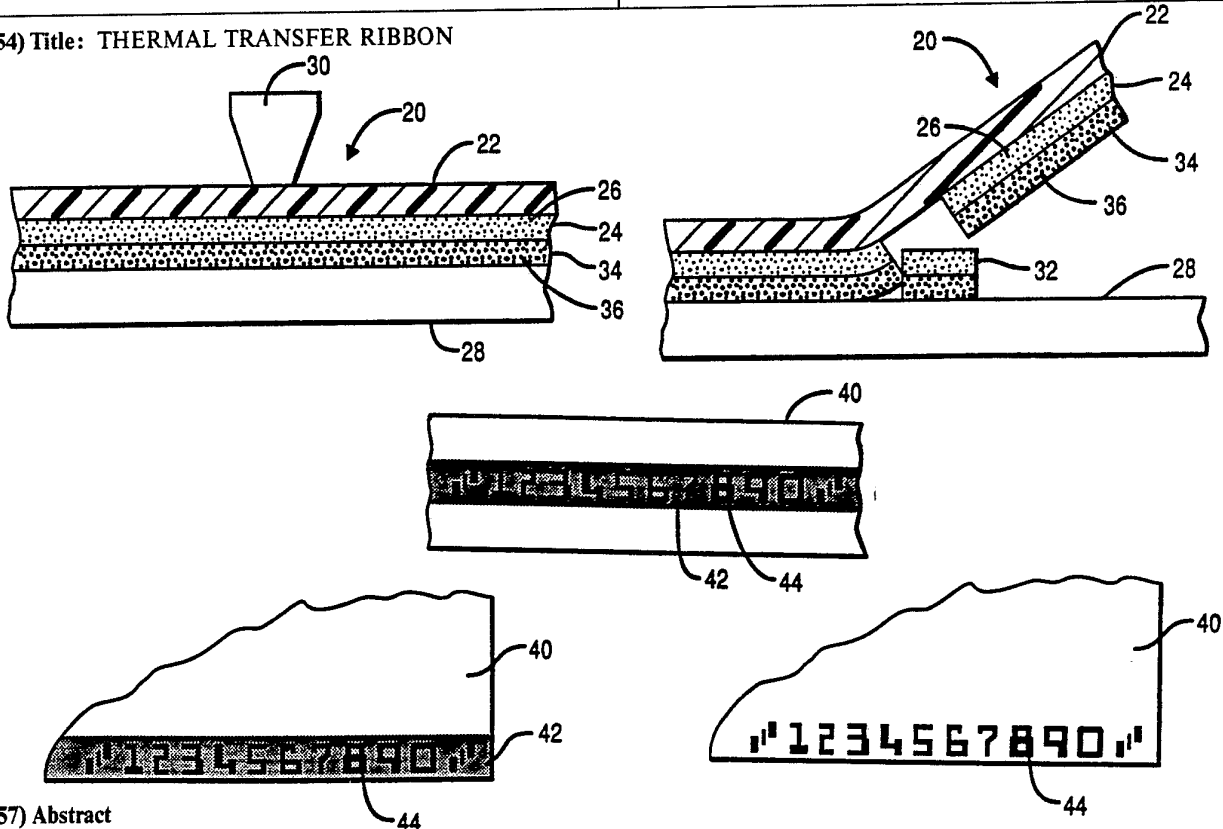




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<p>(21) International Application Number: PCT/US89/01750 (22) International Filing Date: 26 April 1989 (26.04.89) (30) Priority data: 192,795 10 May 1988 (10.05.88) US (71) Applicant: NCR CORPORATION [US/US]; World Headquarters, Dayton, OH 45479 (US). (72) Inventor: WEHR, Mary, Ann ; 2377 Oxford-Middletown Road, Hamilton, OH 45013 (US). (74) Agents: SESSLER, Albert, L., Jr. et al.; Law Department, Intellectual Property Section, NCR Corporation, World Headquarters, Dayton, OH 45479 (US).</p>		<p>(81) Designated States: DE (European patent), FR (European patent), GB (European patent), JP.  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: THERMAL TRANSFER RIBBON



(57) Abstract

A thermal transfer ribbon (20) includes a substrate (22) which has a thermally sensitive coating (24) and a protective coating (34). The thermally sensitive coating (24) is a wax mixture dispersed in a binder mix along with pigments (26). The protective coating (34) is a wax-copolymer mixture for which substantially eliminates ribbon offset, resists smudging and provides a bond between the thermally sensitive coating (24) and a receiving paper (28).

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THERMAL TRANSFER RIBBONTechnical Field

The present invention relates to nonimpact printing. More particularly, the invention provides a thermal transfer ribbon for use in imaging or encoding characters on paper or like record media documents which enable machine, human, or reflectance reading of the imaged or encoded characters. The thermal transfer ribbon enables printing in quiet and efficient manner and makes use of the advantages of thermal printing on documents with a signal inducible ink.

Background Art

In the printing field, the impact type printer has been the predominant apparatus for providing increased throughput of printed information. The impact printers have included the dot matrix type wherein individual print wires are driven from a home position to a printing position by individual and separate drivers. The impact printers also have included the full character type wherein individual type elements are caused to be driven against a ribbon and paper or like record media adjacent and in contact with a platen.

The typical and well-known arrangement in a printing operation provides for transfer of a portion of the ink from the ribbon to result in a mark or image on the paper. Another arrangement includes the use of carbonless paper wherein the impact from a print wire or a type element causes rupture of encapsulated material for marking the paper. Also known are printing inks which contain magnetic particles wherein certain of the particles are transferred to the record media for encoding characters in manner and fashion so as to be machine readable in a subsequent operation. One of the known encoding systems is MICR (Magnetic Ink

Character Recognition) utilizing the manner of operation as just mentioned.

While the impact printing method has dominated the industry, one disadvantage of this type of printing is the noise level which is attained during printing operation. Many efforts have been made to reduce the high noise levels by use of sound absorbing or cushioning materials or by isolating the printing apparatus.

More recently, the advent of thermal printing which effectively and significantly reduces the noise levels has brought about the requirements for heating of extremely precise areas of the record media by use of relatively high currents. The intense heating of the localized areas causes transfer of ink from a ribbon onto the paper. Alternatively, the paper may be of the thermal type which includes materials that are responsive to the generated heat.

The use of thermal transfer printing, especially when printing in a serial manner, can result in ribbon offset to unprinted areas of the receiving substrate. Ribbon offset is a term used to describe the unintentional transfer of ink from the ribbon onto unprinted areas of the paper or other record media which is adjacent the ribbon during printing operation. This ribbon offset can make character recognition, such as OCR (Optical Character Recognition) or MICR (Magnetic Ink Character Recognition), difficult and sometimes impossible.

#### Disclosure of the Invention

It is an object of the present invention to provide a thermal transfer ribbon which eliminates or substantially reduces ribbon offset during the printing operation.

Thus, according to the invention, there is provided a thermal transfer ribbon comprising a

substrate, a thermally sensitive coating which is a mixture comprising the combination of a wax mixture including 5-35% hydrocarbon wax, 25-65% paraffin wax, and 5-35% carnauba wax; of 5-25% acetate copolymer or hydrocarbon resin, and of up to 55% pigment and up to 25% sucrose benzoate; and a protective layer including 10-60% acetate copolymer and 40-90% paraffin wax.

In the preferred embodiment, the ribbon comprises a thin, smooth substrate, such as tissue paper or polyester, on which is applied a thermally sensitive coating that generally includes a wax mixture dispersed in a binding mix of an acetate copolymer or a hydrocarbon resin to form a wax emulsion. The copolymer or the hydrocarbon resin and the solids of the wax emulsion are mixed or dispersed into solution with dyes and coloring pigments in an attritor or other conventional dispersing equipment. The coloring pigments or dyes may include colors such as magenta, cyan, yellow or black and such pigments may also include a magnetic oxide. The thermal sensitive coating is then applied to the substrate by well-known or conventional coating techniques.

A protective layer or coating is applied over the thermal sensitive coating to substantially reduce or eliminate ribbon offset of a serially printed magnetic or a nonmagnetic thermal transfer ribbon. A preferred formulation of the protective coating comprises a mixture of approximately 50% ethylene-vinyl acetate copolymer and approximately 50% paraffin wax which is applied on the thermal reactive coating at a weight of about 2-5 grams per square meter.

#### Brief Description of the Drawings

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

Fig. 1 illustrates a thermal element operating with a ribbon base having a transfer coating and a protective coating thereon incorporating the ingredients as disclosed in the present invention;

Fig. 2 shows the receiving paper with a part of the coatings transferred in the form of a character or other mark onto the receiving paper;

Fig. 3 is a diagrammatic view of a portion of a thermal material receiving medium wherein ribbon offset occurs in unprinted areas;

Fig. 4 is a view of a portion of a document showing ribbon offset in the unprinted areas; and

Fig. 5 is a similar view of a portion of a document when using the protective coated or layered ribbon of the present invention.

#### Best Mode for Carrying Out the Invention

The transfer ribbon 20, as illustrated in Figs. 1 and 2, comprises a base or substrate 22 of thin, smooth, tissue-type paper or polyester-type plastic or like material having a coating 24 which is thermally activated and includes either magnetic or nonmagnetic pigment or particles 26 as an ingredient therein for use in imaging or encoding operations to enable machine reading, or human reading, or reflectance reading, of characters or other marks. Each character that is imaged on a receiving paper 28 or like record media produces a unique pattern or image that is recognized and read by the reader. In the case of thermal transfer ribbons relying on the nonmagnetic thermal printing concept, the particles 26 include coloring materials such as pigments or dyes, and fillers. In the case of ribbons relying on the magnetic thermal printing concept, the pigment or particles 26 include magnetic oxides or like sensible materials.

As alluded to above, it is noted that the use of a thermal printer having a print head element, as 30, substantially reduces noise levels in the printing operation and provides reliability in imaging or encoding of paper or like documents 28. The thermal transfer ribbon 20 provides the advantages of thermal printing while encoding or imaging the document 28 with a magnetic or with a nonmagnetic signal inducible ink. When the heating elements 30 of a thermal print head are activated, the imaging or encoding operation requires that the pigment or particles of material 26 on the coated ribbon 20 be transferred from the ribbon to the document 28 in manner and form to produce precisely defined characters 32 for recognition by the reader. In the case of nonmagnetic thermal printing, the imaging or encoding material 26 is transferred to the document 28 to produce precisely defined characters or marks 32 for recognition and for machine, human, or reflectance reading thereof.

In the case of magnetic thermal printing, the thermal sensitive coating 24 includes magnetic pigment or particles 26 for use in imaging or encoding operations to enable optical, human, or machine reading of the characters. The magnetic thermal transfer ribbon 20 provides the advantages of thermal printing while encoding or imaging the document 28 with a magnetic signal inducible ink.

The thermal transfer ribbon of the present invention is produced in a two coating or layer process wherein the first coating 24 is a thermal functional coating and includes a specific wax emulsion or formulation, and the second coating 34 is a protective coating or layer.

The protective coating or layer 34 is provided on the thermal reactive coating 24 on the side away or distal from the ribbon substrate 22, as seen in Figs. 1 and 2. The protective coating 34 exhibits the

following characteristics, namely, the coating must be resistant to rubbing and smudging, the coating must not inhibit transfer of the thermal-sensitive material 26 in the coating 24 at normal print head voltage, pulse width and temperature, and the coating must provide a bond between the thermal-sensitive material 26 in the coating 24 and the receiving paper 28 after transfer of such material.

Fig. 3 shows a portion of a document 40 with a strip portion 42 of the document and several of the thermally transferred characters 44. The ribbon offset is illustrated as the darkened area strip portion 42 in the unprinted areas adjacent the characters 44.

Fig. 4 shows a portion of a document 40 such as a bank check having a plurality of encoded characters 44 along the lower edge of the check. The darkened strip portion 42 surrounding the characters is illustrated as an example of ribbon offset on a printed document, as 40, using a ribbon without a protective layer or coating.

Fig. 5 shows the portion of the document 40 with the encoded characters 44 and illustrating an example of a printed document using a ribbon with the protective layer or coating 34. The protective layer 34 substantially reduces or prevents ribbon offset during printing or encoding operations.

The thermal functional coating 24 includes adhesive ingredients and thermal ingredients. A wax adhesive emulsion of 20-30% solids uses hydrocarbon wax, paraffin wax, carnauba wax, microcrystalline wax and ethylene/vinyl acetate copolymer or a hydrocarbon resin soluble in aliphatic solvents. The thermal ingredients may include pigments, such as iron oxide, a transfer agent and an additive, which are added to the wax emulsion.

A preferred wax emulsion or formulation to satisfy the requirements of the first coating or the



thermal functional coating 24 includes the ingredients in appropriate amounts as set forth in Tables 1 and 2 of Example I.

EXAMPLE ITABLE 1

<u>Wax Emulsion</u>	<u>Percent Dry</u>	<u>Range</u>
Paraffin 162 Wax	42	25-65%
WB-17 Wax	21	5-35%
Carnauba #3 Wax	12	5-35%
Elvax 210	20	5-25%
Polywax 1000	5	0-20%
Mineral Spirits	-	-
	<u>100.0</u>	

20-30% Solids

TABLE 2

<u>Ingredient</u>	<u>Percent Dry</u>	<u>Range</u>
Wax Emulsion	40	35-90%
(from above)		
Iron Oxide	40	1-55%
Sucrose Benzoate	20	1-25%
X-14 Oleate	0	0-5%
Permablak LS-60	<u>0</u>	0-35%
	100.0	

25-50% Solids

The nonvolatile or solid materials in the above formulation for the thermal transfer coating 24 are controlled or kept within a range of 25-55%, and it is here noted that Lacolene, or VM and P Naptha, can be substituted in place of the mineral spirits. The wax adhesive emulsion is heated to 94°C for a period of about 15 minutes while mixing the above solution and then is allowed to cool to 44°C at the end of the first stage of the process. After cooling the wax emulsion of Table 1 to 44°F, the ingredients of Table 2 are added to the emulsion using conventional grinding or dispersing equipment.

A preferred formulation for the protective layer 34 is made as an emulsion with the ingredients in appropriate amounts as set forth in Table 3 of Example I.

TABLE 3

<u>Protective Coating</u>	<u>Percent Dry</u>	<u>Range</u>
Elvax 210	50	10-60%
Paraffin 162 Wax	50	40-90%
Mineral Spirits	-	-
	<u>100.0</u>	

5-35% Solids

Paraffin 162 wax is a mixture of solid hydrocarbons chiefly of the methane series derived from the paraffin distillate portion of crude petroleum and is soluble in benzene, ligroine, alcohol, chloroform, turpentine, carbon disulfide and olive oil. WB-17 is an oxidized, isocyanated hydrocarbon wax. Carnauba #3 is a hard, amorphous wax derived by exudation from leaves of the wax palm and is soluble in ether, boiling alcohol and alkalies. Elvax 210 is an ethylene vinyl acetate copolymer of high vinyl acetate content that is used as binding material. Different color (magenta, cyan, yellow or black) dyes or pigments can be mixed into the formulation to provide proper color or toning for monochrome printing or for color printing. Magnetic iron oxide is preferred as a pigment or sensible material in the magnetic style ribbon for MICR printing. Polywax 1000 is a low molecular weight polyethylene. Iron oxide is a reddish or bluish-black (or brown or brownish-black) amorphous powder, soluble in acids, insoluble in water, alcohol and ether, and is used as a pigment or sensible material. Sucrose benzoate is a transfer agent that is compatible with waxes and copolymers. X-14 oleate is used as a filler and also as a coloring agent. Permablak LS-60 is a black amorphous powder of relatively coarse particles,

insoluble in solvents and is used as a pigment. It is noted that a pigment is defined as a solid that reflects light of certain wavelengths, without producing appreciable luminescence; in effect, pigments are used to impart color to other materials.

The nonvolatile materials of the thermal transfer coating 24 are controlled or kept within a range of 25-55% for proper viscosity. It should be noted that all ingredients are carefully weighed and solubilized in the mineral spirits using appropriate heat and agitation. After the solution is complete, it is slowly cooled to form a viscous wax dispersion to prepare a thermally active, transfer coating.

The substrate or base 22, which may be 30-40 gauge capacitor tissue, manufactured by Glatz, or 14-35 gauge polyester film as manufactured by E. I. duPont under the trademark Mylar, should have a high tensile strength to provide for ease in handling and coating of the substrate. Additionally, the substrate should have properties of minimum thickness and low heat resistance to prolong the life of the heating elements 30 of the thermal print head by reason of reduced print head actuating voltage and the resultant reduction in burn time.

The thermal functional coating 24 is applied to the substrate 22 by means of conventional coating techniques such as a Meyer rod or like wire-wound doctor bar set up on a typical solvent coating machine to provide a coating weight of between 4-11 grams per square meter. An overall coating thickness of 12-20 microns includes the protective coating of between 2-5 grams per square meter.

The coating 24 is made up of approximately 25-55% nonvolatile material and is maintained at a desired temperature and viscosity throughout the coating process. A temperature of 40-50°C is maintained during the entire coating process. After the thermal

functional coating 24 is applied to the substrate 22 and the protective layer 34 is applied to the coating 24, the web of ribbon 20 is passed through a dryer at an elevated temperature in the range between 80 and 120°C for approximately 5-10 seconds to ensure good drying and adherence of the protective layer 34 on the thermal coating 24 and of the thermal coating 24 onto the substrate 22 in making the transfer ribbon 20. The above-mentioned coating weight, as applied by the Meyer rod onto a preferred 4-7 microns thick substrate, overall translates to a total thickness of 7-14 microns. The thermal functional coating 24 can be fully transferred onto the receiving substrate 28 in the range of 50-120°C by changing the ranges of the waxes used in the wax adhesive emulsion portion of the coating.

The availability of the various ingredients used in the present invention is provided by the following list of companies.

<u>Material</u>	<u>Supplier</u>
WB-17 Wax	Bareco
Paraffin 162 Wax	Boler
Carnauba #3 Wax	Baldini & Co., Inc.
Elvax 210 Wax	E. I. duPont
Polywax 1000	Bareco
Iron Oxide	BASF
Sucrose Benzoate	Velsicol
X-14 Oleate	BASF
Permablak LS-60	Mono-Chem
Mineral Spirits	Ashland Chemical Co.
Magenta Dye	Day-Glo
Cyan Dye	Day-Glo
Calcium Carbonate	Omya
ARC Yellow Dye	Day-Glo

CLAIMS:

1. A thermal transfer ribbon comprising a substrate (22); a thermally sensitive coating (24) which is a mixture comprising the combination of a wax mixture including 5-35% hydrocarbon wax, 25-65% paraffin wax, and 5-35% carnauba wax; of 5-25% acetate copolymer or hydrocarbon resin, and of up to 55% pigment (26) and up to 25% sucrose benzoate; and a protective layer (34) including 10-60% acetate copolymer and 40-90% paraffin wax.

2. Thermal transfer ribbon according to claim 1, characterized in that said pigment (26) is magnetic iron oxide.

3. Thermal transfer ribbon according to claim 1, characterized in that the thermally sensitive coating (24) includes up to 20% polyethylene.

4. Thermal transfer ribbon according to claim 1, characterized in that the thermally sensitive coating (24) includes up to 5% oleate.

5. Thermal transfer ribbon according to claim 1, characterized in that the thermally sensitive coating (24) has a weight of 4-11 grams per square meter.

6. Thermal transfer ribbon according to claim 1, characterized in that the protective layer (34) has a weight of 2-5 grams per square meter.

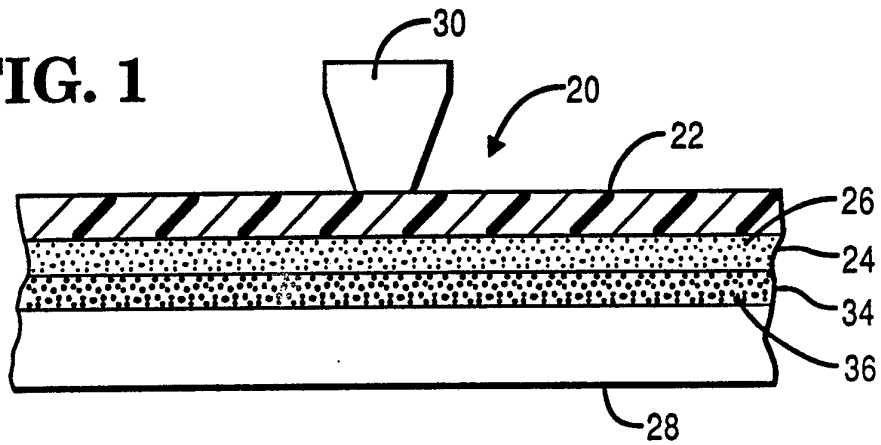
7. Thermal transfer ribbon according to claim 1, characterized in that the hydrocarbon wax is oxidized, isocyanated wax.

8. Thermal transfer ribbon according to claim 1, characterized in that the paraffin wax comprises a mixture of solid hydrocarbons of the methane series.

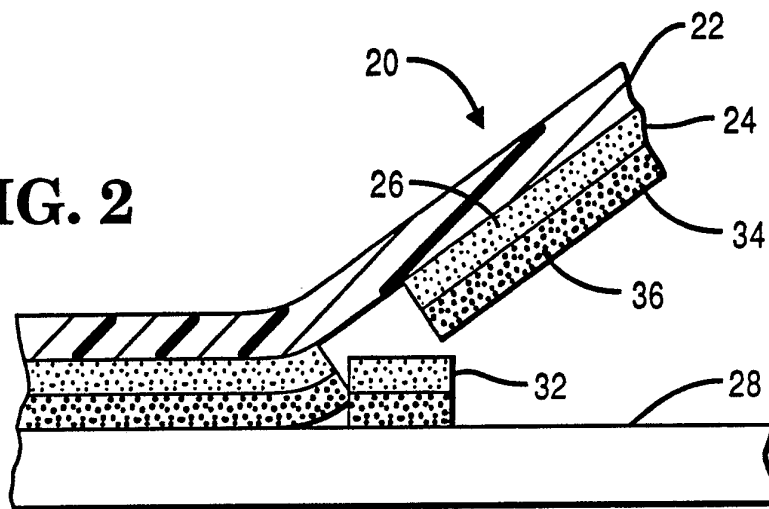
9. Thermal transfer ribbon according to claim 1, characterized in that the acetate copolymer comprises at least one of a series of ethylene vinyl acetate copolymers that are compatible with waxes and resins.

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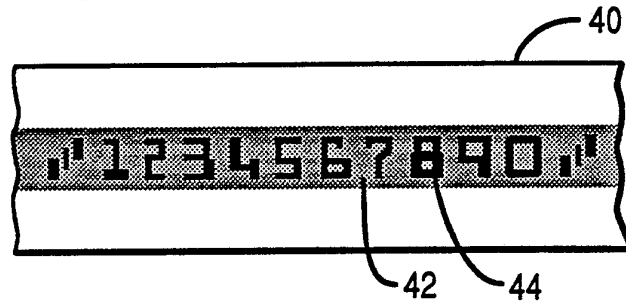
**FIG. 1**



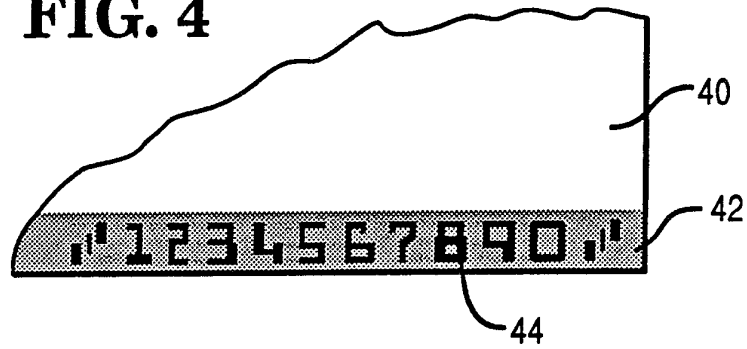
**FIG. 2**



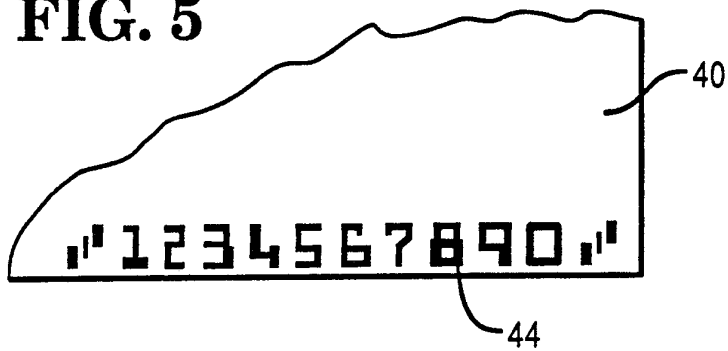
**FIG. 3**



**FIG. 4**



**FIG. 5**

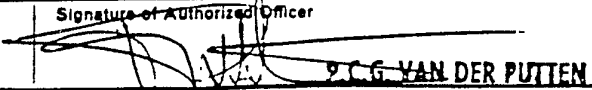




# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 89/01750

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>4</sup> :        B 41 M 5/26		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC <sup>4</sup>	B 41 M 5/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	WO, A, 86/04024 (NCR CORP.) 17 July 1986 see the whole document --	1-9
A	US, A, 4533596 (T.P. BESSELMAN) 6 August 1985 see the whole document --	1-9
A	EP, A, 0154438 (GENERAL COMPANY) 11 September 1985 see the claims --	1-9
A	Patent Abstracts of Japan, volume 11, no. 302 (M-629)(2749), 2 October 1987, & JP, A, 6294387 (YOKOGAWA ELECTRIC CORP.) 30 April 1987 --	1-9
A	Patent Abstracts of Japan, volume 11, no. 295 (M-626)(2742), 24 September 1987, & JP, A, 6285990 (CANON INC.) 20 April 1987 -----	1-9
<p><sup>10</sup> Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the International filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
16th August 1989	05 SEP 1989	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 <b>P.C.G. VAN DER PUTTEN</b>	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8901750

SA 28524

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 30/08/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CA-A- 1234694	05-04-88
		EP-A, B 0205567	30-12-86
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EP-A- 0154438	11-09-85	JP-A- 60178088	12-09-85