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Thermal transfer printing receiver sheet.

A thermal transfer printing receiver sheet comprises a substrate supporting a dye-receiving layer on its surface, characterised in that the main constituent of the dye-receiving layer is a copolyester in which the acid component comprises at least one alicyclic dicarboxylic acid, and the alcohol component comprises at least one alicyclic diol. Such receivers enable a printed sheet with an image of high quality, having a superior balance of properties with respect to optical density, light fastness, storage stability and finger print resistance, to be obtained.

This invention relates to thermal transfer receiver sheets which are used in combination with a thermal transfer dyesheet containing thermal transfer dyes and employing heating means (such as thermal heads) to transfer dye from the dyesheet to a dye-receiving layer on the receiver sheet, according to image signals applied to the heating means. The invention relates especially to an improved dye-receiving composition.

5 Thermal transfer printing systems have been developed in recent years for producing images by causing thermal transfer dyes to transfer to a receiver sheet in response to thermal stimuli. Using a dyesheet comprising a thin substrate supporting a dyecoat containing one or more such dyes uniformly spread over an entire printing area of the dyesheet, printing is effected by heating selected discrete areas of the dyesheet while the dyecoat is pressed against a dye-receptive surface of a receiver sheet, thereby causing dye to transfer to corresponding areas of the receiver. The shape of the image thus formed on the receiver is determined by the number and location of the discrete areas which are subjected to heating.

10 High resolution photograph-like prints can be produced by thermal transfer printing using appropriate printing equipment, such as programmable thermal heads or laser printer, controlled by electronic image signals derived from a video, computer, electronic still camera, or similar signal generating apparatus. Thus for example a thermal print head has a row of individually operable tiny heaters spaced to print typically six or more pixels per millimetre. Selection and operation of these heaters is effected according to the electronic image signals fed to the printer.

15 Full colour prints can be produced by printing with different coloured dyecoats sequentially in like manner, and the different coloured dyecoats are usually provided as discrete uniform print-size areas in a repeated sequence along the same dyesheet.

20 Receiver sheets comprise a substrate sheet supporting a dye-receiving layer containing a material having an affinity for the thermal transfer dye molecules, and into which they can readily diffuse when an adjacent area of dyesheet is heated during printing. Such materials are mainly constituted by various aromatic or aliphatic polyesters, as described for example in JA-A-57-107,885, JA-A-61-258,790, JA-A-1-269,589 and US 4,474,859.

25 When previously known aromatic and aliphatic polyesters were used for the dye-receiving layer of the receiver sheet, one or more of a number of problems were usually experienced. Thus with some polyesters, the maximum optical densities that could be obtained under normal printing conditions, were insufficient, due to inferior dye-receiving properties of the polyester used. Other problems that were often experienced included poor stability of the image, giving deterioration of the image during storage, a fault which can be accelerated for measuring by exposing the printed sheet to high temperature and high humidity conditions. Light fastness of the printed image, and resistance to the development of finger prints, are also desirable properties that are influenced by the material selected for the dye-receiving surface. We have now devised a new receiver sheet having an improved balance of such properties.

30 According to the present invention, a thermal transfer printing receiver sheet comprises a substrate supporting a dye-receiving layer on its surface, characterised in that the main constituent of the dye-receiving layer is a copolyester in which the acid component comprises at least one alicyclic dicarboxylic acid, and the alcohol component comprises at least one alicyclic diol.

35 Materials suitable for use as the substrate of the receiver sheet may variously include for example, thermoplastic films, synthetic papers and cellulose fibre papers. Examples include films or sheets of polyester, polyvinyl chloride, polypropylene, polyethylene, polycarbonate, polyimide, polyamide, polyamideimide, especially biaxially orientated polyethyleneterephthalate film. Examples of synthetic papers include those of fabricated and moulded polyolefines, polystyrene, and polyesters etc. as the polymer component. Cellulose fibre papers, woodfree paper, coated paper, art paper, synthetic rubber latex impregnated paper, cast-coated paper, etc. can also be used. The above may be used on their own, although a laminated substrate using a combination of two or more of the above, may be preferred for some applications.

40 The substrate supports the dye-receiving layer, which is provided as a coating on its surface for the purpose of receiving the dyes transferred from selected areas of the dyesheet, thereby to form an image. The main constituent of the dye-receiving layer of the present invention is a copolyester formed by using an acid component comprising at least one alicyclic dicarboxylic acid.

45 Examples of alicyclic dicarboxylic acids which can be used for this purpose, include cyclopropane dicarboxylic acid, cyclobutane dicarboxylic acid, cyclohexane-1,2-dicarboxylic acid, cyclohexane-1,3-dicarboxylic acid, cyclohexane-1,4-dicarboxylic acid, methylhexahydrophthalic acid, and norbornene dicarboxylic acid. In furtherance of this invention, the alicyclic acid components of the copolyester can be introduced as the acid or as the corresponding anhydride, as appropriate. Examples of such anhydrides, for example, include hexahydrophthalic acid anhydride, and methyl-hexahydrophthalic acid anhydride.

50 The acid component of the copolyester may also include other polybasic carboxylic acids, such as those previously used on their own without the present alicyclic acids. Such other dicarboxylic acids may include, for

example, aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, orthophthalic acid, 2,6-naphthalene dicarboxylic acid, etc, aliphatic dicarboxylic acids, such as succinic acid, adipic acid, azelaic acid, sebacic acid, dodecane dicarboxylic acid, etc. Tri- and tetra-carboxylic acids, such as trimellitic acid, trimesic acid, pyromellitic acid, etc, may also be added to the alicyclic dicarboxylic acid.

5 When the acid component of the copolyester comprises a mixture of alicyclic dicarboxylic acids and other polybasic carboxylic acids, we prefer the molar ratio of the alicyclic dicarboxylic acids to the other carboxylic acids in the mixture to be within the range 5/95 - 95/5, especially within the range 10/90 - 50/50, the range 10/90 - 30/70 being particularly preferred with some acid combinations.

10 The alcohol component of the copolyester of the present invention comprises at least one alicyclic diol. Examples of diols that can be used for this purpose include 1,4-cyclohexanedimethanol, cyclohexane-1,2-diol, cyclohexane-1,3-diol, cyclohexane-1,4-diol, cyclopentane-1,2-diol, cyclopentane-1,3-diol, tricyclocodcanedimethylol, and ethylene oxide adduct of hydrogenated Bisphenol A.

15 The alcohol component of the copolyester may also include other polyols, such as those previously used on their own in the absence of the present alicyclic diols, for example. Such additional other polyols may include ethylene glycol, propylene glycol, butanediol, neopentyl glycol, diethylene glycol, 1,6-hexanediol, 2,2-diethyl-1,3-propanediol, 2-n-butyl-2-ethyl-1,3-propanediol, and ethylene oxide and/or propylene oxide adduct of Bisphenol A, and polyols such as trimethylol propane, glycerin, pentaerithritol, polyglycerin, etc.

20 When the alcohol component of the copolyester comprises a mixture of alicyclic diols and other polyhydric alcohols, we prefer the molar ratio of the alicyclic diols to the other alcohols in the mixture, to be within the range 5/95 - 95/5, especially within the range 10/90 - 50/50, the range 10/90 - 30/70 being particularly preferred with some polyol combinations.

25 Dye-receiving layers of the present invention can be made by coating a substrate with a composition containing the copolyester, using any of the normal coating techniques, such as roll coating or gravure printing, for example. The viscosity of the coating composition can be adjusted by altering the amount of solvents present, and these are subsequently removed from the applied layer by drying. Receivers made according to the invention, can show properties superior to those obtained with previously known polyesters, but such improvements are only shown when both alicyclic dicarboxylic acid and alicyclic diol moieties are present; ie not when only one or the other is present.

30 In order to improve release from the thermal transfer dye-sheet after printing, the thermal printing receiver may be provided with a release agent in the dye-receiving layer or on its surface. Examples of release agents include solid waxes such as polyethylene wax, amide wax, polytetrafluoroethylene powder, fluorine- or phosphate-type surfactants, and especially silicone oils.

35 Both oil type and solid type silicone oils can be used, but curable silicone materials are preferred. Where such release system is to be used on the surface of the receiver, the uncured silicone materials are first applied as an uncured coating composition on the dye-receiving layer, dried as appropriate, and thereafter cured in situ. Where the release system is to be contained in the dye-receiving layer, the curable materials are mixed with the copolyester in a coating composition, which is then applied to the substrate and dried, curing of the release system then being effected in situ. Such cross-linked matrices these produce within the dye-receiving layer help to stabilise it. They can be reaction curing types, photocuring type or catalytic curing type, for example, but the reaction curing type is preferred.

40 Examples of reaction curing release systems include the reaction products of amino-modified silicone oils, such as KF-393, KF-857, KF-858, X-22-3680, X-22-3810 (these being products of Shin-Etsu Chemical), and M468 (ICI), reacted with an epoxy-modified silicone such as KF-100T, KF-101, KF-103 (these also being products of Shin-Etsu Chemical), or with an organic oligoepoxide free from silicone, such as Diepoxide 126, Diepoxide 183 (both being products of Degussa), and Araldite GY 1558 GB (Ciba Geigy). Preferred quantities of such release systems in the dye-receiving layer are 0.05-20% of the copolyester.

45 The cross-linking of the copolyester can also be enhanced, by including an effective amount of a cross-linking agent in the coating composition, applying this as a layer to the substrate, and carrying out the cross-linking reaction in situ, ie in essentially the same manner as that described above for the release system. Examples of crosslinking agents include compounds having isocyanate groups, compounds having active methylol or alkoxy methyl groups, acid anhydride, carboxy groups, or epoxy groups. It is generally preferred to limit the crosslinking agent to 0.5-20 wt % of the copolyester.

50 In addition to the copolyester of the present invention and any polymeric release agent that might be employed, the dye-receiving layer may also contain a minor amount of other polymeric materials intimately mixed with the copolyester. Examples of such other polymeric materials include polyvinyl chloride, polyvinyl acetate, vinyl chloride/vinyl acetate copolymer, polystyrene, polycarbonate, acrylic and methacrylic polymers, cellulosic polymers, polyacetal, polyethylene, and polypropylene; and even thermosetting resins such as epoxy, melamine, urethane and urea type resins can be present in small quantities. By minor amount, we mean

less than 50 % by weight, and prefer there to be less than 20 % of the other polymer. For most purposes we particularly prefer that no such other polymer be included in the dye-receiving layer, any polymeric material in the dye-receiving layer being limited to the copolyester and any polymeric release agent.

5 The dye-receiving layer may also contain stabilisers for combating fading and/or a UV absorber. Suitable quantities are 0.5-20 wt % of the copolyester.

To obtain a smoother gradation of colour, especially when using a hard substrate, can be obtained by providing an intermediate compliant layer between the substrate and the dye-receiving layer. Such layers may be in the form of a compliant cushion or a porous layer, and these may be formed from polyurethane, polyester, polyamide, acrylic or methacrylic polymers, or synthetic rubber. The thickness of such layers may suitably be
10 in the range 1-50 μm .

In order to control the formation of static electricity, during the fabrication process or while travelling through the printer with the dyesheet, an antistatic agent can be coated onto or incorporated with one or more coating of the receiver. We prefer that antistatic treatments be applied to both sides of the substrate.

15 EXAMPLES

Evaluation of thermal printing receiver sheets according to the invention was made by transferring images onto the dye-receiving layer using a thermal head. The receiver sheet was placed against a dyesheet with its dye-receiving layer in contact with the dyecoat of the dyesheet (details of the latter being specified in the
20 example below). Heat was applied to the back of the dyesheet by a thermal head having an output energy of 0.32 W/dot, a head heating time of 6 ms and a dot density of 6 dots/mm. The printed sheets thus formed were evaluated in respect of their optical density, light fastness, storage stability, and finger print resistance, in the following manner.

25 Optical density

The image density was measured on a SAKURA optical density meter PDA 85.

30 Light fastness

The hue of the image was measured before and after accelerated aging of the print by ATRAS HPUV, to determine the change in hue which occurred during the aging cycle.

35 Storage stability

The printed receiver sheet was stored in an atmosphere of 45°C and 85% relative humidity, for 2 weeks. The hue was again measured before and after treatment, to determine the change of hue occurring under those conditions.

40 Finger print resistance

The optical density of the printed image was determined. A finger print was then made on the image surface, and the print left in an atmosphere of 45°C and 85% relative humidity for 2 weeks. After that time the optical density was again measured of the part of the print on which the finger print had been made. The change in
45 optical density was recorded as a percentage of the initial measurement.

Production of copolyester (A)

245.6 parts of dimethyl terephthalic acid, 69.4 parts of ethylene glycol, 2.9 parts of trimethylol propane,
50 211.1 parts of 2-n-butyl-2-ethyl-1,3-propanediol, 118.5 parts of 1,4-cyclohexane dimethanol and 0.1 part of zinc acetate were placed into a flask installed with a thermometer, nitrogen gas inlet tube, reflux dehydrator and stirrer, and it was heated at 170°C - 220°C for 5 hours. During the heating, methanol formed was evaporated outside the system. Then it was cooled at 170°C, 105.1 parts of isophthalic acid and 97.5 parts of hexahydrophthalic anhydride were added and the mixture heated at 170°C - 230°C for 6 hours. During the heating, water
55 formed was evaporated outside the system. The reflux dehydrator was then replaced with a vacuum pressure reducer, and after an addition of 0.1 part of antimony trioxide, it was heated at 260°C and 5 mmHg pressure for 4 hours, to perform the reduced pressure condensation reaction from which the copolyester (A) was obtained.

The reactants used for the production of the copolyester (A) are summarised below.

Copolyester (A)

5	dimethyl terephthalic acid	245.6 parts
	isophthalic acid	105.1 parts
	hexahydrophthalic acid anhydride	97.5 parts
10	ethylene glycol	69.4 parts
	2-n-butyl-2-ethyl-1, 3-propanediol	211.1 parts
	1,4-Cyclohexane dimethanol	118.5 parts
15	trimethylol propane	2.9 parts

Copolyesters (B) and (C) were obtained in similar manner by using the reactants listed below.

Copolyester (B)

20	dimethyl terephthalic acid	360.0 parts
	isophthalic acid	220.4 parts
	hexahydrophthalic acid anhydride	87.6 parts
25	ethylene glycol	73.4 parts
	2-n-butyl-2-ethyl-1, 3-propanediol	177.5 parts
	1,4-cyclohexane dimethanol	158.2 parts
	trimethylol propane	4.4 parts
30	2 mole ethylene oxide adduct of Bisphenol A	510.4 parts

Copolyester (C)

35	dimethyl terephthalic acid	431.8 parts
	isophthalic acid	328.4 parts
	hexahydrophthalic acid anhydride	114.2 parts
40	ethylene glycol	135.5 parts
	neopentyl glycol	100.3 parts
	2-n-butyl-2-ethyl-1,3-propanediol	206.3 parts
45	1,4 cyclohexane dimethanol	277.8 parts
	trimethylol propane	5.7 parts

Example 1

50 Preparation of thermal transfer receiver sheet

Receiver sheet (a') was prepared by wire bar coating one surface of a polyester film with an ink composition (a), and drying this to produce a dye-receiving layer of approximately 5 µm thickness. The polyester film was
55 Melinex 990 (Melinex is a trade mark of Imperial Chemical Industries PLC, hereinafter referred to as ICI). Ink composition (a) contained copolyester (A) as the main constituent of the dye-receiving layer, a release system also being present as a minor constituent. The full composition of ink composition (a), is set out below.

Ink composition (a)

	copolyester (A)	100	parts
5	aminosiloxane (ICI product)	4	parts
	Degacure (Degussa product)	0.7	part
	triethylenediamine	0.5	part
10	methylethylketone/Toluene	200	parts
	(mixing ratio : 4/6 wt/wt)		

Preparation of the thermal transfer dye sheet

15 A slipping layer of silicone oil was formed on one side of a 6 μm polyester substrate film (Lumilar Toray product). Then an ink composition (I) for the thermal transfer printing was prepared as described below, and was coated onto the other surface of the substrate from that coated with the slipping layer. The ink composition (I) was then dried to form a 1.0 μm thick dyecoat, to complete the thermal transfer dye sheet (I'). Details of the ink composition were as follows:

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Ink composition (I)

	dye (Dispersol Red B-2B, ICI product)	4	parts
25	ethyl cellulose resin (Hercules product)	4.4	parts
	tetrahydrofuran	100	parts

30 Then the thermal transfer dye sheet (I') and the thermal transfer printing receiver sheet (a') were held together, and an image was formed in the dye-receiving layer by heating with a thermal head. The optical density, light fastness, storage stability and finger print resistance of the printed sheet thus produced, were evaluated. The results are shown in Table I.

Example 2

35 An ink composition (b) for forming a dye receiving layer was prepared in the similar manner to that in Example 1, but using copolyester (B) as the main constituent. A thermal transfer printing receiver sheet (b') was prepared by coating this ink onto Melinex 990 and drying, as described above. Using the thermal transfer dyesheet (I') to provide the transfer dyes, a printed sheet was obtained by forming an image in the dye-receiving layer of receiver sheet (b'), by heating with a thermal head. The optical density, light fastness, storage stability and finger print resistance were then evaluated. The results are shown in Table I.

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Example 3

45 An ink composition (c) was prepared in the similar manner to the two preceding Examples, but using copolyester (C) as the main constituent, and thermal transfer printing receiver sheet (c') was prepared and printed in like manner. The optical density, light fastness, storage stability and finger print resistance of the resultant print were then evaluated, and the results are shown in Table I

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COMPARATIVE EXAMPLES

Copolyester resins (D) and (E) were prepared from the compositions shown below, in similar manner to those of Examples 1 to 3 above.

Copolyester (D)

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dimethyl phthalic acid	187.0 parts
isophthalic acid	240.0 parts

ethylene glycol 77.0 parts
neopentyl glycol 195.4 parts

Copolyester (E)

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dimethyl phthalic acid 187.0 parts
isophthalic acid 240.0 parts
trimellitic anhydride 13.7 parts
ethylene glycol 77.0 parts
neopentyl glycol 195.4 parts

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Comparative Example C1

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An ink composition (d) for forming the dye-receiving layer was prepared in a similar manner to that of Example I but using copolyester (D) as the main constituent, and a corresponding thermal transfer printing receiver sheet (d') was prepared, again using Melinex 990 as substrate. Thermal transfer dyesheet (l') and thermal transfer printing receiver sheet (d') were passed together through a thermal printer, and a printed sheet was obtained by forming an image in the receiver layer by heating with the thermal head. Optical density, light fastness, storage stability and finger print resistance of the printed sheet, were evaluated. The results are shown in Table 1.

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Comparative Example C2

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An ink composition (e) for forming the dye receiving layer was prepared in similar manner to those of the preceding Examples, but using copolyester (E) as the main constituent. Receiver sheet (e') was prepared by coating Melinex 990 with a layer of e. This was printed as before using thermal transfer dyesheet (l') and the optical density, the light fastness, the storage stability and the finger printing resistance were evaluated. The results are shown in Table I.

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Table 1

	Example			Comparative Example	
	(1)	(2)	(3)	(C1)	(C2)
Optical Density	1.2	1.3	1.2	1.0	0.9
Light Fastness	20.0	20.5	20.0	23.0	24.0
Storage Stability	2.0	3.0	2.5	6.0	7.0
Finger Print Resistance (%)	+3.0	+2.0	+4.0	-8.0	-10.0

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To summarise these observations, when general polyester resins as used previously, were used as the main constituent of the dye receiving layer, it was difficult to satisfy all the required properties of optical density, light fastness, storage stability and finger print resistance. However, by using copolyesters obtained by reacting at least one alicyclic dicarboxylic acid as the acid component for the copolymerization and at least one alicyclic diol as the alcohol component, these properties can be largely improved. Such receivers enable a printed sheet with an image of high quality, having a superior balance of properties with respect to optical density, light fastness, storage stability and finger print resistance, to be obtained.

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Claims

1. A thermal transfer printing receiver sheet comprising a substrate supporting a dye-receiving layer on its

surface, characterised in that the main constituent of the dye-receiving layer is a copolyester in which the acid component comprises at least one alicyclic dicarboxylic acid, and the alcohol component comprises at least one alicyclic diol.

- 5 **2.** A thermal transfer printing receiver sheet as claimed in claim 1, characterised in that the acid component of the copolyester comprises a mixture of alicyclic dicarboxylic acids and other polycarboxylic acids having a molar ratio within the range 5/95 - 95/5.
- 10 **3.** A thermal transfer printing receiver sheet as claimed in either of the preceding claims, characterised in that the alcohol component of the copolyester comprises a mixture of alicyclic diols and other polyhydric alcohols having a molar ratio within the range 5/95 - 95/5.
- 15 **4.** A thermal transfer printing receiver sheet as claimed in any one of the preceding claims, characterised in that in addition to the copolyester and any polymeric release agent that might be employed, the dye-receiving layer contains a minor amount of other polymeric materials intimately mixed with the copolyester.
- 20 **5.** A thermal transfer printing receiver sheet as claimed in any one of the preceding claims, characterised in that the polyester-type cross-linking of the copolyester is enhanced by reaction with an effective amount of a cross-linking agent therefor.
- 25 **6.** A thermal transfer printing receiver sheet as claimed in any one of the preceding claims in which an anti-static agent is coated onto or is incorporated within one or more coatings of the receiver.
- 30 **7.** A thermal transfer printing receiver sheet as claimed in claim 6 characterised in that the antistatic treatments are applied to both sides of the substrate.

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