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(54) **Thermal transfer imaging.**

- (57) A method of forming a colour image comprising the steps of :
- (i) assembling in face-to-face contact a) a colourant donor element comprising a thermally transferable colourant and an infrared absorber and b) a receptor element ;
 - (ii) subjecting the assembly to image-wise exposure to infrared radiation whereby said radiation is absorbed by the infrared absorber, causing localised heating in the donor element and transfer of colourant to the receptor ;
 - (iii) separating the donor element from the image bearing receptor ;
 - (iv) optionally repeating steps (i) to (iii) one or more times using donor elements comprising different colourants and the same receptor in order to form a multicolour image ;
- in which a thermal bleaching agents capable of bleaching the infrared absorber is present in one or both of the donor and receptor elements, or is brought into contact with the transferred image in a subsequent step.

FIELD OF THE INVENTION

This invention relates to methods of thermal transfer imaging in which a donor element comprising a colourant and an infrared (IR) absorber is assembled in face-to-face contact with a receptor element and the assembly exposed imagewise to IR radiation to effect transfer of colourant from the donor to the receptor.

BACKGROUND TO THE INVENTION

There is growing interest in the generation of colour images via thermal transfer, and in particular via thermal transfer that is mediated by IR radiation. In such a system, a donor sheet comprising a layer of colourant and an IR absorber is placed in contact with a receptor and the assembly exposed to a pattern of IR radiation, normally from a scanning laser source. The radiation is absorbed by the IR absorber, causing a rapid build-up of heat in the exposed areas of the donor which in turn causes transfer of colourant from those areas to the receptor. By repeating the process with one or more different coloured donors, a multi-colour image can be assembled on a common receptor. The system is particularly suited to the colour proofing industry, where colour separation information is routinely generated and stored electronically and the ability to convert such data into hardcopy via digital address of "dry" media is seen as a great advantage.

The heat generated in the donor element may cause colourant transfer by a variety of mechanisms. For example, there may be a rapid build up of pressure as a result of decomposition of binders or other ingredients to gaseous products, causing physical propulsion of colourant material to the receptor ("ablation transfer"), as disclosed in U.S. 5,171,650 and WO90/12342. Alternatively, the colourant and associated binder materials may transfer in a molten state ("melt-stick transfer"), as disclosed in JP63-319192. Both of these mechanisms produce mass transfer, i.e. there is essentially 0% or 100% transfer of colourant depending on whether the applied energy exceeds a certain threshold. Diffusion or sublimation transfer involves a different mechanism in which a colourant is diffused (or sublimed) to the receptor without co-transfer of binder. This process enables the amount of colourant transferred to vary continuously with the input energy. Examples of this process are disclosed in U.S. 5,126,760 and numerous other patents.

A problem common to all these imaging methods is that of transfer of some or all of the IR absorber along with the colourant. Unless the IR absorber is completely colourless, the final image is contaminated and not a true colour reproduction, and hence unacceptable for high quality proofing purposes. Attempts have been made to minimise co-transfer by placing the IR absorber in a layer separate from the colourant (which may affect the sensitivity) and to find IR absorbers with minimal visible absorption, see, for example, EP 0157568. In practice, however, there is always some residual absorption, which has limited the usefulness of the technology.

U.S. 5,219,703 discloses laser-induced thermal dye transfer using heat transferable dyes, bleachable and heat transferable near-infrared absorbing sensitisers, acid photogenerating compounds and optional near-ultraviolet absorbing sensitisers. The combination of the near-infrared absorbing sensitiser and acid photogenerating compounds effects transfer of the heat transferable dyes and bleaching of the near-infrared absorbing sensitiser to eliminate unwanted visible light absorption. The acid photogenerating compound may be present in either the dye donor or dye receiver element. If the acid photogenerator is in the dye donor, bleaching will occur upon initial exposure of the dye donor to near-infrared or near-ultraviolet radiation. If present in the dye receiver element, bleaching will occur upon subsequent exposure of the dye receiver to near-infrared or near-ultraviolet radiation.

It has now been found that the use of thermal bleaching agents with bleachable IR absorbers provides an effective system for reducing residual absorption for IR absorber in a thermal transfer imaging process.

BRIEF SUMMARY OF THE INVENTION

Therefore according to the present invention there is provided a method of forming a colour image comprising the steps of:

- (i) assembling in face-to-face contact a) a colourant donor element comprising a thermally transferable colourant and an infrared absorber and b) a receptor element;
- (ii) subjecting the assembly to image-wise exposure to infrared radiation whereby said radiation is absorbed by the infrared absorber, causing localised heating in the donor element and transfer of colourant to the receptor;
- (iii) separating the donor element from the image bearing receptor;
- (iv) optionally repeating steps (i) to (iii) one or more times using donor elements comprising different colourants and the same receptor in order to form a multicolour image;

in which a thermal bleaching agent capable of bleaching the infrared absorber is present in one or both of the donor and receptor elements, or is brought into contact with the transferred image in a subsequent step.

The term "thermal bleaching agent" used herein refers to bleaching agents which do not require exposure to light to become active but will bleach dyes at ambient or elevated temperatures.

5 The term "bleaching" means a substantial reduction in absorption(s) giving rise to colour visible to the human eye, regardless of how this is achieved. For example, there may be an overall reduction in the intensity of the absorption, or it may be shifted to non-interfering wavelengths, or a change in shape of the absorption band (a narrowing) may be sufficient to render the IR absorber colourless.

10 Preferably the thermal bleaching agent is present in a receptor layer on the surface of the receptor element, or in the donor element, but it is also possible to deposit the thermal bleaching agent on the transferred image by appropriate means in an additional step subsequent to step (iii) or step (iv). In a further embodiment, the image residing on the receptor element after step (iii) or step (iv) may be further transferred to a second receptor which comprises a layer containing a thermal bleaching agent.

15 Thermal bleaching of IR dyes is known in fields unrelated to that of thermal transfer imaging, notably in antihalation layers of IR-sensitive photothermographic media, as described, for example, in U.S. 5,135,842 and U.S. Patent Application Serial No. 07/993650, filed 21st December, 1992. U.S. Patent Application Serial No. 07/993642, filed 21st December, 1992 discloses thermal carbanion generating agents for use in such systems. Also, various patents disclose IR dye-bleach systems for optical data storage, e.g., U.S. 5,166,041 and U.S. 5,185,233, and Japanese Patent Application 05-024342 discloses laser addressed recording materials involving an amine dye-bleach step subsequent to the laser exposure, but colourant transfer is not involved.

20 The IR absorber should have the properties normally required for use in thermal transfer media, i.e., strong absorption in the desired region (normally in the range 650 to 1200 nm), ability to be incorporated in a uniform layer in the donor (with or without other ingredients), stability to normal conditions of heat, light, humidity etc., yet should be rapidly and irreversibly bleached by the action of the bleaching agent.

25 Likewise, the bleaching agent should be compatible with the resins commonly used in donor and receptor elements for thermal colourant transfer, should be stable under normal conditions of temperature, light and humidity, and must not give rise to any visible colouration of the receptor, yet it should, when required, react rapidly and irreversibly with the IR absorber to cause bleaching of the latter.

30 A variety of IR absorber/bleaching agent combinations are possible. For example, U.S. 5,185,233, discloses the bleaching of IR dyes by free radicals released by thermal decomposition of species such as azo compounds, diacyl peroxides, dialkyl peroxides, hydroperoxides, carbonyl compounds, halogen compounds, organometallic compounds and persulphates. Hence one or more of these species may be incorporated in the receptor layer or in the donor as the thermal bleaching agent.

35 The preferred bleaching method for use in this invention is bleaching by nucleophiles, such as, amines and carbanions. A large number of dyes of different structural types are known to be bleached by amines, see for example, EP 0518470. Dyes known in the art to be amine-bleachable include triarylmethane, styryl, benzylidene, indophenol, polymethine, merocyanine and azine dyes, hence IR-absorbing members of these classes are potentially suitable for use in the invention. Not all members of the above classes are necessarily amine-bleachable, but the suitability of a particular dye may be assessed by treating a solution of the dye in question with at least an equivalent quantity of an amine and recording any change in the absorption spectrum, after warming the mixture if necessary.

40 A preferred class of IR absorbing dyes that is known to be bleachable by nucleophiles are the tetraarylpolymethine (TAPM) dyes. These generally absorb in the 700 to 900 nm region, making them suitable for diode laser address. JP63-319191, JP63-319192 and U.S. 4,950,639 disclose their use as absorbers in laser addressed thermal transfer media. However, none of these references addresses the problem of co-transfer of these dyes with the colourant which gives a blue cast to the transferred image because the TAPM dyes generally have absorption peaks which tail into the red region of the spectrum.

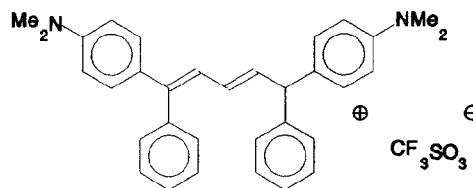
45 The general formula for TAPM dyes is disclosed in U.S. 5,125,842. Dyes of this class have been shown to be bleachable by free amines (EP 05118470), thermally-generated amines (U.S. 5,135,842) and thermally-generated carbanions (U.S. Serial No. 07/993650).

50 A preferred dye of this class is Dye I:-

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Dye I has the unexpected property of partially autobleaching during the imaging process, so that the bleaching process requires lower concentrations of bleaching agent and/or shorter reaction times. Another class of dye found to be susceptible to nucleophilic bleaching is that of the diamine dication dyes, disclosed for example in WO90/012342 and JP51-88016, an example of which is commercially available under the trade name CYASORB IR165 (American Cyanamid). Although these dyes show peak absorptions at relatively long wavelengths (ca. 1050 nm, suitable for YAG laser address), the absorption band is broad and tails into the red region. This unwanted absorption may be bleached in the manner described for the TAPM dyes, but in some cases a new absorption appears at around 450nm, which restricts the usefulness unless further bleaching agents or optical brighteners are employed.

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With regard to the construction of the donor elements, apart from the choice of IR absorber the only constraint is that the colourant should be substantially inert towards the bleaching agent. Within these constraints, any of the donor element constructions known in the art of laser thermal transfer imaging may be used. Thus, the donor may be adapted for sublimation transfer, ablation transfer or melt-stick transfer. Typically, the donor element comprises a substrate (such as polyester sheet), a layer of colourant and the IR absorber, which may be in the same layer as the colourant, in a separate layer, or both. Other layers may be present, such as dynamic release layers as disclosed in U.S. 5,171,650. Alternatively, the donor may be self-sustaining, as taught in EP 0491564. The colourant generally comprises one or more dyes or pigments of the desired colour dissolved or dispersed in a binder, although binder-free colourant layers are also possible, as disclosed in International Patent Application No. PCTGB92/01489. Preferably, the colourant comprises dyes or pigments that reproduce the colours shown by standard printing ink references provided by the International Prepress Proofing Association, known as SWOP colour references.

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The preferred bleaching agents for use with the invention are amines and carbanions, and many types of dye are known to be bleachable by such species. Therefore, colourant dyes, e.g., for sublimation transfer, must be chosen with care and screened for possible interactions with the bleaching agent. For this reason, preferred donor elements comprise a colourant layer in the form of a dispersion of pigment particles in a binder as this greatly reduces the likelihood of unwanted colourant bleaching. Particularly preferred donor elements are of the type disclosed in British Patent Application No. 9225724 in which the colourant layer comprises a fluoro-carbon compound in addition to pigment and binder.

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In certain embodiments, the bleaching agent is incorporated in the donor element. In such situations it is vital that the bleaching reaction does not occur prematurely, i.e., during coating or storage of the element and so such embodiments preferably employ the bleaching agent in "masked" form, i.e., a compound that decomposes thermally to release the active bleaching agent. Examples include the free-radical generators disclosed in U.S. 5,185,233 and thermal amine and carbanion generators referred to previously. These include salts which decompose thermally to release amines. Suitable examples include the salts of arylsulphonylacetic acids with amines such as guanidine, dicyclohexylamine etc., as disclosed in U.S. 5,135,842. The preferred class of bleaching agent for incorporation in the donor are quaternary ammonium phenylsulphonylacetates, such as tetramethylguanidinium nitrophenylsulphonylacetate, as disclosed in U.S. Serial No. 07/993642. These compounds are stable at room temperature, but decompose rapidly at elevated temperatures to produce carbanionic species which react rapidly and irreversibly with dyes of the TAPM class to give colourless products.

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Masked bleaching agents can be coated in the same layer of the donor element as the IR absorber. If a "free" bleaching agent is included in the donor, then it must be contained in a layer separate from that containing the IR absorber, e.g., by adopting the technology described in EP 0518470.

Apart from the optional presence of the bleaching agent, the receptor elements used in the invention are entirely conventional. The elements typically comprise a substrate, such as paper or plastic sheet, bearing one or more resin coatings containing the thermal bleaching agent. The choice of the resin for the receptor layer e.g. in terms of Tg, softening point etc., may depend on the type of transfer involved (ablation, melt-stick or

sublimation), but for use with the preferred donor elements, Butvar B76 (Monsanto) and similar thermoplastic materials are highly suitable.

In the embodiments of the invention in which the bleaching agent is not present initially in the receptor, the receptor need not comprise a resin layer, e.g., plain paper may be used as the receptor.

The preferred bleaching agents are nucleophiles such as amines and carbanions. If a free amine is incorporated in the receptor layer, it is preferably non-volatile. Suitable examples are disclosed in EP 0518470, e.g., diethylenetetramine, triethylenepentamine etc. Polymeric amines such as polyethyleneimine are also suitable. An alternative to the use of free amines is the use of amine salts which decompose thermally to release amines. Suitable examples include the salts of arylsulphonylacetate acids with amines such as guanidine, dicyclohexylamine etc. as disclosed in U.S. 5,135,842. The preferred class of bleaching agent for incorporation in the receptor layer are quaternary ammonium phenylsulphonylacetates, such as tetramethylguanidinium nitrophenylsulphonylacetate, as described in U.S. Serial No. 07/993642. These compounds are stable at room temperature, but decompose rapidly at elevated temperatures to produce carbanionic species which react rapidly and irreversibly with dyes of the TAPM class to give colourless products.

The amount of bleaching agent employed may vary considerably, depending on the concentration and characteristics of the IR absorber used, e.g. its propensity for co-transfer with the colourant, the intensity of its visible colouration etc. Generally, loadings of from 1 to 10 wt% of the solids in the receptor layer are suitable, normally 3 to 5 wt%.

The procedure for imagewise transfer of colourant from donor to receptor is conventional. The two elements are assembled in intimate face-to-face contact, e.g. by vacuum hold down or alternatively by means of the cylindrical lens apparatus described in British Patent Application No. 9220271 and scanned by a suitable laser. The assembly may be imaged by any of the commonly used lasers, depending on the absorber used, but address by near infrared emitting lasers such as diode lasers and YAG lasers, is preferred. Any of the known scanning devices may be used, e.g. flat-bed scanners, external drum scanners or internal drum scanners. In these devices, the assembly to be imaged is secured to the drum or bed, e.g., by vacuum hold-down, and the laser beam is focused to a spot, e.g., of about 20 microns diameter on the IR-absorbing layer of the donor. This spot is scanned over the entire area to be imaged while the laser output is modulated in accordance with electronically stored image information. Two or more lasers may scan different areas of the donor receptor assembly simultaneously, and if necessary, the output of two or more lasers may be combined optically into a single spot of higher intensity. Laser address is normally from the donor side, but may be from the receptor side if the receptor is transparent to the laser radiation.

Peeling apart the donor and receptor reveals a monochrome image on the receptor that will in most cases be contaminated by co-transfer of the IR absorber. The process may be repeated one or more times using donor sheets of different colours so as to build a multi-colour image on a common receptor. In the embodiments in which a bleaching agent is present in the receptor layer, all that is required to produce a "clean" image is an overall heat treatment of the image to activate or accelerate the bleach chemistry. In the embodiments in which the bleaching agent is present in the donor, further thermal treatment may not be necessary.

In certain embodiments, the bleaching agent is present initially in neither the donor nor the receptor, and an additional step is required to bring it into contact with the contaminated image. Whilst this technique requires an extra step, it does allow the use of an uncoated receptor, such as plain paper. Any suitable means may be employed to apply the bleaching agent to the transferred image, but "wet" methods such as dipping, spraying etc. are not preferred. A suitable dry method is thermal lamination and subsequent peeling of a separate donor sheet containing the thermal bleaching agent. Any of the thermal bleaching agents described previously are suitable for use in this embodiment.

In some situations, the receptor to which the colourant image is initially transferred is not the final substrate on which the image is viewed. For example, U.S. 5,126,760 discloses thermal transfer of the image from the first receptor to a second receptor for viewing purposes. In such cases, it may be convenient to provide the thermal bleaching agent in the second receptor. The invention will now be illustrated by the following Examples.

In the following Examples all donor sheets are made in accordance with British Patent Application No. 9225724. "FC" refers to N-methyl perfluorooctanesulphonamide (U.S. 2,732,398). "Millbase" refers to a dispersion produced from 36 parts by weight 2-butanone and 4 parts by weight pigment chips. The pigment chips were made by conventional methods and comprised pigment particles and VAGH resin in 3 : 2 ratio by weight. (VAGH resin is a copolymer of vinyl chloride and vinyl acetate which is partially hydrolysed and commercially available from Union Carbide).

Coatings were made using wire-wound bars and were dried at ambient temperature.

Example 1

The following solution was coated at 12 micron wet thickness on unsubbed polyester base:-

5	magenta millbase	5.5g
	2-butanone	1.0g
	ethanol	1.0g
10	Dye I	0.075g
	FC	0.1g

The first four ingredients were mixed for 1 hour before adding the FC.

15 The resulting coating showed an absorption maximum at 830nm due to the IR dye with a shoulder at 750nm and a tail extending below 700nm (in addition to the magenta pigment absorptions).

A sheet comprising a layer of bleaching agent was prepared by coating plain photocopier paper with the following solution at 36 micron wet thickness:

20 0.2g tetramethylguanidinium nitrophenylsulphonylacetate
2.5g methanol
5.0g Butvar B76 (10 wt% solution in 2-butanone)

Samples of each coating were held in face-to-face contact and heated at 100°C for 1 minute then peeled apart. The absorption spectrum of the pigmented coating showed complete disappearance of the IR dye absorptions, with no change in the magenta pigment absorptions.

25 The process was repeated using cyan and yellow coatings with the same result.

This Example demonstrates the selective bleaching of the IR dye, and that the bleaching agent can be applied from a separate sheet.

Example 2

30 This Example demonstrates the selective bleaching of a different class of IR dye. The following dispersion was prepared:-

27.5g magenta millbase
7.5g 2-butanone
35 2.5g ethanol
1.0g Cyasorb IR165

To 3.85g of this dispersion was added 0.05g FC and the mixture coated at 12 micron wet thickness on unsubbed polyester. The resulting coating showed an absorption from the IR dye extending from below 700nm to beyond 1200nm. After treatment with the guanidinium salt as described above, this absorption was found to have disappeared, although there was a slight increase in absorption in the range 400 to 500nm as a result of this treatment.

Example 3

45 A sample of the yellow coating from Example 1 was assembled with a plain paper receptor on an external drum scanner with vacuum hold down, and imaged via a laser diode delivering 100mW at 810nm focused to a 20 micron spot, and scanned at 200cm/sec. A 2mm stripe image was transferred to the receptor, and contamination by the IR dye was apparent both visually and by spectrometric analysis.

50 The process was repeated using the coated paper of Example 1 as receptor, and the transferred image was subjected to 30 second heating from a hot air blower. In this case no contamination by the IR dye was detectable. The process was repeated using the yellow, magenta and cyan coatings of Example 1 singly and in all possible overprinted combinations. In each case, transfer to the guanidinium-coated paper, followed by heat treatment, produced pure, uncontaminated colours.

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Claims

1. A method of forming a colour image comprising the steps of:

- (i) assembling in face-to-face contact a) a colourant donor element comprising a thermally transferable colourant and an infrared absorber and b) a receptor element;
(ii) subjecting the assembly to image-wise exposure to infrared radiation whereby said radiation is absorbed by the infrared absorber, causing localised heating in the donor element and transfer of colourant to the receptor;
(iii) separating the donor element from the image bearing receptor;
(iv) optionally repeating steps (i) to (iii) one or more times using donor elements comprising different colourants and the same receptor in order to form a multicolour image;
in which a thermal bleaching agent capable of bleaching the infrared absorber is present in one or both of the donor and receptor elements, or is brought into contact with the transferred image in a subsequent step.
2. A method as claimed in Claim 1 in which the donor element comprises a layer containing a thermal bleaching agent and/or the receptor element comprises a layer containing a thermal bleaching agent.
 3. A method as claimed in Claim 1 in which a thermal bleaching agent is brought into contact with the transferred colourant in a separate step.
 4. A method as claimed in any preceding Claim in which the thermal bleaching agent is a nucleophile.
 5. A method as claimed in Claim 4 in which the thermal bleaching agent is an amine, a carbanion or a compound capable of thermally generating an amine or carbanion.
 6. A method as claimed in any preceding Claim in which the thermal bleaching agent is selected from amine salts of arylsulphonylacetates and quaternary ammonium nitrophenylsulphonylacetates.
 7. A method as claimed in any preceding Claim in which the infrared absorber is a tetraarylpolymethine dye.
 8. A thermal dye transfer assemblage comprising a colourant donor element comprising a thermally transferable colourant and an infrared absorber; and a receptor element comprising a substrate for receiving colourant from the donor element, in which the assemblage contains a thermal bleaching agent in the donor element and/or the receptor element.
 9. A thermal dye transfer assemblage as claimed in Claim 8 in which the donor element comprises a layer containing a thermal bleaching agent and/or the receptor element comprises a layer containing a thermal bleaching agent.
 10. A thermal dye transfer assemblage as claimed in Claim 8 or Claim 9 in which the thermal bleaching agent is a nucleophile.
 11. A thermal dye transfer assemblage as claimed in Claim 10 in which the thermal bleaching agent is an amine, a carbanion or a compound capable of thermally generating an amine or carbanion.
 12. A thermal dye transfer assemblage as claimed in any one of Claims 8 to 11 in which the thermal bleaching agent is selected from amine salts of arylsulphonylacetates and quaternary ammonium nitrophenylsulphonylacetates.
 13. A thermal dye transfer assemblage as claimed in any one of Claims 9 to 12 in which the infrared absorber is a tetraarylpolymethine dye.
 14. A donor element comprising a substrate bearing a transferable colourant, an infrared absorber and a thermal bleaching agent.
 15. A donor element as claimed in Claim 14 in which the thermal bleaching agent is a nucleophile.
 16. A donor element as claimed in Claim 15 in which the thermal bleaching agent is an amine, a carbanion or a compound capable of thermally generating an amine or carbanion.

17. A donor element as claimed in any one of Claims 14 to 16 in which the thermal bleaching agent is selected from amine salts of arylsulphonylacetates and quaternary ammonium nitrophenylsulphonylacetates.

5 18. A donor element as claimed in any one of Claims 13 to 17 in which the infrared absorber is a tetraaryl-polymethine dye.

10 19. A modification of the method as claimed in Claim 1 which comprises the additional step of thermally transferring the colour image from the receptor to a final receptor wherein a thermal bleaching agent is present on the final receptor.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 2102

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	EP-A-0 563 886 (EASTMAN KODAK COMPANY) * page 2, line 34 - page 5, line 17 * * page 7, line 58 - page 8, line 7 * * claims 1-8 *	1-19	B41M5/38
X	EP-A-0 535 608 (KONICA CORPORATION) * page 11, line 52 - page 18, line 50 * * page 19, line 33 - line 41; example 3 *	1-19	
X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 459 (M-770) (3306) 2 December 1988 & JP-A-63 185 680 (OKI ELECTRIC INDUSTRIAL K.K.) 1 August 1988 * abstract *	1-19	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B41M G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 July 1995	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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