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(54) **Dye donor element and method for making an image according to thermal dye transfer printing**

(57) The present invention discloses a dye donor element comprising on a support a dye donor layer comprising a dye dispersed in a binder, characterised in that said dye donor element has a relative elongation δL in the main direction and a relative elongation δB in the transverse direction such that the angle α between the resultant of the vector sum of δL and δB and the vector δL is less than 82° , said relative elongations δL and δB being measured under conditions of 200°C with a load of 200g for 10 minutes. Less wrinkles are formed in a thermal transfer printing process using a dye donor element according to the invention.

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Description

1. Field of the invention

5 The present invention relates to a dye donor element for use in thermal dye sublimation transfer printing.

2. Background of the invention

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

15 A dye donor element for use according to thermal dye sublimation transfer usually comprises a very thin support e.g. a polyester support, one side of which has been covered with a dye layer comprising the printing dyes. Usually, an adhesive or subbing layer is provided between the support and the dye layer.

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 dye layer) is typically provided with a heat-resistant layer to facilitate passage of the dye-donor element past the thermal printing head. An adhesive layer may be provided between the support and the heat-resistant layer.

25 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 02/128,899 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).

30 It has been observed that when prints have to be made using high printing energies, wrinkles are formed in the dye donor element during printing which may cause malfunction of the printing device and defects such as jamming or defects in the printed image. This phenomenon occurs in particular when the average printing power of said heat generating elements exceeds 4.5 W/mm^2 . 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. Conventional thermal printers usually operate with a maximum average printing power of 3 to 4.5 W/mm^2 . However, if higher print densities and/or faster printing speeds are wanted, the average printing power has to be higher than 4.5 W/mm^2 .

35 These high printing energies are used in thermal sublimation printers, which for the sublimation (or diffusion) of dye require substantially higher printing energies than thermal wax printers, in which delamination and fusion of the dye layer are caused.

40 The problem of wrinkles was also addressed in EP-A 383267 in which it was proposed to set the elastic modulus in at least one of the main and sub scanning directions of the dye donor element to 280 kg/mm^2 or more and to keep the ratio of elastic modulus of the main to the sub scanning direction between 0.8 and 1.3. However, it was found that wrinkles may still be formed with a dye donor element according to EP-A 383267.

3. Summary of the invention

45 Accordingly, it is an object of the present invention to provide a solution to the problem of wrinkles formed in a dye donor element during printing.

Further objects of the present invention will become clear from the description hereinafter.

50 According to the present invention there is provided a dye donor element comprising on a support a dye donor layer comprising a dye dispersed in a binder, characterised in that said dye donor element has a relative elongation δL in the main direction and a relative elongation δB in the transverse direction such that the angle α between the resultant of the vector sum of δL and δB and the vector δL is less than 82° , said relative elongations δL and δB being measured under conditions of 200°C with a load of 200g for 10 minutes.

According to the present invention there is further provided a thermal imaging system and a method for making an image as set out in the claims.

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4. Detailed description of the invention

The relative elongations δB and δL are determined as follows. A sample having a size of 200 by 40mm is cut from the dye donor element. On this sample two markers are provided at a distance of approximately 150mm. The sample

is then conditioned for half an hour at 24°C and 50% relative humidity and the distance between the markers is measured with an accuracy of 10µm. Subsequently the sample is put hanging with a weight of 200g on the bottom of the sample in an oven at 200°C for 10 minutes. Due to opening of the oven, the temperature inside drops to about 190°C. Accordingly, the time was not started before the oven temperature reached 197°C. Subsequently, the sample was again conditioned at 24°C and 50% relative humidity before measuring the distance between the markers again. From the distance between the markers before and after the oven a relative elongation is calculated. This test is performed in the main and sub scanning direction to obtain the relative elongations in these directions. The angle α between the resultant of the vector sum of δL and δB and the vector δL can then be calculated. According to the present invention, this angle should be less than 82°.

The angle α can be obtained by adjusting manufacturing parameters of the support of the dye donor element and/or the conditions at which the dye layer is applied to the support of the dye donor element, in particular, the temperature and time of drying when applying the dye donor element. Parameters in the production process of the support are e.g. the composition of the support, tensions applied during transport and winding of the support, heat set conditions and stretching. Preferably, the support is a polyester film support that is biaxially stretched. In particular, a polyethylene terephthalate film and polyethylene naphthalate film are preferred. Generally, a support for a dye donor element is produced at a larger width than the actual width needed for a dye donor element and several bands are cut from a produced film. It has been found that the angle α varies along the produced film and that generally the bands cut from both outsides of a produced film tend to have an angle that is outside the scope of the present invention whereas bands towards the center of a produced film tend towards angle values below 82°. During coating of the dye layer, this value may be further reduced depending on the actual coating conditions.

In accordance with a preferred embodiment, the dye donor element comprises a heat-resistant layer on the backside, i.e. the side opposite to the side containing the dye layer. The heat-resistant layer preferably comprises a binder and particles that may be meltable or non-meltable.

Non-meltable particles are e.g. talc particles, China clay particles, dolomite particles, silica particles and the like.

Meltable particles can be wax particles such as polyolefin particles such as polyethylene, polypropylene, amid wax particles such as stearamide and ethylenebisstearamide, ester wax particles such as carnauba wax, bees wax and glycerine monostearate, metal soap particles of fatty acids such as lithium stearate, magnesium stearate, zinc stearate and the like.

Particular useful particle mixtures are mixtures of talc, calcined aluminium silicate and a salt of a fatty acid and particle mixtures of calcined aluminium silicate and a salt of a fatty acid. In the above mentioned mixtures, the salt of the fatty acid is preferably zinc stearate.

The total amount of particles in the heat-resistant layer is generally not higher than 1 g/m² and smaller amounts usually suffice to clean the thermal printing head during the printing operation.

Colloidal silica such as Aerosil™ R972 (Degussa) can further be added to the heat-resistant layer.

The binder for the heat-resistant layer can be a cured binder or a polymeric thermoplast.

A cured binder can be produced by a chemical reaction as described in e.g. EP 153,880 and EP 194,106, or by the influence of moisture as described in e.g. EP 528 074, or by irradiation of a radiation-curable composition as described in e.g. EP 314,348 and EP 458,538.

Thanks to the fact that the coating procedure of polymeric thermoplasts is very convenient, they are preferably used as binder for the heat-resistant layer. Preferred polymeric thermoplasts are those having a glass transition temperature above 100°C; these thermoplasts are suited for use as binder in the heat-resistant layer, because they are dimensionally stable at higher temperatures. Polymers having a glass transition temperature above 170°C are especially preferred. Even more preferred polymeric thermoplasts are those that are soluble in ecologically acceptable solvents such as ketones (e.g. ethyl methyl ketone and acetone) and alcohols (e.g. isopropanol).

Representatives of polymeric thermoplasts that are suited for use as binder in the heat-resistant layer are e.g. poly(styrene-co-acrylonitrile), polycarbonates derived from bisphenol A, polyvinyl butyral, polyvinyl acetal, ethyl cellulose, cellulose acetate butyrate, cellulose acetate propionate, and polyparabanic acid. Especially preferred polymeric thermoplasts are the polycarbonates derived from a bis-(hydroxyphenyl)-cycloalkane.

A heat-resistant layer of a dye-donor element according to the present invention may in addition to said particles and the binder comprise minor amounts of such other agents like surface-active agents and liquid lubricants.

A heat-resistant layer may contain other additives provided such materials do not inhibit the anti-sticking properties of the heat-resistant layer and provided that such materials do not substantially scratch, erode, contaminate, or otherwise damage the thermal printing head or harm image quality. Examples of suitable additives have been described in EP 389,153.

Suitable surface-active agents for a heat-resistant layer of the dye-donor element according to the present invention are i.a. : alkyl phenyl polyalkylene oxides e.g. Antarox™ CO 630 (GAF), alkyl polyalkylene oxides e.g. Renex™ 709 (ICI), and sorbitol esters e.g. Span™ 85 (ICI) and Tween™ 20 (ICI).

Preferred lubricants for use in a heat-resistant layer of the dye-donor element according to the present invention are polysiloxan-based lubricants. Among these polyalkylene oxide-modified polydimethylsiloxans such as Byk™ 320,

Byk™ 307, and Byk™ 330 (Byk Cera) and Tegoglide™ 410 (Goldschmidt) are especially preferred.

A heat-resistant layer of the dye-donor element according to the present invention is formed preferably by adding the polymeric thermoplastic binder or binder mixture and other optional components to a suitable solvent or solvent mixture, dissolving or dispersing the ingredients to form a coating composition, applying said coating composition to a support, which may have been provided first with an adhesive or subbing layer, and drying the resulting layer. It can be advantageous to use a ball mill to reduce the particle size of the particles in the coating solution.

A heat-resistant layer may be coated on the support or printed thereon by a printing technique such as a gravure process. A heat-resistant layer thus formed has a thickness of about 0.1 to 3 µm, preferably 0.3 to 1.5 µm.

Although the above-mentioned ingredients of a heat-resistant layer can be incorporated in one single layer, it is sometimes preferred to incorporate at least part of the additives such as lubricants and/or surface-active agents in a separate topcoat on top of the heat-resistant layer. As a result the lubricants and/or surface-active agents are in direct contact with the thermal printing head and thus lead to improved slipping properties of the dye donor element. It is highly preferred to add a polysiloxane based lubricant and/or a metal salt of a fatty acid to the heat-resistant layer and/or top coat layer. It is even more preferred to add a polymethylsiloxane based lubricant and zinc stearate to the heat-resistant layer and/or top coat layer.

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, EP 546 010, US 4,567,113, US 4,572,860, US 4,717,711, US 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 subbing layer may further comprise an aromatic polyol such as e.g. 1,2 dihydroxybenzene as described in EP 433,496.

Any dye can be used in the dye layer of the dye-donor element of the present invention provided it is transferable to the receiver sheet by the action of heat. Examples of suitable dyes have been described in e.g. EP 432,829, EP 400,706 and in the references mentioned therein. The amount ratio of dye or dye mixture to binder generally ranges from 9:1 and 1:3 by weight, preferably from 3:1 and 1:2 by weight.

The following polymers can be used as polymeric binder : cellulose derivatives, such as ethyl cellulose, hydroxyethyl cellulose, ethylhydroxy cellulose, ethylhydroxyethyl cellulose, hydroxypropyl 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, cellulose triacetate; vinyl-type resins and derivatives, such as polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral, copolyvinyl butyral-vinyl acetal-vinyl alcohol, polyvinyl pyrrolidone, polyvinyl acetoacetal, polyacrylamide; polymers and copolymers derived from acrylates and acrylate derivatives, such as polyacrylic acid, polymethyl methacrylate and styrene-acrylate copolymers; polyester resins; polycarbonates such as the polycarbonates described above for the heat resistant layer; copoly(styrene/acrylonitrile); polysulfones; polyphenylene oxide; organosilicones, such as polysiloxans; epoxy resins and natural resins, such as gum arabic. Preferably, the binder for the dye layer of the present invention comprises copoly(styrene/acrylonitrile).

The dye layer may also contain other additives such as i.a. thermal solvents, stabilizers, curing agents, preservatives, organic or inorganic fine particles, dispersing agents, antistatic agents, defoaming agents, and viscosity-controlling agents, these and other ingredients being described more fully in EP 133,011, EP 133,012, EP 111,004, and EP 279,467.

Dendrimers, also called highly branched non-crosslinked polymers can be added as a density improving agent or thermal solvent to the dye layer of the dye donor element in order to improve the dye transfer efficiency during printing. Highly branched, non-crosslinked polymers have been prepared by "multiple generation" and "single generation" procedures. Dendrimeric latices suitable for use in the present invention, can be prepared by a multiple generation procedure. Such procedures have been described e.g. by Tomalia, D.A. and others in *Angewandte Chemie, Int. Ed. in English*, 29, 138-175 (1990), in EP-A 66366 and in WO 84/2705 etc.. In these disclosures, highly branched non-crosslinked polymers or oligomers are described, in particular polyamido amines and polybenzyl ethers.

Further methods for preparing dendrimers are disclosed in EP-A 582842, EP-A 583608, EP-A 583609 and WO 93/017060. Dendrimers are also commercially available from DSM (Netherlands) and DENDRITECH (USA).

Addition of beads of polyolefin waxes or amid waxes, and/or of polymethylsilylsesquioxan particles, as described in EP 554 583, to the dye layer, said beads and/or particles protruding from the surface of said layer, is especially preferred.

A dye-barrier layer comprising a hydrophilic polymer may also be employed between the support and the dye layer of the dye-donor element to enhance the dye transfer densities by preventing wrong-way transfer of dye backwards to the support. The dye barrier layer may contain any hydrophilic material that is useful for the intended purpose. In general, good results have been obtained with gelatin, polyacrylamide, polyisopropylacrylamide, butyl methacrylate-grafted

gelatin, ethyl methacrylate-grafted gelatin, ethyl acrylate-grafted gelatin, cellulose monoacetate, methyl cellulose, polyvinyl alcohol, polyethyleneimine, polyacrylic acid, a mixture of polyvinyl alcohol and polyvinyl acetate, a mixture of polyvinyl alcohol and polyacrylic acid or a mixture of cellulose monoacetate and polyacrylic acid. Suitable dye barrier layers have been described in e.g. EP 227,091 and EP 228,065. Certain hydrophilic polymers e.g. those described in EP 227,091 also have an adequate adhesion to the support and the dye layer so that the need for a separate adhesive or subbing layer is avoided. These particular hydrophilic polymers used in a single layer in the dye-donor element thus perform a dual function, hence are referred to as dye-barrier/subbing layers.

The support for the image receiving element that is used with the dye-donor element 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 a baryta-coated paper, polyethylene-coated paper or white polyester i.e. white-pigmented polyester. Blue-coloured polyethylene terephthalate film can also be used as support.

To avoid poor adsorption of the transferred dye to the support of the image receiving element this support must be coated with a special layer called dye-image-receiving layer, into which the dye can diffuse more readily. The dye-image-receiving layer may comprise e.g. a polycarbonate, a polyurethane, a polyester, a polyamide, polyvinyl chloride, polystyrene-co-acrylonitrile, polycaprolactone, or mixtures thereof. The dye-image receiving layer may also comprise a heat-cured product of poly(vinyl chloride/co-vinyl acetate/co-vinyl alcohol) and polyisocyanate. Suitable dye-image-receiving layers have been described in e.g. EP 133,011, EP 133,012, EP 144,247, EP 227,094, and EP 228,066.

Dendrimers can be added as a plasticizer to the receiving layer in order to increase the density of the printed image. Moreover, it can act as a coreactant in the cross-linking process when a cured image-receiving layer is used. In this case, functional groups such as e.g. carboxyl groups, hydroxyl groups or amino groups are required.

In order to improve the light resistance and other stabilities of recorded images, UV absorbers, singlet oxygen quenchers such as HALS-compounds (Hindered Amine Light Stabilizers) and/or antioxidants may be incorporated into the dye-image-receiving layer.

The dye layer of the dye-donor element or the dye-image-receiving layer of the image receiving element may also contain a releasing agent that aids in separating the dye-donor element from the receiving element after transfer. The releasing agents can also be applied in a separate layer on at least part of the dye layer or of the dye-image-receiving layer. Suitable releasing agents are solid waxes, fluorine- or phosphate-containing surfactants and silicone oils. Suitable releasing agents have been described in e.g. EP 133,012, JP 85/19,138, and EP 227,092.

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

Preferably, the average printing power applied by means of a thermal printing head during the image-wise heating of the dye-donor element is higher than 4.5 W/mm².

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

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

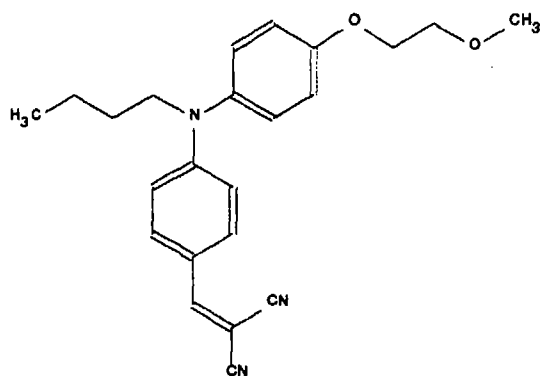
EXAMPLE 1

A series of dye-donor elements having different angles α for use according to thermal dye sublimation transfer were prepared as follows.

Polyethylene terephthalate film having a thickness of 6 μ m was provided on both sides with a subbing layer from a solution of copolyester comprising isophthalic acid units/terephthalic acid units/ethylene glycol units/neopentyl glycol units/adipic acid units/glycerol units in ethyl methyl ketone.

A solution comprising 6% by weight of dye A, 6 % by weight of dye B, and 10 % by weight of poly(styrene-co-acrylonitrile) as binder in ethyl methyl ketone as solvent was prepared :

C.I. Disperse Yellow 201 Dye A



Dye B

From the resulting solution a layer having a wet thickness of 9 μm was coated on the subbed polyethylene terephthalate film. The resulting dye layer was dried by evaporation of the solvent.

A heat-resistant layer having a wet thickness of 4.8 μm was coated on the subbed back of the polyethylene terephthalate film from a solution in ethyl methyl ketone containing a polycarbonate binder PCI (13% by weight), 0.5% zinc stearate particles having an average particle size of 3.5 μm , 1% Tegoglide 410 (Goldsmidt), and talc particles in an amount of 0.5%.

PCI: A polycarbonate derived from 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane having a molecular weight such that a relative viscosity of 1.295 (measured in a 0.5% by weight solution in dichloromethane) is obtained.

Receiver sheets were prepared by coating a polyethylene terephthalate film support having a thickness of 175 μm with a dye-image-receiving layer from a solution in ethyl methyl ketone of 3,6 g/m² of poly(vinyl chloride/co-vinyl acetate/co-vinyl alcohol) (Vinylite VAGD supplied by Union Carbide), 0,200 g/m² of diisocyanate (Desmodur N75 supplied by Bayer AG), and 0,2 g/m² of hydroxy-modified polydimethylsiloxan (Tegomer H SI 2111 supplied by Goldschmidt).

Each dye-donor element was printed in combination with a receiver sheet in a printer set-up using a Kyocera thermal printing head, Type KGT-219-12MP4-75PM at an average power of 60 mW per dot (total amount of energy applied to one resistor element divided by the total line time, 80 mW with a duty cycle of 75%). The surface of the heater element measured 68 by 152 mm. Consequently, the average printing power applied to the heater elements was 5.8 W/mm².

The results obtained were as follows:

Sample no.	angle α	wrinkles
1	64	no
2	71	no
3	73	no
4	81	no
5	84	yes
6	85	yes
7	86	yes

EXAMPLE 2

The same experiment as set out in example 1 was repeated with the exception however that a polyethylene naphthalate film was used as support having an angle α of 51°. No wrinkles were found.

Claims

1. Dye donor element comprising on a support a dye donor layer comprising a dye dispersed in a binder, characterised in that said dye donor element has a relative elongation δL in the main direction and a relative elongation δB in the transverse direction such that the angle α between the resultant of the vector sum of δL and δB and the vector δL is less than 82° , said relative elongations δL and δB being measured under conditions of 200°C with a load of 200g for 10 minutes.
2. A dye donor element according to claim 1 wherein said support is a polyester film support.
3. A dye donor element according to claim 2 wherein said polyester is a polyethylene terephthalate or a polyethylene naphthalate.
4. A dye donor element according to claim 1 further comprising a lubricant layer provided on a side of the support opposite to the side comprising said dye donor layer.
5. A thermal imaging system comprising a dye donor element as defined in any of the above claims and a receiving element for use in combination with said dye donor element, said receiving element comprising on a support a receiving layer.
6. A method for making an image comprising the steps of:
 - (i) bringing a dye layer of a dye donor element as defined in any of claims 1 to 5 in face-to-face relationship with a receiving layer of a receiving element;
 - (ii) image-wise heating a thus obtained assemblage thereby transferring dye from said dye donor element to said receiving layer of said receiving element in accordance with an amount of heat supplied;
 - (iii) separating said dye donor element from said receiving element.



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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 0077

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,D	EP-A-0 383 267 (DAI NIPPON INSATSU KABUSHIKI KAISHA) * page 2, line 45 - page 3, line 10 * * page 5, line 25 - line 52 * * claim 1; table 1 * ---	1-6	B41M5/38
X	PATENT ABSTRACTS OF JAPAN vol. 11, no. 205 (M-603), 3 July 1987 & JP-A-62 023789 (MATSUSHITA ELECTRIC INDUSTRIAL COMPANY LIMITED), 31 January 1987, * abstract * -----	1-6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11 June 1996	Examiner Bacon, A
CATEGORY OF CITED DOCUMENTS 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 T : 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			

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