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

(11) Publication number: **0 228 294**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **86310159.8**

(22) Date of filing: **24.12.86**

(51) Int. Cl.⁴: **B 41 M 5/26**

(30) Priority: **26.12.85 JP 295826/85**

(43) Date of publication of application: **08.07.87**
Bulletin 87/28

(84) Designated Contracting States: **DE FR GB NL**

(71) Applicant: **SONY CORPORATION,**
7-35 Kitashinagawa 6-Chome Shinagawa-ku,
Tokyo 141 (JP)

(72) Inventor: **Abe, Tetsuya, Patents Division Sony**
Corp. 6-7-35 Kitashinagawa, Shinagawa-ku
Tokyo 141 (JP)
Inventor: **Kobayashi, Naotake, Patents Division Sony**
Corp. 6-7-35 Kitashinagawa, Shinagawa-ku
Tokyo 141 (JP)
Inventor: **Shinohara, Satoru, Patents Division Sony**
Corp. 6-7-35 Kitashinagawa, Shinagawa-ku
Tokyo 141 (JP)
Inventor: **Sugai, Naoki, Patents Division Sony**
Corp. 6-7-35 Kitashinagawa, Shinagawa-ku
Tokyo 141 (JP)

(74) Representative: **Plich, Adam John Michael et al, c/o D.**
Young & Co. 10 Staple Inn, London WC1V 7RD (GB)

(54) Dye carrier ribbons.

(57) A dye carrier ribbon for hard copy sublimation transfer is formed of a substrate with an ink layer formed on a surface of the substrate. The ink layer mainly comprises a sublimation dye and a binder resin. The binder resin has a glass transition point which is not lower than 55°C, and comprises a resin having bisphenol units therein.

EP 0 228 294 A2

DYE CARRIER RIBBONS

This invention relates to dye carrier ribbons, and in particular to such ribbons 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 on printing paper by thermal transfer of sublimable dyes.

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.

In the accompanying single figure drawing, 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.

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.

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 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 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 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 the head elements 4a of the head 4.

Dye carrier ribbons for hard copy sublimation transfer have previously been made by dissolving or dispersing sublimable dyes and binder resins in solvents to obtain inks, and applying each of the inks on to a substrate of a uniform thin paper of a high density or a heat-resistant plastics film, such as a polyimide or polyester film. Printing paper has been made by applying, on to a substrate, a resin having good dyeing properties for sublimable dyes, such as, for example, a polyester resin. When a thermal head is applied from the substrate side of the dye carrier ribbon, only the dye in the ribbon is sublimated and transferred to the printing paper to form an image of the desired colours, or a black and white image, on the printing paper.

With existing dye carrier ribbons for hard copy sublimation transfer, the following problem arises with respect to storage stability. The dye carrier ribbons cannot stand high temperature and high humidity conditions and are not resistant to oils and fats including plasticisers, so that the sublimable dye may migrate or crystallise on the surface of the ribbon. The crystallised dye is transferred to the printing paper as it is, and not only in response to thermal transfer signals, and thus the resultant image is degraded in sharpness and fineness, leading to a lowering of the image quality. Moreover, a sublimable dye which has become unstable migrates on to the back surface of the substrate of the ribbon when the ribbon is wound in a roll, causing the thermal head to be contaminated and/or causing a lowering of the density or hue of the colour to be transferred.

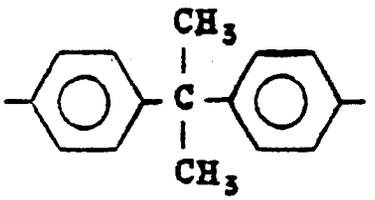
According to the present invention there is provided a dye carrier ribbon for hard copy sublimation transfer, the dye carrier ribbon comprising a substrate and an ink layer formed on a surface of said substrate, said ink layer mainly comprising a sublimation dye and a binder resin, said binder resin comprising a resin having bisphenol units therein, and said binder resin having a glass transition point not lower than $55^{o}C$.

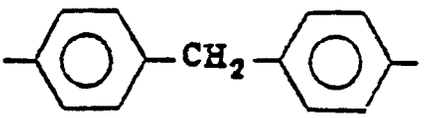
A preferred embodiment of the present invention, to be described in greater detail hereinafter, provides a dye carrier ribbon with improved storage stability, and which is capable of forming a high quality print image.

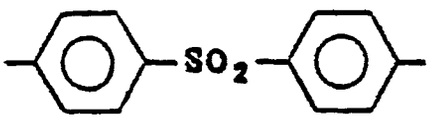
The invention will now be described by way of example with reference to the accompanying single figure drawing which is a schematic illustration of a printer showing a printing mechanism for printing images on printing paper by thermal transfer of sublimation dyes.

Embodiments of the invention provide dye carrier ribbons for hard copy sublimation transfer in which an ink layer provided on a substrate mainly comprises a binder resin and a sublimable dye, and in which the binder resin is mainly composed of a resin having a glass transition point Tg not lower than $55^{o}C$ and bisphenol units therein.

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

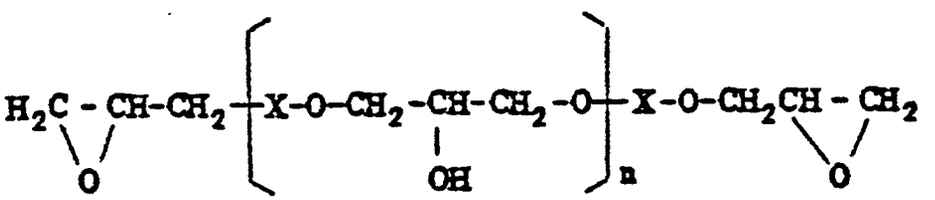


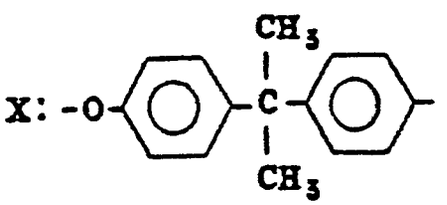




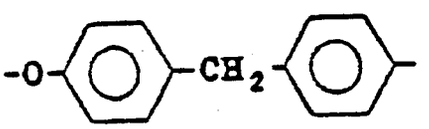
Examples of resins having bisphenol units and their formulae are as follows:

Bisphenol-type epoxy resins

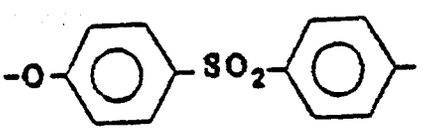




bisphenol A

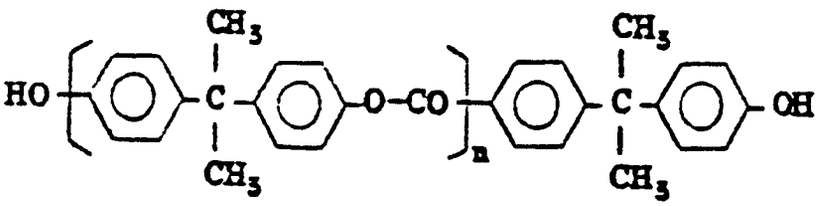


bisphenol F

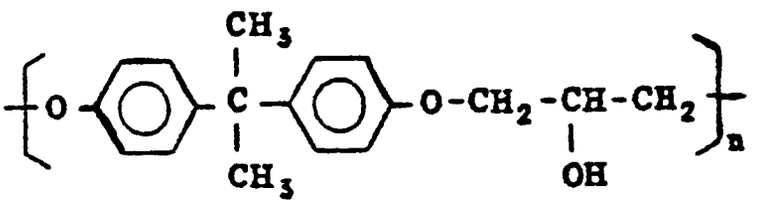


bisphenol S

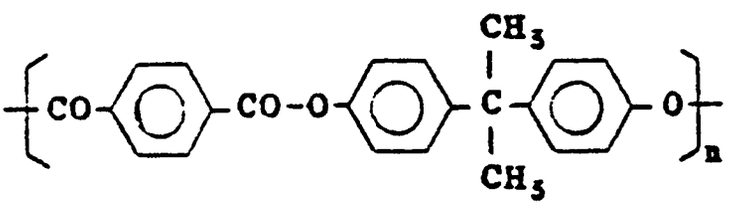
Polycarbonate resins



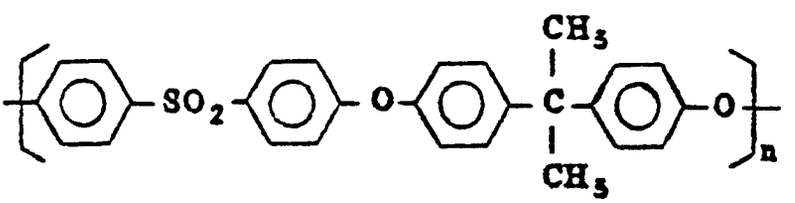
Phenoxy resins (high molecular weight product of bisphenol A-type epoxy compound)



Polyarylate resins



Polysulphone resins



The resin having bisphenol units is used in amounts not less than 70 wt% of the total amount of the binder resin. The binder resin may further comprise, apart from the resin having bisphenol units, up to 30 wt% of other types of resin such as polyesters, epoxy resins, nylon and cellulose acetate resins. In this case, the binder resin should be arranged to have a glass transition point Tg not lower than 55°C.

The sublimable dyes may be disperse dyes, oil-soluble dyes and the like, and are used in amounts of 10 to 200 parts, more preferably 30 to 120 parts, by weight per 100 parts by weight of the binder resin. Additives such as, for example, surface active agents, fillers, crosslinking agents and the like, may be added as required. The substrate may be a thin paper having a high density and a smooth surface, for example condenser paper, or a heat-resistant film of a plastics resin such as a polyester, polyimide, polyamide or the like. The thickness is generally in the range of 3 - 25 µm, preferably 3 - 10 µm.

A resin having bisphenol units is chosen as a main component for the binder resin, which has a glass transition point Tg not lower than 55°C. As a result, crystallisation of a sublimable dye and migration of the sublimable dye towards either side of the ink ribbon can be prevented. Accordingly, the storage stability of the ink ribbon increases providing a prolonged life of the ribbon, and a clear image can be obtained by using the ribbon for thermal transfer of the sublimation dyes.

EXAMPLES

Example 1

An ink having the following formulation was prepared and was coated on one side of a condenser paper by the use of a gravure plate having a screen ruling of 185/inch (about 72.8/cm) and a depth of 40 µm, thereby forming a dye carrier ribbon.

Panlite L1225 (Tradename, made by Teijin Ltd., polycarbonate resin, Tg 145°C)	..... 10 parts by weight
Sumiplast Yellow FC (made by Sumitomo Chem. Ind. Co., Ltd., sublimation dye)	..... 10 parts by weight
Methylene chloride (solvent)	..... 80 parts by weight

Example 2

An ink having the following formulation was prepared and a dye carrier ribbon was made in the same manner as in Example 1.

Epikote 1007 (Tradename, made by Yuka Shell Epoxy K.K., bisphenol A-type epoxy resin, Tg 77°C) ..... 3.3 parts by weight

Kayaset Yellow G (made by Nippon Kayaku Co.. Ltd., sublimable dye) ..... 3.3 parts by weight

Fine silica powder R972 (made by Nippon Aerosil Co., Ltd.) ..... 3.3 parts by weight

Methyl ethyl ketone (solvent) ..... 62.4 parts by weight

Diacetone alcohol (solvent) ..... 26.7 parts by weight

Example 3

An ink having the following formulation was prepared and a dye carrier ribbon was made in the same manner as in Example 1.

YP-50 (made by Toto Kasei Co., Ltd., phenoxy resin, Tg 100°) ..... 10 parts by weight

Sumiplast Blue OA (made by Sumitomo Chem. Ind. Co., Ltd., sublimable dye) ..... 10 parts by weight

Methyl ethyl ketone (solvent) ..... 56 parts by weight

Toluene (solvent) ..... 24 parts by weight

Example 4

An ink having the following formulation was prepared and applied onto a 10 µm thick condenser paper in a layer having a thickness of 1 µm, thereby forming a dye carrier ribbon.

U-100 (made by Unitika Ltd., polyacrylate resin, Tg 190°C) ..... 10 parts by weight

Sumiplast Red 3B (made by Sumitomo Chem. Ind. Co., Ltd., sublimable dye) ..... 10 parts by weight

Methyl ethyl ketone (solvent) ..... 80 parts by weight.

Example 5

Example 4 was repeated except that Epotot YD-012 (made by Toto Kasei Co., Ltd., bisphenol A-type epoxy resin, Tg 60°C) was used instead of U-110, thereby obtaining a dye carrier ribbon.

Example 6

Example 4 was repeated except that Epotot YD-017 (made by Toto Kasei Co., Ltd., bisphenol A-type epoxy resin, Tg 77°C) was used instead of U-110, thereby obtaining a dye carrier ribbon.

Example 7

Example 4 was repeated except that there was used, instead of U-100, a mixed resin (Tg 62°C) of 9 parts by weight of Epotot YD-014 (made by Toto Kasei Co., Ltd., bisphenol A-type epoxy resin, Tg 65°C) and 1 part by weight of TP-219 (made by Nippon Synthetic Chem. Ind. Co., Ltd., polyester resin, Tg 40°C), thereby obtaining a dye carrier ribbon.

Example 8

Example 4 was repeated except that there was used, instead of U-100, a mixed resin (Tg 57°C) of 7 parts by weight of YD-012 (Tg 60°C) and 3 parts by weight of UE-3300 (made by Unitika Ltd., polyester resin, Tg 50°C), thereby forming a dye carrier ribbon.

Example 9

Example 4 was repeated except that there was used, instead of U-100, a mixed resin (Tg 83°C) of 7 parts by weight of Phenototo YP-50 (made by Toto Kasei Co., Ltd., phenoxy resin, Tg 100°C) and 3 parts by weight of UE-3300 (Tg 50°C), thereby forming a dye carrier ribbon.

Example 10

Example 4 was repeated except that there was used, instead of U-100, a mixed resin (Tg 75°C) of 7 parts by weight of Epotot YD-014 (Tg 65°C) and 3 parts by weight of MH-101-2 (made by Fujikura Kasei Co. Ltd., Polymethyl methacrylate resin, Tg 105°C), thereby forming a dye carrier ribbon.

Comparative Example 1

An ink having the following formulation was prepared and printed on one side of a condenser paper by means of a gravure plate having a screen ruling of 183/inch (about 72.0/cm) and a depth of 40 μm, thereby forming a dye carrier ribbon.

Ethyl cellulose N-7
(made by Hercules Inc., Tg 47°C) ..... 10 parts by weight
Sumiplast Yellow FC
(Sumitomo Chem. Ind. Co., Ltd., sublimable dye)
..... 10 parts by weight
Methyl ethyl ketone (solvent) ..... 80 parts by weight

Comparative Example 2

An ink having the following formula was prepared and used to make a dye carrier ribbon in the same manner as in Comparative Example 1.

Cellulose acetate
(made by Daicell Chem. Co., Ltd., Tg 140°C)
..... 3.3 parts by weight
Kayaset Yellow G
(made by Nippon Kayaku Co., Ltd., sublimable dye)
..... 3.3 parts by weight
Fine silica powder R972
(made by Nippon Aerosol Co., Ltd.) ..... 3.3 parts by weight
Methyl ethyl ketone (solvent) ..... 62.4 parts by weight
Diacetone alcohol (solvent) ..... 26.7 parts by weight

Comparative Example 3

An ink having the following formulation was prepared and used to make a dye carrier ribbon in the same manner as in Comparative Example 1.

Vyron #200 (made by Toyobo Co., Ltd.,
saturated polyester, Tg 67°C)
..... 10 parts by weight
Sumiplast Blue A (made by Sumitomo Chem., Ind. Co., Ltd.,
sublimable dye) ..... 10 parts by weight
Methyl ethyl ketone (solvent) ..... 10 parts by weight
Toluene (solvent) ..... 10 parts by weight

The dye carrier ribbons of Examples 1 to 10 and Comparative Examples 1 to 3 were each applied with a 10% stearic acid solution in ethanol on the surface thereof in an amount of 0.1 g/m^2 after drying, and were aged by allowing them to stand for 1 week under conditions of 40°C and 90% R.H. (relative humidity). The dye carrier ribbon aged by this process was used for printing on printing paper by the use of a thermal print head. As a result, it was found that no crystal growth of the dyes took place in the dye carrier ribbons of Examples 1 to 10 and accordingly the ribbons could yield good images similar to those obtained prior to ageing. On the other hand, with the dye carrier ribbons of Comparative Examples 1 to 3 in which crystals of the dyes were formed, roughness which was considered to arise from irregularities in density resulting from the influence of the crystals was observed at half-tone portions on the obtained print. Also, colour was developed at portions other than the portions which were intended to be printed, thus lowering the image quality.

When the binder resin in the dye carrier ribbon has a glass transition point Tg not lower than 55°C and is mainly composed of a resin having bisphenol units, the storage stability of the dye carrier ribbon increases, and a prolonged life is obtained. The degree of freedom in selection of the sublimable dye to be mixed with the binder resin increases. When this type of dye carrier ribbon is used to transfer an image on to printing paper, a clear and very fine image is obtained.

CLAIMS

1. A dye carrier ribbon for hard copy sublimation transfer, the dye carrier ribbon comprising a substrate (9) and an ink layer (Y, M, C or B) formed on a surface of said substrate (9), said ink layer (Y, M, C or B) mainly comprising a sublimation dye and a binder resin, said binder resin comprising a resin having bisphenol units therein, and said binder resin having a glass transition point (Tg) not lower than 55°C.

2. A dye carrier ribbon according to claim 1, wherein said resin having bisphenol units therein is present in a proportion which is more than 70 percent by weight of said binder resin.

3. A dye carrier ribbon according to claim 1 or claim 2, wherein said sublimation dye is present in said ink layer in a proportion between 10 and 200 parts by weight for 100 parts by weight of said binder resin.

0228294

FIGURE