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54 **Printing paper.**

57 A printing paper for hard copy sublimation transfer comprises a substrate and a dye acceptor layer formed on a surface of the substrate, the dye acceptor layer being formed of a resin layer mainly composed of a resin having bisphenol units, and the resin forming the resin layer having a glass transition point not lower than 55°C. The dye acceptor layer may be a single layer, or it may have a multi-layer structure with the top layer including the resin having bisphenol units.

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PRINTING PAPER

This invention relates to printing paper, and in particular to such paper for hard copy sublimation transfer, which may be used for making a hard copy of an image picked up by a video camera or a television picture image by thermal transfer of sublimable dyes.

5 As is known in the art, hard copies may be obtained by thermal transfer printing by superposing a dye carrier ribbon having a colorant layer, in which sublimable dyes are contained, on to printing paper, and heating the ribbon according to a pattern corresponding to image information, for example, image information picked up by a video camera or television picture image information, thereby causing the sublimable dyes to be transferred to the printing paper.

10 In Figure 1 of the accompanying drawings, there is shown a printer for obtaining a hard copy by thermal transfer printing. The printer has a platen 2 around which printing paper 1 is wound and which is rotated in the direction of an arrow a, and a heating head 4 arranged to press a dye carrier ribbon 3 against the platen 2 and the printing paper 1. At the tip of the heating head 4 are arranged heating elements 4a corresponding to the number of required picture elements, which in turn correspond to the number of elements in one scanning line of, for example, a television picture image.

20 The dye carrier ribbon 3 sandwiched under pressure between the heating head 4 and the printing paper 1 has a sheet substrate 9 on which there are formed colorant layers in a form corresponding, for example, to the frame of a television picture image, and which each contain a respective one of four sublimable dyes which are yellow, magenta, cyan and black in colour. In other words, the respective colorant layers including yellow Y, magenta M, cyan C and black B are successively formed on the sheet substrate 9 in a repeating fashion. In order to permit the respective colours to be detected, detection marks 5 (5Y, 5M, 5C and 5B for each of the respective colorant layers) from which the position of each colorant layer is detected, are provided along one side edge of the substrate 9 as shown.

Likewise, for detection of a block consisting of one of each of the dye colorant layer portions Y, M, C and B, a block position-detecting mark 6 is provided along the other side edge of the substrate 9.

5 In the case where, for example, the dye portion Y is in pressure contact with the printing paper 1 and the respective head elements 4a of the head 4 are heated in a pattern corresponding to picture elements of one scanning line according to information corresponding to yellow, for example a colour television picture signal corresponding to yellow, the sublimable yellow dye in the dye portion Y is thermally transferred to the printing
10 paper according to the heating pattern.

When the platen 2 is intermittently rotated in the direction of the arrow a with every line corresponding to the respective scanning line, information relating to each line is thermally transferred in turn until the transfer of the yellow colour corresponding to one complete frame has been
15 carried out during one cycle of rotation of the platen 2. Subsequently, a similar transfer process is conducted with respect to magenta M, followed by thermal transfer with respect to cyan C and finally with respect to black B. The transferred images of the sublimable dyes of yellow Y, magenta M, cyan C and black B are therefore superposed and thus a colour
20 image is developed on the printing paper, providing a hard copy.

A light source 7 (for example an infrared light emission diode) and a photo detector 8 constitute a detector means for detecting the detection marks 5 (5Y, 5M, 5C and 5B) and 6 in order that signals corresponding to the respective colour signals in the dye portions Y, M, C and B are supplied to
25 the head elements 4a of the head 4.

Printing paper for transfer-by-sublimation type hard copies has previously been constituted of a substrate such as paper, synthetic paper, a plastics film or the like, with a dye accepting layer formed on the substrate and mainly composed of a polyester resin such as polyethylene
30 terephthalate. In general, polyester resins have good exhaustion properties for sublimable dyes and are stable under ordinary storage conditions. Therefore, printing paper with a dye accepting layer mainly composed of a polyester resin such as polyethylene terephthalate has good stability under ordinary storage conditions. However, when the paper is placed under high
35 temperature and high humidity conditions, for example when the paper is allowed to stand near a window or in a car in summer, a stability problem

will arise in that the dye in the paper migrates and may contaminate adjacent sheets of paper in a stack. In order to overcome this problem, it is usual to resort to a specific treatment such as formation of a laminate film as a surface protective layer.

5 According to the present invention there is provided printing paper for hard copy sublimation transfer, the paper comprising a substrate and a dye acceptor layer formed on a surface of said substrate, said dye acceptor layer being formed at least in part of a resin layer mainly comprising a resin having bisphenol units, and the resin forming said resin layer having a glass
10 transition point not lower than 55°C .

 A preferred embodiment of the present invention, to be described in greater detail hereinafter, provides printing paper for hard copy sublimation transfer having storage stability of picture images made by thermal transfer of a sublimation dye, and having superior dyeing properties with respect to
15 the sublimation dye.

 The invention will now be described by way of example with reference to the accompanying drawings, in which:

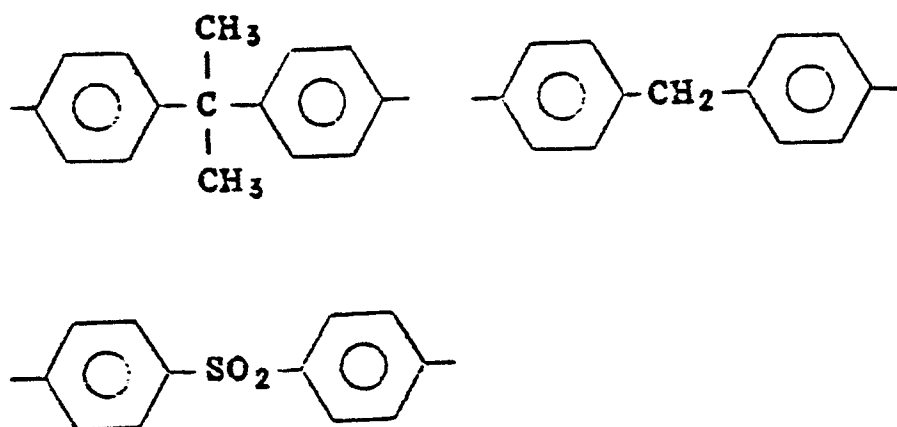
 Figure 1 is a schematic illustration of a printer showing a printing mechanism for printing images on printing paper by thermal transfer of sublimation dyes;
20

 Figures 2 and 3 are cross-sectional views of two types of printing paper; and

 Figure 4 is a cross-sectional view showing a method of measuring the stability of an image on printing paper.

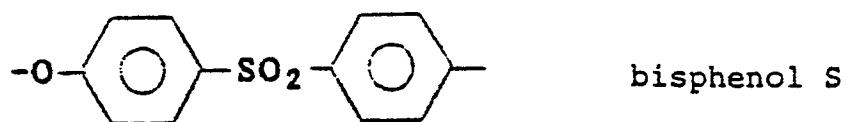
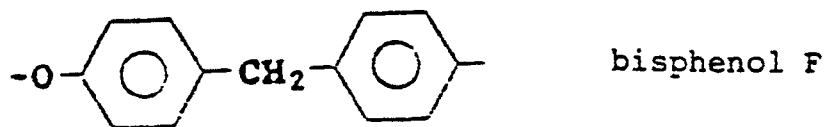
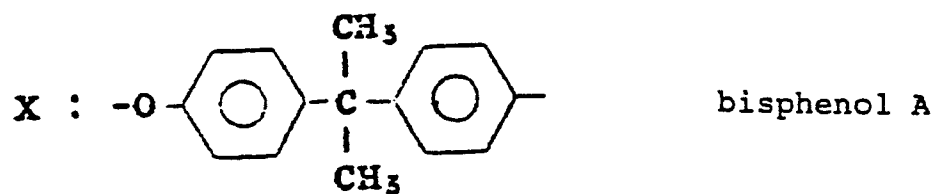
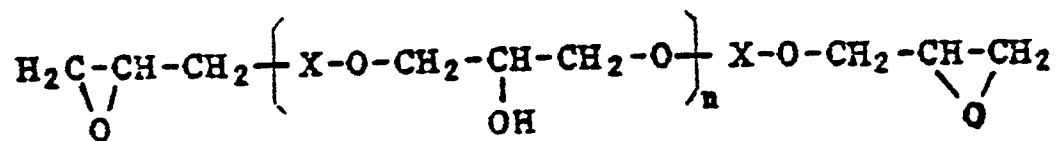
25 Two types of printing paper according to embodiments of the present invention are shown in Figures 2 and 3. Printing paper 13 comprises a substrate 11 and a dye acceptor layer 12 formed on the substrate 11. The dye acceptor layer 12 may be formed by a single coating layer as shown in Figure 2 or by a multi-layer structure formed of coating layers 12a and 12b
30 as shown in Figure 3. The dye acceptor layer 12 (Figure 2) or the uppermost layer 12a (Figure 3) is formed of a resin layer mainly composed of a resin having bisphenol units, the resin in the resin layer having a glass transition temperature T_g not lower than 55°C .

 The term "bisphenol units" is intended to mean those units having the
35 following structural formulae:

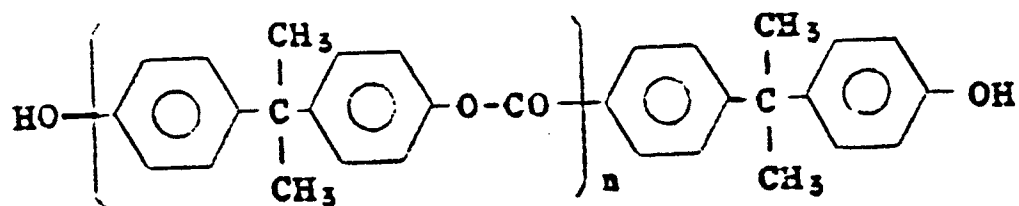


Examples of resins having the above bisphenol units are indicated below by their names and structural formulae:

5 Bisphenol-type epoxy resins

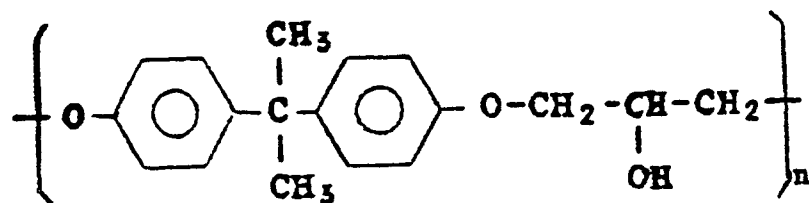


Polycarbonate resins

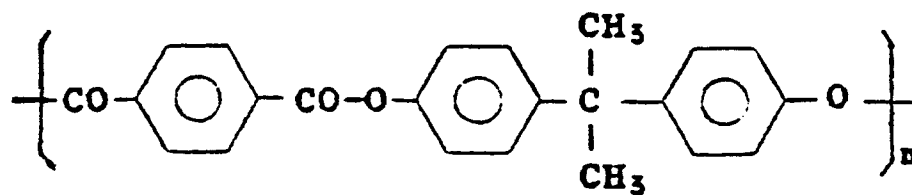


Phenoxy resins (high molecular weight product of bisphenol A-type epoxy compound)

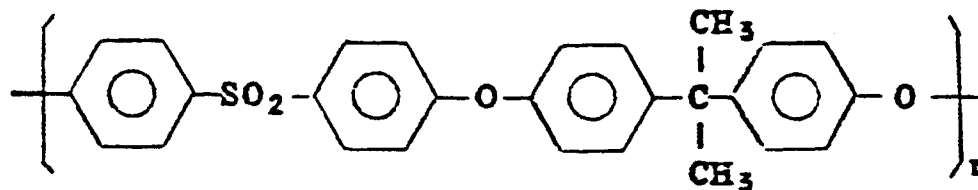
5



Polyarylate resins



Polysulphone resins



The resin having bisphenol units is used in amounts not less than 70 wt% of the total amount of the resin in the resin layer or the uppermost resin layer. If the amounts are less than 70 wt%, the dyeing property of a sublimable dye and the storage stability are unfavourably degraded. The
5 (uppermost) resin layer may further contain, apart from the resin having bisphenol units, up to 30 wt% of other types of resin such as polyesters, epoxy resins, nylon or cellulose acetate resins. In this case, the resin layer should be arranged to have a glass transition temperature T_g of not lower than 55°C.

10 If necessary, the (uppermost) resin layer may further comprise fillers (for example SiO_2 , TiO_2 , CaCO_3 or the like), ultra-violet (UV) absorbers, antioxidants, fluorescent brighteners, surface active agents and the like.

In the case where the dye accepting layer 12 is formed of a multi-layered structure, for example a double-layered structure as shown in Figure
15 3, a dye accepting layer 12b of a polyester resin is first formed on the substrate 11, on which a dye accepting resin layer 12a mainly composed of a resin having bisphenol units and having a glass transition temperature not lower than 55°C is further formed. With the double-layered structure of the dye accepting layer 12, the upper dye accepting resin layer 12a may have a
20 thickness of 0.5 - 5.0 μm .

A resin having bisphenol units has a high absorptivity for sublimable dyes and exhibits good storage stability of picture images formed thereon when the temperature is maintained at or lower than its glass transition point T_g . The main component of the (uppermost) dye accepting layer
25 should be a resin having bisphenol units and the layer should have a glass transition point T_g not lower than 55°C, so that stable storage is ensured even under high temperature and higher humidity conditions than in an ordinary state. Accordingly, although, for example, a polyester resin may be mixed with the resin having bisphenol units in order to increase the
30 colour concentration, the resultant resin layer should have a glass transition point T_g not lower than 55°C. However, even though the glass transition point T_g is over 55°C, a polyester content over 30 wt% results in a strong tendency for the composition to develop properties of the polyester. This leads to a deterioration of the storage stability. Accordingly, the resin
35 having bisphenol units has to be used in amounts not less than 70 wt% of the total amount of the resin layer.

EXAMPLES

Example 1

Phenoate YP-50 (Trade name of Toto Kasei Co., Ltd., phenoxy resin, Tg 100°C) was dissolved in a solvent and applied onto art paper used as a substrate 11 in a dry thickness of 10 μm, thereby obtaining printing paper 13 for printing hard copies by thermal transfer of sublimation dye, the printing paper 13 being composed of the substrate 11 and a dye accepting layer 12 as shown in Figure 2.

Example 2

Panlite L1225 (Trade name of Teijin Ltd., polycarbonate resin, Tg 145°C) was dissolved in a solvent and applied onto art paper used as a substrate 11 in a dry thickness of 10 μm, to obtain printing paper 13 composed of the substrate 11 and a dye accepting layer 12 as shown in Figure 2.

Example 3

A resin layer was formed in the same manner as in Example 1 using U-100 (Trade name of Unitika Ltd., polyarylate resin, Tg 190°C), thereby making printing paper 13 which was composed of a dye accepting layer 12 and a substrate 11.

Example 4

A resin layer was formed in the same manner as in Example 1 using Epototo YD-012 (Trade name of Toto Kasei Co., Ltd., bisphenol A-type epoxy resin, Tg 60°C), thereby making printing paper 13 composed of a dye accepting layer 12 and a substrate 11.

Example 5

A resin layer was formed in the same manner as in Example 1 using Epototo YD-017 (Trade name of Toto Kasei Co., Ltd., epoxy resin, Tg 77°C), thereby making printing paper 13 composed of a dye accepting layer 12 and a substrate 11.

Example 6

A resin layer was formed in the same manner as in Example 1 using a mixed resin (Tg 62°C) of 9 parts by weight of Epototo YD-014 (Trade name of Toto Kasei Co., Ltd., bisphenol A-type epoxy resin, Tg 65°C) and 1 part by weight of TP-219 (Trade designation of Nippon Synthetic Chem. Ind. Co., Ltd., polyester resin, Tg 40°C), thereby making printing paper 13 composed of a dye accepting layer 12 and a substrate 11.

Example 7

A resin layer was formed in the same manner as in Example 1 using a mixed resin (Tg 57⁰C) of 7 parts by weight of Epototo YD-012 (Tg 65⁰C) and 3 parts by weight of UE-3300 (Trade designation of Unitika Ltd., polyester resin, Tg 50⁰C), thereby making printing paper 13 composed of a dye accepting layer 12 and a substrate 11.

Example 8

A resin layer was formed in the same manner as in Example 1 using a mixed resin (Tg 75⁰C) of 7 parts by weight of Epototo YD-014 (Trade name of Toto Kasei Co., Ltd., bisphenol A-type epoxy resin, Tg 65⁰C) and 3 parts by weight of MH-101-2 (Trade designation of Fujikura Kasei Co., Ltd., methyl polymethacrylate, Tg 105⁰C), thereby making printing paper 13 composed of a dye accepting layer 12 and a substrate 11.

Example 9

Vyron No. 200 (Trade name of Toyobo Co., Ltd., polyester resin, Tg 67⁰C) dissolved in a solvent was applied onto a substrate 11 to form a first dye accepting layer 12b having a dry thickness of 10 μm. Thereafter, a mixed resin (Tg 83⁰C) consisting of 7 parts by weight of Phenototo YP-50 (Tg 100⁰C) and 3 parts by weight of UE-3000 (Tg 50⁰C) was used to form a second dye-accepting layer 12a having a dry thickness of 1 μm, thereby obtaining printing paper 13 composed of a double-layered dye accepting layer 12 as shown in Figure 3.

Comparative Example 1

Vyron No. 200 (Toyobo, polyester, Tg 67⁰C) was dissolved in a solvent and applied onto an art paper, used as a substrate, in a dry thickness of 10 μm, thereby obtaining printing paper for printing by thermal transfer of sublimation dye which was composed of the substrate and a dye accepting layer.

Comparative Example 2

A resin layer was formed in the same manner as in Comparative Example 1 using XA5535 (made by Unitika Ltd., polyester, Tg 105⁰C), thereby obtaining printing paper which was composed of a dye accepting layer and a substrate.

Comparative Example 3

A resin layer was formed in the same manner as in Comparative Example 1 using Epototo YD-011 (Trade name of Toto Kasei Co., Ltd.,

polyester resin, Tg 10⁰C), thereby forming printing paper which was composed of a dye accepting layer and a substrate.

Comparative Example 4

5 A resin layer was formed in the same manner as in Comparative Example 1 using a mixed resin (Tg 53⁰C) of 7 parts by weight of Epototo TD-012 (Trade name of Toto Kasei Co., Ltd., bisphenol A-type epoxy resin, Tg 60⁰C) and 3 parts by weight of TP-219 (Trade designation of Nippon Synthetic Chem. Ind. Co., Ltd., polyester resin, Tg 40⁰C), thereby obtaining printing paper composed of a dye accepting layer and a substrate.

10 Evaluation of Materials to be Transferred

An ink having the following composition was prepared and applied onto a 10 μ m thick condenser paper substrate in a dry thickness of 1 μ m to make an ink ribbon.

15	Cellulose acetate (binder resin)	 10 parts by weight
	Sumiplast Red 3B	
	(made by Sumitomo Chem. Ind. Co., Ltd., Sublimation dye)	
		 10 parts by weight
	Methyl ethyl ketone (solvent)	 80 parts by weight

20 This ink ribbon was used for printing on the printing papers of Examples 1 to 9 and Comparative Examples 1 to 4 by the use of a thermal head, thereby obtaining print samples. Thereafter, as shown in Figure 4, the printed surface of each print sample was brought into intimate contact with art paper 15 to provide a layer structure 14 which was allowed to stand in atmospheres of 65⁰C and a relative humidity (R.H.) of 80%, 55⁰C and a relative humidity (R.H.) of 85%, and 40⁰C and a relative humidity (R.H.) of 90% for one week, to test for ageing. After the ageing process, the density of dye transferred to the art paper was measured by means of a Macbeth densitometer. Density on the art paper 15 resulting from transfer of sublimation dye from the print which was found to be below 0.03 was taken as "o", whereas such density which was found to be over 0.03 was taken as "x". The results of the measurements are shown in the Table below.

TABLE

		40°C 90% R.H.	55°C 85% R.H.	65°C 80% R.H.
5	Example 1	o	o	o
	Example 2	o	o	o
	Example 3	o	o	o
	Example 4	o	o	x
	Example 5	o	o	o
	Example 6	o	o	x
10	Example 7	o	o	x
	Example 8	o	o	o
	Example 9	o	o	o
	Comp. Ex. 1	o	x	x
	Comp. Ex. 2	o	x	x
15	Comp. Ex. 3	o	x	x
	Comp. Ex. 4	o	x	x

According to the embodiments of the invention, the (uppermost) dye
 accepting layer is a resin layer mainly composed of a resin having bisphenol
 units and having a glass transition point T_g not lower than 55°C.
 Accordingly, the dyeing property of the dye accepting layer is enhanced, so
 that an image of a higher quality can be obtained, which has good stability
 even under high temperature and higher humidity conditions than is the case
 under ordinary storage conditions. This does not require an additional
 specific type of surface protective film, such as a laminate film, as has been
 necessary with the previously-proposed types of printing paper.

CLAIMS

1. Printing paper for hard copy sublimation transfer, the paper comprising a substrate (11) and a dye acceptor layer (12) formed on a surface of said substrate (11), said dye acceptor layer (12) being formed at least in part of a resin layer mainly comprising a resin having bisphenol units, and the resin forming said resin layer having a glass transition point (Tg) not lower than 55°C.
5
2. Printing paper according to claim 1, wherein said resin layer contains more than 70 parts by weight of said resin having bisphenol units for 100 parts by weight of the resins forming said resin layer.
10
3. Printing paper according to claim 1 or claim 2, wherein said resin having bisphenol units is at least one of bisphenol type epoxy resin, polycarbonate resin, polyarylate resin, or polysulphone resin.
15
4. Printing paper according to claim 1, claim 2 or claim 3, wherein said dye acceptor layer (12) comprises a first resin layer (12b) formed on the surface of said substrate (11), and a second resin layer (12a) formed on the first resin layer (12b), said second resin layer (12a) comprising the resin having bisphenol units.
20

FIG. 2

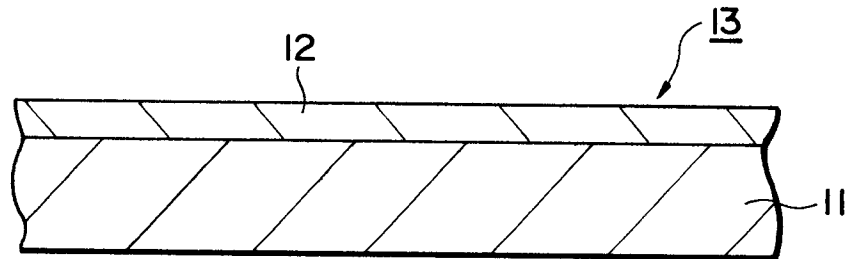


FIG. 3

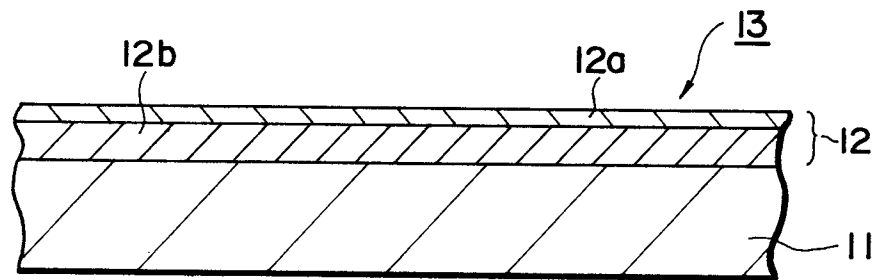


FIG. 4

