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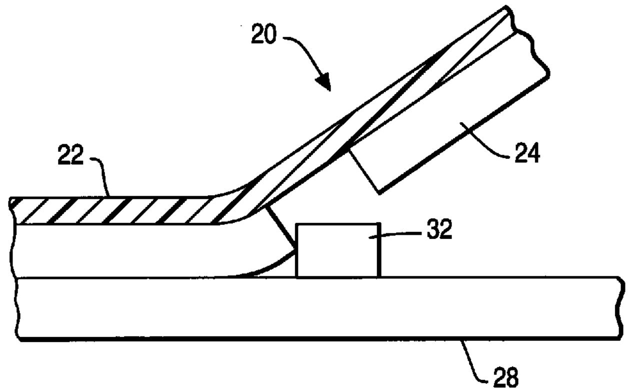
(54) Thermal transfer formulations

(57) A coating formulation for a thermal transfer ribbon (20) which provides images (100) which change color when exposed to U.V. light. The formulations and ribbons contain photochromic dyes/pigment that are responsive to U.V. light. In preferred embodiments the layers are initially transparent and become visible upon exposure to U.V. light.

FIG. 2



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Description

The present invention relates to thermal transfer printing wherein images are formed on a receiving substrate by heating extremely precise areas of a print ribbon with thin film resistors. This heating of the localized area causes transfer of ink or other sensible material from the ribbon to the receiving substrate. Sensible material is typically a pigment or dye which can be detected optically or magnetically.

More particularly, the present invention is directed to coating formulations (thermal transfer ink formulations) and thermal transfer media (ribbons) obtained therefrom which produce printed images with photochromic properties.

Thermal transfer printing has displaced impact printing in many applications due to advances such as the relatively low noise levels which are attained during the printing operation. Thermal transfer printing is widely used in special applications such as in the printing of machine readable bar codes and magnetic alpha-numeric characters. The thermal transfer process provides great flexibility in generating images and allows for broad variations in style, size and color of the printed image.

Photochromic compounds have been employed in various articles such as window glasses, sunglasses and films. It would be advantageous to provide images having photochromic properties (photochromism) which are generated by thermal transfer printing.

Photochromism means such characteristics of a material that the material develops a color under irradiation with excitation rays such as ultraviolet rays and returns to the initial uncolored state when allowing the material to stand. That is, photochromism means that the material is reversibly colored and discolored repeatedly.

It is an object of the present invention to provide images on articles by thermal transfer printing, wherein the images are hidden or invisible to the naked eye for purposes of security and identification but detectable under special conditions.

According to the invention a coating formulation for a thermal transfer layer which transfers an image basis to a receiving substrate when exposed to heat, characterized in that said coating formulation comprises wax, binder resin, solvent and a sensible material which comprises a photochromic pigment, a mixture of photochromic pigments, a photochromic dye, a mixture of photochromic dyes or a combination of one or more photochromic pigments and one or more photochromic dyes in an amount sufficient to change the color of the image basis upon subsequent exposure to U.V. light.

Also according to the invention a thermal transfer medium comprising a flexible substrate and a thermal transfer layer positioned thereon, said layer having a softening point in the range of 40°C to 250°C, said layer comprises a coating formulation according to any preceding claim.

Further to the invention an article carrying an image basis, said image basis changing colour when subsequently exposed to U.V. light so as to produce an image, characterized in that said image basis is produced from a thermal transfer medium.

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

Fig. 1 illustrates a thermal transfer medium of the present invention in a printing operation prior to thermal transfer;
Fig. 2 illustrates a thermal transfer medium of the present invention in a printing operation after thermal transfer;
Fig. 3 is a representation of a transparent image of the present invention on a substrate following exposure to U.V. light; and
Fig. 4 is a representation of another transparent image of the present invention on a substrate following exposure to U.V. light.

Thermal transfer ribbon 20, as illustrated in Figs. 1 and 2, comprises substrate 22 of a flexible material which is preferably a thin smooth paper or plastic-like material. Tissue type paper materials such as 30-40 gauge capacitor tissue, manufactured by Glatz and polyester-type plastic materials such as 14-35 gauge polyester film manufactured by Dupont under the trademark Mylar® are suitable. Polyethylene naphthalate films, polyamide films such as nylon, polyolefin films such as polypropylene film, cellulose films such as triacetate film and polycarbonate films are also suitable. The substrates should have high tensile strength to provide ease in handling and coating and preferably provide these properties at minimum thickness and low heat resistance to prolong the life of heating elements within thermal print heads. The thickness is preferably 3 to 10 μm. The substrate or base film may be provided with a backcoating (not shown) on the surface opposite the thermal transfer layer. Positioned on substrate 22 is thermal transfer layer 24, also referred to as a functional layer. The thermal sensitivity of thermal transfer layer 24 is determined by the softening point of the wax and binder resin therein. This thermal transfer layer has a softening point below 250°C, preferably below 200°C and most preferably from 50°C to 125°C. Softening temperatures within this range enable the thermal transfer medium to be used in conventional thermal transfer printers, which typically have print heads which operate at temperatures in the range of 50°C to 300°C, more typically, temperatures in the range of 60°C to 125°C. The thermal transfer layer 24 contains a wax and binder resin which are preferably compatible so that exposure to heat from print head 30 uniformly transfers thermal transfer layer 24 from substrate 22 to synthetic resin receiving substrate 28 and forms image 32.

The coating formulation of this invention comprises the components of conventional coating formulations such as one or more waxes, binder resins and solvents. However, the sensible material (pigment or dye) employed is a photochromic dye, a mixture of photochromic dyes, a photochromic pigment, a mixture of photochromic pigments or a combination of one or more photochromic dyes and one or more photochromic pigments.

Photochromic compounds suitable for use in this invention are those classified as organic photochromic compounds. Many of such compounds are known to be homogeneously mixed with organic high molecular weight compounds in the preparation of photochromic films and laminates . Suitable photochromic compounds include the spiro compounds of formula V disclosed by Takahashi et al. in U.S. Patent No. 5,266,447. These include spiroxazine compounds, spiropyran compounds and thiopyran compounds of the formulae in columns 5-6 of U.S. Patent No. 5,266,447.

Other examples of suitable photochromic compounds include the benzopyran compounds disclosed by Kumar in U.S. Patent No. 5,429,774, the benzothioxanthone oxides disclosed by Fischer et al. in U.S. Patent No. 5,177,218, the dinitrated spiropyrans disclosed by Hibino et al. in U.S. Patent No. 5,155,230, the naphthacenequinones disclosed by Fischer et al. in U.S. Patent No. 5,206,395 and U.S. Patent No. 5,407,885, the naphthopyran compounds disclosed by Knowles in U.S. Patent No. 5,384,077, the spiro(indoline) naphthoxazine compounds disclosed by VanGemert in U.S. Patent No. 5,405,958, the ring compounds disclosed by Tanaka et al. in U.S. Patent No. 5,106,988 and the spiro-benzoxazine compounds disclosed by Rickwood et al. in U.S. Patent No. 5,446,151. Mixtures of such compounds are preferred and are available commercially from sources such as Color Change Corp. of Illinois and Xytronyx Inc. of San Diego, California. Mixtures are typically used to provide variations in color.

The photochromic pigments/dyes are preferably added to the formulation in manner consistent with conventional methods for introducing conventional pigments or dyes. However, alternative (non-conventional) methods for preparing the coating formulations of this invention may also suitable. The photochromic dye/pigment is employed in an amount sufficient to change the color of the thermal transfer layer formed therefrom when exposed U.V. light. The photochromic dye/pigment is typically employed in an amount in the range of about .01 to 50 wt.%, preferably 0.1-25 wt.% based on the of dry components. More preferably the amount employed ranges from about 1 to 10 wt. % and most preferably about 1 wt. % based on dry components.

The coating formulation of the present invention can be prepared in conventional equipment. The preferred method is to mix the solvent, wax components and binder resin at an elevated temperature, preferably about 65°C. When thoroughly mixed, the photochromic pigment/dye is added and the resulting mixture mixed at an elevated temperature, preferably from about 60°C to 65°C. The pigments are typically ground in an attritor.

The coating formulation comprises wax as a main dry component. Suitable waxes provide temperature sensitivity and flexibility. Examples include natural waxes such as carnauba wax, rice bran wax, bees wax, lanolin, candelilla wax, motan wax and ceresine wax; petroleum waxes such as paraffin wax and microcrystalline waxes; synthetic hydrocarbon waxes such as low molecular weight polyethylene and Fisher-Tropsch wax; higher fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid and behenic acid; higher aliphatic alcohol such as stearyl alcohol and esters such as sucrose fatty acid esters, sorbitane fatty acid esters and amides. The wax-like substances have a melting point less than 200°C and preferably from 40°C to 130°C. The amount of wax in the coating formulation is preferably above 25 wt.% and most preferably ranges from 25 to 85 percent by weight, based on the weight of dry ingredients.

The coating formulation of this invention also comprises a binder resin. Suitable binder resins are those conventionally used in coating formulations. These include thermoplastic resins and reactive resins such as epoxy resins.

Suitable thermoplastic binder resins include those described in U.S. Patent Nos. 5,240,781 and U.S. 5,348,348 which have a melting point of less than 300°C, preferably from 40°C to 225°C. Examples of suitable thermoplastic resins include polyvinyl chloride, polyvinyl acetate, vinyl chloride-vinyl acetate copolymers, polyethylene, polypropylene, polyacetal, ethylene-vinyl acetate copolymers, ethylene alkyl (meth)acrylate copolymers, ethylene-ethyl acetate copolymers, polystyrene, styrene copolymers, polyamide, ethylcellulose, epoxy resin, xylene resin, ketone resin, petroleum resin, terpene resin, polyurethane resin, polyvinyl butyryl, styrene-butadiene rubber, saturated polyesters, styrene-alkyl (meth)acrylate copolymer, ethylene alkyl (meth)acrylate copolymers. Suitable saturated polyesters are further described in U.S. Patent No. 4,983,446. Thermoplastic resins are preferably used in an amount of from 2 to 35 wt.% based on the total dry ingredients of the coating formulation.

Suitable reactive binder components include epoxy resins and a polymerization initiator (crosslinker). Suitable epoxy resins include those that have at least two oxirane groups such as epoxy novolak resins obtained by reacting epichlorohydrin with phenol/formaldehyde condensates or cresol/formaldehyde condensates. Another preferred epoxy resin is polyglycidyl ether polymers obtained by reaction of epichlorohydrin with a polyhydroxy monomer such as 1,4 butanediol. A specific example of suitable epoxy novolak resin is Epon 164 available from Shell Chemical Company. A specific example of the polyglycidyl ether is available from Ciba-Geigy Corporation under the trade name Araldite® GT 7013. The epoxy resins are preferably employed with a crosslinker which activates upon exposure to the heat from a thermal print head. Preferred crosslinkers include polyamines with at least two primary or secondary amine groups. Examples being Epi-cure P101 and Ancamine 2014FG available from Shell Chemical Company and Air Products, respectively. Accelerators such as triglycidylisocyanurate can be used with the crosslinker to accelerate the reaction. When used, the epoxy resins typically comprise more than 25 wt.% of the coating formulation based on dry components in view of their low viscosity. Waxes are typically not necessary when reactive epoxy resins form the binder.

The solvents employed in coating formulations of this invention can vary widely and are dependent on the solubility of the binder resin. A preferred solvent is mineral spirits. Other suitable solvents include esters, ketones, ethers, alcohols, aliphatics and aromatics. The solids content of the coating formulation is typically within the range of 15 to 100 wt.% (hot melt), depending on the viscosity of the dry components therein.

Although not preferred, the coating formulation may also contain another sensible material or pigment in addition to the photochromic pigments/dye discussed above. These are preferably colorless pigments used as filler or light in color so as not to interfere with the photochromic effect. The photochromic pigments may be used to change the color of light colored pigments. The additional sensible material is typically a coloring agent, such as a dye or pigment or magnetic particles; however any coloring agent used in conventional ink ribbons is suitable, including carbon black and a variety of organic and inorganic coloring pigments and dyes, examples of which include phthalocyanine dyes, fluorescent naphthalimide dyes and others such as cadmium, primrose, chrome yellow, ultra marine blue, titanium dioxide, zinc oxide, iron oxide, cobalt oxide, nickel oxide, etc. Examples of sensible materials include those described in U.S. 3,663,278 and U.S. 4,923,749. Reactive dyes such as leuco dyes are also suitable. In the case of magnetic thermal printing, the thermal transfer layer includes a magnetic pigment or particles for use in imaging to enable optical human or machine reading of the characters. Use of magnetic pigment particles is expected conflict with the objects of the present invention in most cases, but the use of such particles is not excluded from this invention. The additional sensible material or pigment is typically used in an amount of from 0 to 40 parts by weight based on the total dry ingredients of the coating formulation.

The coating formulations may contain conventional additives such as plasticizers, viscosity modifiers, tackifiers, etc.

A preferred formulation is that containing a mixture of rice bran wax in an amount ranging from 60 to 95 wt.% based on the total dry ingredients, an ethyl vinyl acetate copolymer binder resin and the photochromic pigment. Mineral spirits are a preferred solvent. This preferred formulation is made by mixing the solution of mineral spirits, rice bran wax and ethyl vinyl acetate copolymer binder resin for about 15 minutes at a temperature of about 65°C, after which the photochromic dye is added at about 60°C to 70°C for about two hours.

The thermal transfer ribbon of the present invention comprises a substrate as described above, preferably polyethylene terephthalate, and a thermal transfer layer comprised of wax, binder resin, sometimes residual solvent and a photochromic pigment. The thermal transfer layer is preferably obtained from the coating formulation of the present invention. Suitable waxes, binder resins and photochromic pigments are as described above. The thermal transfer layer (functional layer) preferably has a softening point within the range of about 50°C to 250°C which enables transfer at normal print head energies which range from about 100°C to 250°C and more typically from about 100°C to 150°C. The thermal transfer ribbon of the present invention can be prepared from formulations of the present invention in the form of either a solution, dispersion or emulsion. Once applied to the substrate, a portion of the solvent can remain in the coating. The ribbons can be prepared by conventional techniques and equipment such as a Meyer Rod or like wire round doctor bar set up on a conventional coating machine to provide the coating weights described above. The coating weight of the thermal transfer layer typically ranges from 1.9 to 4.3 g/m^2. A temperature of about 65°C is maintained during the entire coating process. After the coating formulation is applied, it is optionally passed through a dryer at an elevated temperature to ensure drying and adherence of the functional layer to the substrate. The thermal transfer layer can be fully transferred onto a receiving substrate such as paper or synthetic resin at a temperature in the range of 75°C to 200°C.

The thermal transfer ribbon of the present invention provides the advantages of thermal printing. When the thermal transfer ribbon is exposed to the heating elements of the thermal print head, the thermal transfer layer softens and transfers from the ribbon to the receiving substrate with some of the silicone resin backcoating therein.

The images of this invention are preferably derived from the thermal transfer ribbons of this invention and comprise a single layer of the wax, binder resin and photochromic pigments/dyes, as described above, transferred from the thermal transfer layer onto a substrate. The images of this invention are preferably transparent until exposed to U.V. light which is achieved by excluding colored pigments.

The images can be patterned in fine detail as shown in Fig. 3, which is an image 100 of this invention in the pattern of a bar code. When transparent, this image enables the identification of goods or authentication of articles without disrupting the appearance/packaging of the goods or articles. The image 100 can also be a decorative pattern for novelty items such as cards shirts, etc. as shown in Fig. 4.

EXAMPLES

Coating Formulation

A coating formulation of the present invention is prepared by mixing mineral spirits, wax and binder resin in the proportions indicated in Table 1 and heating the mixture to 60°C for 15 minutes. A mixture of photochromic dyes available from Xytronyx Inc. in the amount indicated in Table 1 is added to the resultant mixture at a temperature of from about 140°F to 150°F for about 2 hours.

TABLE 1

Material	Wt.% Dry	Wt.% Dry - Range	Grams Dry	Grams Wet
Rice Bran Wax[1]	78.0	40 - 85%	93.6	93.6
Ethyl Vinyl Acetate Copolymer Resin[2]	7.0	2 - 30%	8.4	8.4
Photochromic Mixture[3]	15.0	1 - 30%	18	18
Mineral Spirits	--	--	--	480
Total	**100.0**		**120.0**	**600**

[1] Rice Bran Wax available from Strahl & Pitsch Inc. in West Babylon, N.Y.
[2] Ethyl Vinyl Acetate Copolymer Resin = "Elvax 260 Ethyl Vinyl Acetate Copolymer Resin" by Chemcentral in Atlanta Georgia.
[3] Photochromic Mixture = #117-21-A

Thermal Transfer Medium

A thermal transfer medium of the present invention is prepared by coating a formulation as defined above onto a 4.5 µm Polyester Mylar Film by E. I. Dupont de Nemours & Co., Incorporated at a coat weight of from 1.9 to 4.3 g/m^2. The solution is coated onto the mylar film at 70°C using a doctor bar and subsequently dried.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding example.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

Claims

1. A coating formulation for a thermal transfer layer (24) which transfers an image basis (100) to a receiving substrate when exposed to heat, characterized in that said coating formulation comprises wax, binder resin, solvent and a sensible material which comprises a photochromic pigment, a mixture of photochromic pigments, a photochromic dye, a mixture of photochromic dyes or a combination of one or more photochromic pigments and one or more photochromic dyes in an amount sufficient to change the color of the image basis upon subsequent exposure to U.V. light.

2. A coating formulation as in claim 1, characterized by providing a colorless image basis which becomes colored upon exposure to U.V. light.

3. A coating formulation as in claim 1, characterized by providing an invisible image basis which becomes visible upon exposure to U.V. light.

4. A coating formulation as in any preceding claim, characterized in that the wax has a melting point in the range of 40°C to 130°C; and the binder resin is a thermoplastic polymer resin having a melting point in the range of 40°C to 250°C and comprises 2 to 35 wt.% of the dry components.

5. A coating formulation as in claim 4, characterized by comprising 2 to 35 wt. % thermoplastic polymer resin, 25 to 85 wt.% wax, and 1 to 50 wt.% sensible material, all based on dry components.

6. A coating formulation as in any preceding claim, characterized in that the photochromic dye and photochromic pigment are selected from the group consisting of:

spiroxazine compounds and derivatives thereof;
spiropyran compounds and derivatives thereof;
thiopyran compounds and derivatives thereof;
naphthopyran compounds and derivatives thereof;
spiro(indoline) naphthoxazine compounds and derivatives thereof;
spiro benzoxazine compounds and derivatives thereof;
benzothioxanthone compounds and derivatives thereof;
naphthacenequinones compounds and derivatives thereof; and mixtures thereof.

7. A coating formulation as in any preceding claims, characterized in that the amount of photochromic dye and photochromic pigment ranges from 0.01 to 25 wt.% based on dry components.

8. A thermal transfer medium (20) comprising a flexible substrate (22) and a thermal transfer layer (24) positioned thereon, said layer having a softening point in the range of 40°C to 250°C, characterized in that said layer comprises a coating formulation according to any preceding claim.

9. A thermal transfer medium as in claim 8, characterized in that the thermal transfer layer has a coat weight within the range of 1.9 - 4.3 g/m^2.

10. An article carrying an image basis, said image basis changing color when subsequently exposed to U.V. light so as to produce an image, characterized in that said image basis is produced from a thermal transfer medium according to claim 8 or claim 9.

FIG. 1

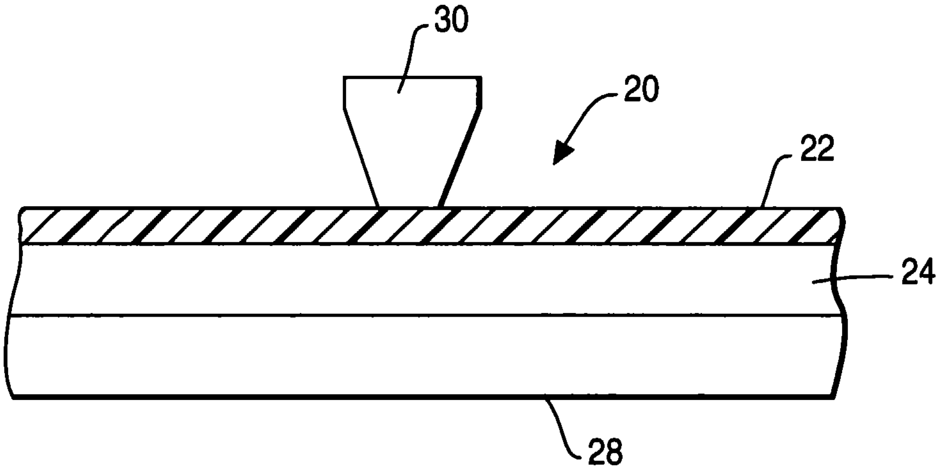


FIG. 2

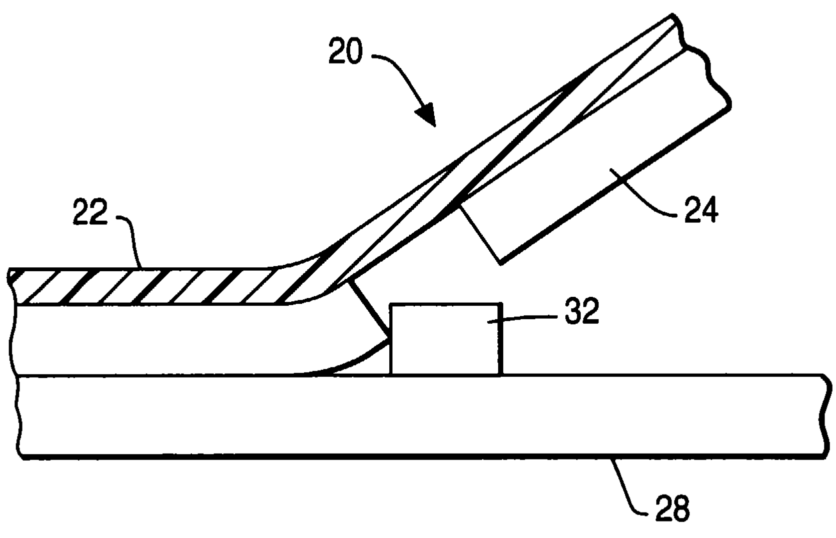


FIG. 3

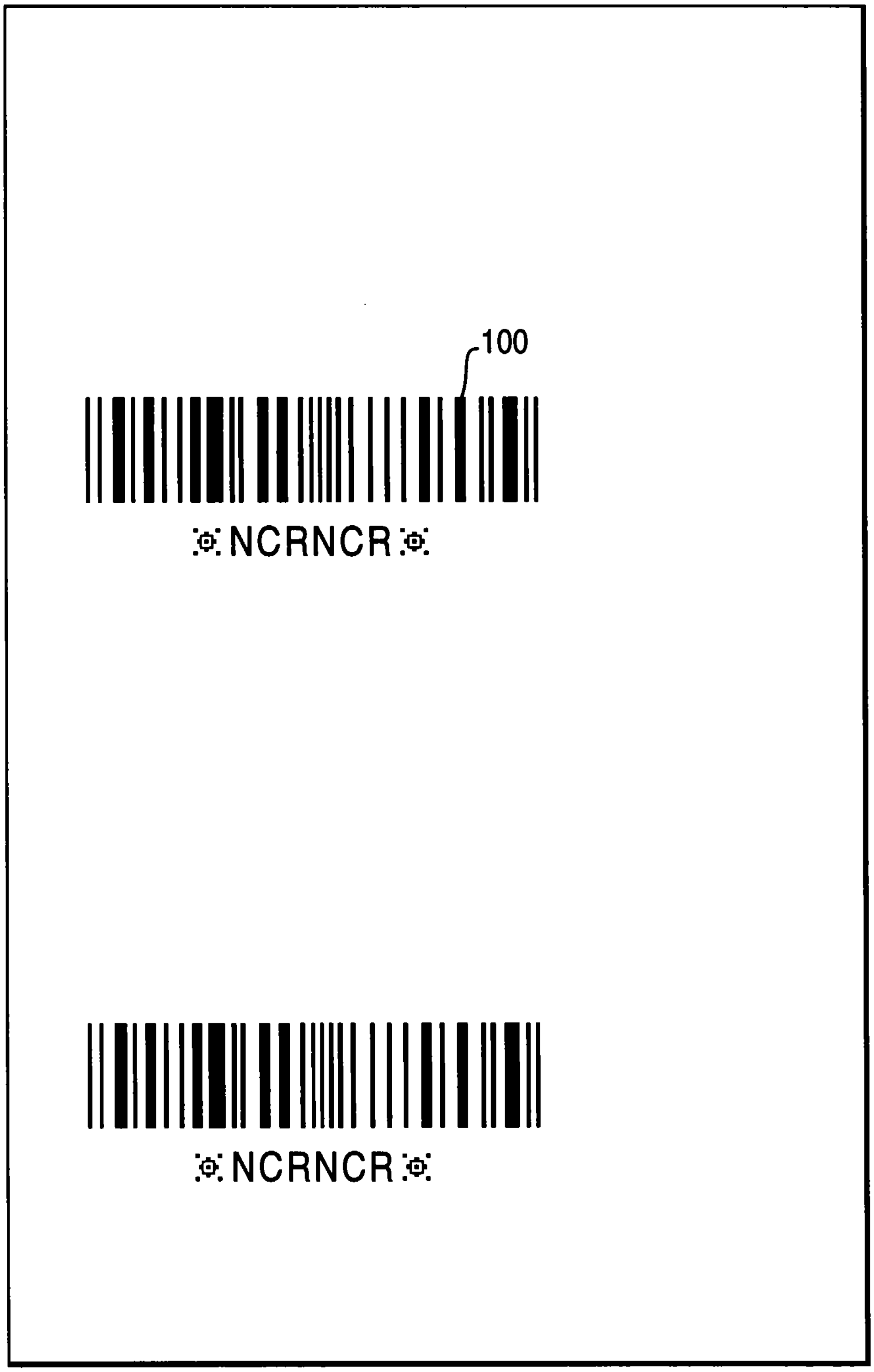
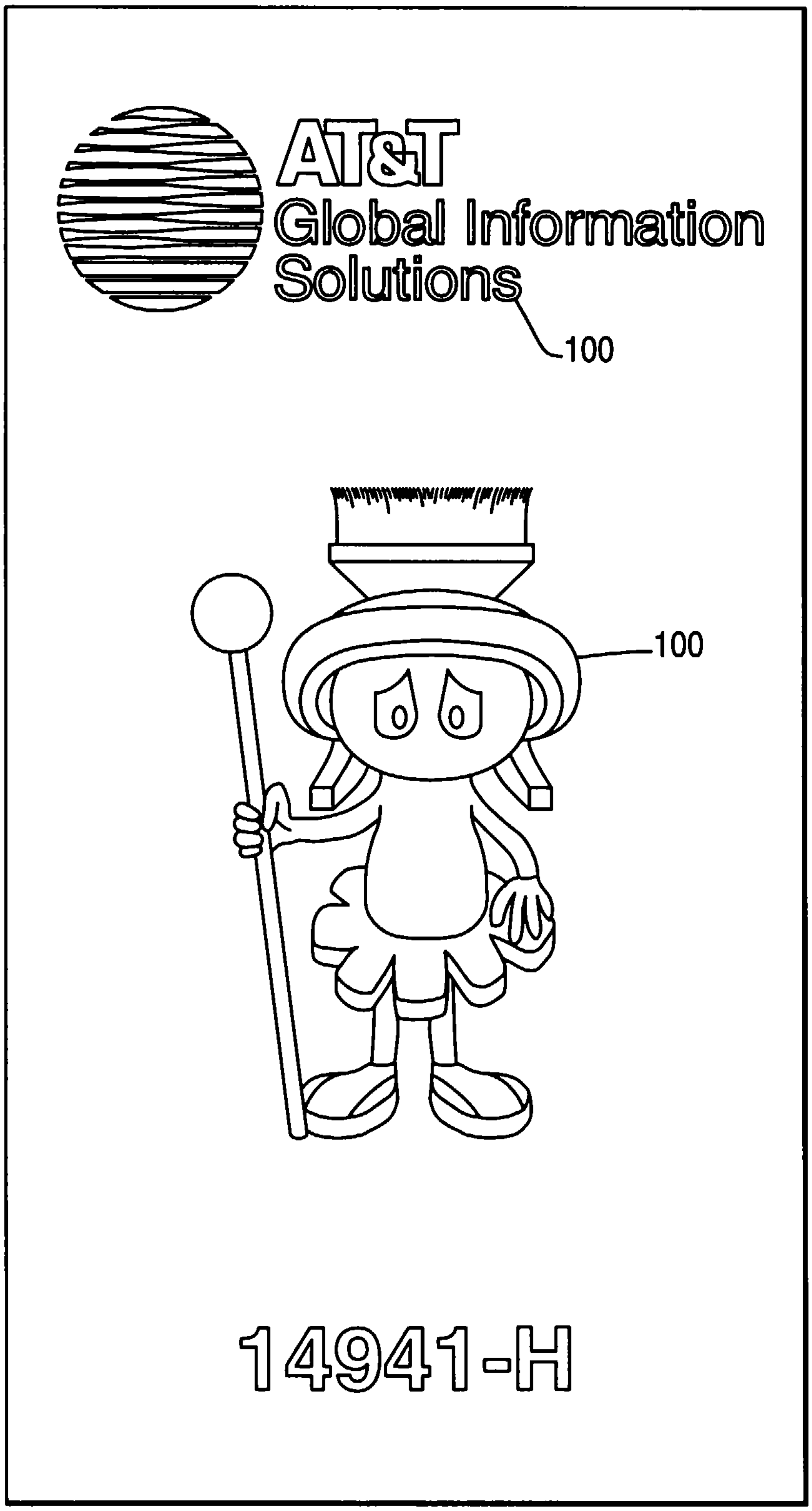


FIG. 4



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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 4195

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 Y	DATABASE WPI Section Ch, Week 8912 Derwent Publications Ltd., London, GB; Class A89, AN 89-088805 XP002035860 & JP 01 038 283 A (TOYO INK MFG CO) , 8 February 1989 * abstract *	1-3,6,10 4,5	B41M5/38
X	DATABASE WPI Section Ch, Week 9117 Derwent Publications Ltd., London, GB; Class A89, AN 91-121702 XP002035861 & JP 03 061 084 A (TOYO INK MFG CO) , 15 March 1991 * abstract *	1,6	
Y	US 5 516 590 A (OLMSTEAD MICHAEL W ET AL) 14 May 1996 * column 4, line 57 - column 5, line 43 * * claims 1-4 * * the whole document *	4,5	TECHNICAL FIELDS SEARCHED (Int.Cl.6) B41M
A	US 5 244 524 A (YAMANE MITSUO) 14 September 1993 * column 6, line 24 - column 7, line 19 * * column 9, line 18 - line 47 * * the whole document *	1-10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 July 1997	Martins-Lopes, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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