.

With hydrophobic backcoat layers, it can be useful to provide an intermediate hydrophilic layer between the subbing layer and the backcoat layer, such as those mentioned for use at the receiving side of the receiving element, in order to improve the removal of the backcoat layer in the recycling procedure.

The printing method of the present invention preferably uses a thermal head to selectively heat specific portions of the donor element in contact with a receiving element. The thermal head can be a thick or thin film thermal head although the use of a thin film thermal head is preferred, since this offers more opportunities to obtain appropriate gradation. The pressure applied to the thermal head is preferably between 120 and 400 g/cm heater line. A spatial resolution of 150 dpi or higher is preferred. The average printing power is calculated as the total amount of energy applied during one line time divided by the line time and by the surface area of the heat-generating elements.

Although a higher average printing power results in higher optical densities of the final image, it is preferred to use an average printing power below 10 W/mm². At higher printing energies, deformation of the receiving layer and/or receiving sheet occurs.

The time needed for printing one single line with the thermal head, also called the line time, is preferably below 45 ms. Longer line times result in longer printing times and more deformation of the receiving sheet and/or receiving layer.

In order to increase the density of the final image after printing line-by-line with a thermal head, an overall heat treatment of the receiving element may be performed. This heat treatment can be e.g. done with an infrared source, a heated air stream or a hot plate, but is preferably done by means of a heated roller.

It is believed that during the overall heat treatment, the transferred reducing agents can further react with the reducible silver source.

By selecting the appropriate diameter and speed of the heated roller, the heat treatment time for the overall heating can be adjusted. Moreover, the heated rollers can be used to uncurl the receiving sheet after printing.

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

EXAMPLES

55 Preparation of the receiving element

A subbed polyethylene terephthalate support having a thickness of 100 μm was coated in order to obtain the following receiving layer :

silver behenate	4.5 g/m ²
compound I mentioned above	0.34 g/m ²
polyvinylbutyral (Butvar B79, Monsanto)	4.5 g/m ²

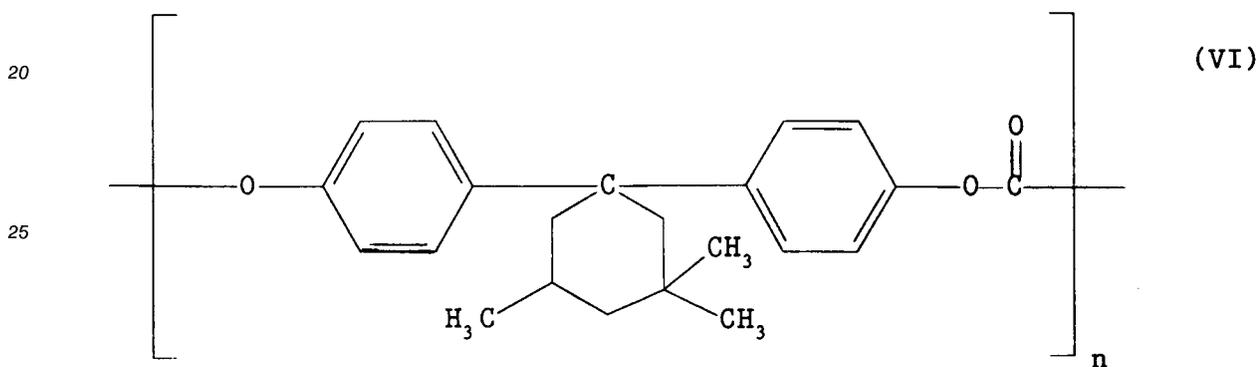
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After drying, a release layer was coated from hexane comprising 0.03 g/m² Tegoglide 410 (polyether-polysiloxane blockcopolymer from Goldschmidt). This receiving element was used in the following printing examples.

10 Preparation of the donor elements

Both sides of a 5.7 μm thick polyethylene terephthalate support were coated with a subbing layer of a copolyester comprising ethylene glycol, adipic acid, neopentyl glycol, terephthalic acid, isophthalic acid, and glycerol.

15 The resulting subbing layer was covered with a solution in methyl ethyl ketone of 13% of a polycarbonate having the following structural formula (VI):



wherein n represents the number of units to obtain a polycarbonate having a relative viscosity of 1.30 as measured in a 0.5% solution in dichloromethane, 0.5% of talc (Nippon Talc P3, Interorgana) and 0.5% of zinc stearate.

35 Finally, a top layer of polyether-modified polydimethylsiloxane (Tegoglide 410, Goldschmidt) was coated from a solution in isopropanol on the resulting heat-resistant polycarbonate layer.

The other side of the support was provided with a donor layer. The nature of the ingredients is mentioned in table I. The binder (Luran 388 S, BASF) was used at 10 weight % in butanon in combination with the reducing agents A, B, C and D. 0.5 % Tospearl 145 (Toshiba Silicone) was added to the coating solution. These coating solutions were applied at a wet thickness of 10 μm by means of a wire bar. The resulting layer was dried by evaporation of the solvent.

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Printing of the combination of donor and receiving elements

45 Printing was performed by contacting the donor layer of the donor element with the receiving layer of the receiving element, followed by heating by means of a thermal head. The thermal head was a thin film thermal head heated (pulse wise activation) at an average printing power of 5 Watt/mm² and a line time of 18 ms, a duty cycle of 75 % and with a resolution of 300 dpi. The pressure applied between the thermal head and the rotating drum carrying the receiving and donor element was 160 g/cm heater line. After printing, the receiving element was separated from the donor element.

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The printed image was a 16-step grey scale between data level 0 and 255 (8 bit). The data levels of the different steps were chosen equidistant with respect to the input data level in order to obtain the native sensitometry.

55 Overall heat treatment

After image-wise heating, the receiving elements were reheated on a hot plate of 118 °C for 10 seconds in order to increase the density of the final image.

Measurement of the optical density of the prints

The optical maximal densities of the prints were measured behind a visual filter in a Macbeth TR924 densitometer in the grey scale part corresponding to data level 255.

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Evaluation of the degree of crystallization.

Crystallization of the reducing agent in the donor layer was evaluated after coating and after storage for 1 day at 45° C and 70 % relative humidity. The following criteria were used:

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- B : Extensive crystallization
 - M : Moderate : Some crystals visible
 - G : Good : No crystals visible on the donor element
- The results are summarized in Table 1

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Table 1

	Reducing agents								Vis. density	Crys after	Crys after storage
	A	%	B	%	C	%	D	%			
Comp1	R1	15	-	-	-	-	-	-	2.87	B	B
Comp2	R2	15	-	-	-	-	-	-	1.66	B	B
Comp3	R3	15	-	-	-	-	-	-	2.24	B	B
Comp4	R4	15	-	-	-	-	-	-	2.02	B	B
1	R1	7	R5	4	R2	4	-	-	3.55	E	G
2	R1	7	R5	4	R4	4	-	-	3.85	M	M
3	R1	9	R2	4	R6	2	-	-	3.05	G	M
4	R1	5	R5	3	R2	3	R6	4	2.90	G	M
5	R5	9	R2	6	-	-	-	-	2.56	G	M
R1 : 4-methoxynaphthol R2 : propylgallate R3 : 3,4-dihydroxybenzoic acid ethyl ester R4 : methylgallate R5 : 4-phenylpyrocatechol R6 : n.octylgallate											

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It is clear from table 1 that high optical densities can be obtained by using a donor element of the present invention. It is also clear that the stability of the donor elements is improved as compared to donor elements having only one reducing agent.

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Claims

1. A donor element for use in thermal transfer printing wherein said donor element comprises on a support (a) a donor layer comprising a binder and a mixture of at least two thermotransferable reducing agents capable of reducing a silver source to metallic silver upon heating, and (b) on the side of the support opposite to the side comprising said donor layer, a heat-resistant backing layer.
2. Donor element according to claim 1 wherein said donor layer comprises a mixture of at least three thermotransferable reducing agents capable of reducing a silver source to metallic silver upon heating.
3. Donor element according to claim 1 or 2 wherein said donor layer comprises from 40 to 80 weight % of said thermotransferable reducing agents relative to the total weight of said donor layer.

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4. Donor element according to claim 1 or 3 wherein said thermotransferable reducing agents are selected from the group consisting of 4-methoxynaftol, pyrocatechol and pyrocatechol derivatives, pyrogallol and pyrogallol derivatives.
- 5 5. A thermal imaging process using (i) a donor element according to any of the above claims and (ii) a receiving element comprising on a support a receiving layer comprising a silver source capable of being reduced by means of heat in the presence of a reducing agent, said thermal imaging process comprising the steps of
- 10 - bringing said donor layer of said donor element into face to face relationship with said receiving layer of said receiving element,
- image-wise heating a thus obtained assemblage, thereby causing image-wise transfer of an amount of said thermotransferable reducing agents to said receiving element in accordance with the amount of heat supplied and
- separating said donor element from said receiving element.
- 15 6. A thermal imaging process according to claim 5 wherein said receiving element subsequent to said image-wise heating is overall heated.
- 20 7. A thermal imaging process according to claim 6 wherein said overall heating is performed by means of a heated roller.
- 25 8. A thermal imaging system consisting of a donor element and a receiving element for use in combination with said donor element, said donor element comprising on a support (a) a donor layer comprising a binder and a mixture of at least two thermotransferable reducing agents capable of reducing a silver source to metallic silver upon heating (b) on the side of the support opposite to the side comprising said donor layer, a heat-resistant backing layer and said receiving element comprising on a support a receiving layer comprising a silver source capable of being reduced by means of heat in the presence of a reducing agent.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 95 20 0413

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X,Y	EP-A-0 582 144 (MINNESOTA MINING AND MANUFACTURING COMPANY) * page 6, line 46 - line 47; example 12 * ---	1-8	G03C1/498 B41M5/32 B41M5/38 G03C8/40
Y	US-A-3 767 414 (HUFFMAN ET AL.) * column 1, line 53 - line 67; claim 4 * ---	1-8	
Y	US-A-3 795 532 (NEWMAN ET AL.) * examples 5,6 * ---	1-8	
Y	GB-A-2 203 563 (FUJI PHOTO FILM COMPANY LTD.) * p.58, last paragraph - p.63, third paragraph * ---	1-8	
Y	RESEARCH DISCLOSURE, vol. 177, no. 06, January 1979 HAVANT GB, 'Photothermographic materials' * the whole document * ---	1	
Y	GB-A-2 083 726 (MINNESOTA MINING AND MANUFACTURING COMPANY) * claims 1,3,4,19 * -----	6,7	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 1 August 1995	Examiner Buscha, A
CATEGORY OF CITED DOCUMENTS		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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