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- **PATENT ABSTRACTS OF JAPAN**, vol. 11, no. 316 (M-631)[2763], 15th October 1987; JP-A-62 99 195 (Mitsui Toatsu Chem., Inc.) 08.05.1987
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**EP 0 235 939 B2**

## Description

This specification describes an invention relating to thermal transfer printing and more particularly to a thermal transfer printing sheet carrying a dye or a mixture of dyes and to a thermal transfer printing process in which dye is transferred from the transfer sheet to a receiver sheet by the application of heat.

EP-A-0001068 describes a thermal transfer printing sheet comprising certain azo dyes and a thermal transfer printing process suitable for printing textile materials. Under the process conditions described the sheet is heated to a temperature from 60°C to 260°C for a period from 0.5 to 75 seconds in order to cause the dye to sublime and thereby to be transferred non-selectively to the textile material.

GB-A-2159971 describes a transfer printing process and is concerned with the problem of preventing the dyes migrating from the receiver sheet after transfer by introducing a reactive group into the dye so that the dye is capable of reacting with a compound bound into the receiver.

In the form of thermal transfer printing with which the present application is concerned, a heat-transferable dye is applied to a sheet-like substrate, in the form of an ink, usually containing a polymeric or resinous binder to bind the dye to the substrate, to form a transfer sheet. This is then placed in contact with the material to be printed, the receiver sheet, and selectively heated in accordance with a pattern information signal whereby dye from the selectively heated regions of the transfer sheet is transferred 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 transfer sheet.

Important criteria in the selection of a dye for TTP are its thermal properties, brightness of shade, fastness properties, such as light and heat fastness, and facility for application to the substrate in the preparation of the transfer sheet. For suitable performance the dye should transfer evenly, in a predetermined relationship to the heat applied to the transfer sheet so that the depth of shade on the receiver sheet is smoothly related to the heat applied and a good density gradation can be achieved on the receiver sheet. Brightness of shade is important in order to obtain as wide a range of shades with the three primary dye shades of yellow, cyan and magenta.

As the dye must be sufficiently mobile to migrate from the transfer sheet to the receiver sheet at the temperatures employed, typically 150-400°C, more especially 300-400°C, it is generally free from ionic and water-solubilising groups, and is thus not readily soluble in aqueous or water-miscible media, such as water and alkanols. Many suitable dyes are also not readily soluble in the solvents which are commonly used in, and thus acceptable to, the printing industry, such as aromatic hydrocarbons, alkanols and alkyl- and cycloalkyl-ketones. Although the dye can be applied as a dispersion in a suitable solvent, it has been found that brighter, glossier and smoother final prints can often be achieved on the receiver sheet if the dye is applied to the substrate from a solution. To apply sufficient dye to the transfer sheet, and thereby to achieve the potential for a deep shade on the receiver sheet, it is desirable that the dye should be readily soluble in the ink medium, particularly if it has a relatively low extinction coefficient. It is also important that a dye which has been applied to a transfer sheet from a solution should be resistant to crystallisation so that it remains as an amorphous layer on the transfer sheet for a considerable time.

According to the present invention there is provided a thermal transfer printing sheet comprising a substrate having a coating comprising a dye of the formula:

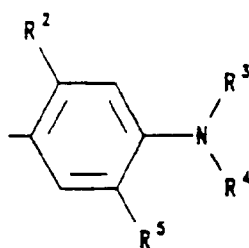


wherein

A is a phenyl group substituted by two or three electron-withdrawing groups selected from NO<sub>2</sub>, CN, and -SO<sub>2</sub>-C<sub>1-4</sub>-alkyl, and optionally by one or more groups selected from C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkoxy; and

E is selected from,

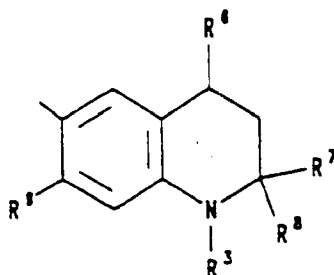
(i) an amino group of the formula:



wherein:

- $R^2$  is selected from H,  $C_{1-4}$ -alkyl,  $C_{1-4}$ -alkoxy,  $C_{1-4}$ -alkylthio,  $NH_2-CO-NH-$ ,  $HCONH-$ , phenyl- $CONH-$ ,  $C_{1-4}$ -alkyl- $CO-NH-$ ,  $C_{1-4}$ -alkyl- $SO_2-NH-$ , CN,  $CF_3$ , and halogen;
- $R^3$  &  $R^4$  are independently selected from H;  $C_{1-6}$ -alkyl and  $C_{4-8}$ -cycloalkyl, each of which is unsubstituted or substituted by a group independently selected from halogen, CN, phenyl mono- or bicyclic heteroaryl,  $-OCO-C_{1-4}$ -alkyl,  $-COO-C_{1-4}$ -alkyl,  $C_{2-4}$ -alkenyl, and  $C_{1-4}$ -alkoxy; or
- $R^3$  &  $R^4$  together with the nitrogen atom to which they are attached form a heterocyclic ring, such as morpholine, piperazine or thiomorpholine; and
- $R^5$  is selected from H,  $C_{1-4}$ -alkyl and  $C_{1-4}$ -alkoxy;

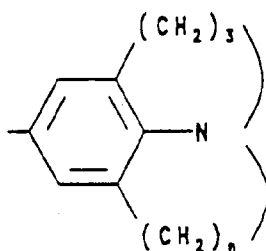
(ii) a tetrahydroquinoliny group of the formula:



wherein:

- $R^3$  is selected from H;  $C_{1-6}$ -alkyl and  $C_{4-8}$ -cycloalkyl, each of which is independently unsubstituted or substituted by a group selected from halogen, CN, phenyl, mono- or bicyclic heteroaryl,  $-OCO-C_{1-4}$ -alkyl,  $-COO-C_{1-4}$ -alkyl,  $C_{2-4}$ -alkenyl, and  $C_{1-4}$ -alkoxy, and
- $R^6$  to  $R^9$  are independently selected from H and  $C_{1-4}$ -alkyl; and

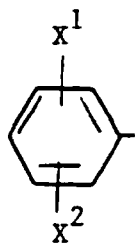
(iii) lilolidinyl or julolidinyl of the formula:



wherein:  $n = 2$  (lilolidine) or  $3$  (julolidine). With the disclaimers as defined in the two sets of claims.

Where the phenyl group A optionally carries a C<sub>1-4</sub>-alkyl group, this preferably CH<sub>3</sub>, or C<sub>1-4</sub>-alkoxy, this is preferably -OCH<sub>3</sub>. The substituents in phenyl group A are preferably in the ortho and/or para positions with respect to the azo link.

A preferred substituted phenyl group, A, in the dyes of Formula I, giving orange to violet shades, is of the formula:



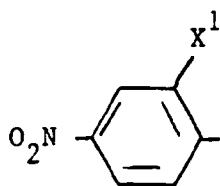
II

wherein

X<sup>1</sup> is NO<sub>2</sub>, CN or -SO<sub>2</sub>CH<sub>3</sub>; and

X<sup>2</sup> is NO<sub>2</sub>, CN, -SO<sub>2</sub>CH<sub>3</sub>

and an especially preferred substituted phenyl group is of the formula:

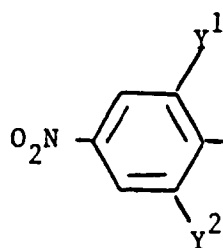


III

wherein

X<sup>1</sup> is NO<sub>2</sub>, CN or -SO<sub>2</sub>CH<sub>3</sub>, gives strong magenta dyes of Formula I.

A preferred substituted phenyl group A in dyes of Formula I, giving blue shades, is of the formula:



IV

wherein

Y<sup>1</sup> & Y<sup>2</sup> are independently selected from CN, NO<sub>2</sub> provided that they are not both NO<sub>2</sub>

In a dye of Formula IV, it is especially preferred that Y<sup>1</sup> and Y<sup>2</sup> are both CN or that Y<sup>1</sup> is CN and Y<sup>2</sup> is NO<sub>2</sub>.

Specific examples of the substituted phenyl group, A, are: 2,4-dinitrophenyl, 2-cyano-4-nitrophenyl, 2,4-dicyano-phenyl, 2-nitro-4-cyanophenyl, 3,4-dicyanophenyl, 2,4-dinitro-6-cyanophenyl, 2,6-dicyano-4-nitrophenyl, 2-methyl-sulphonyl-4-nitrophenyl, 2,6-dicyano-4-methylphenyl

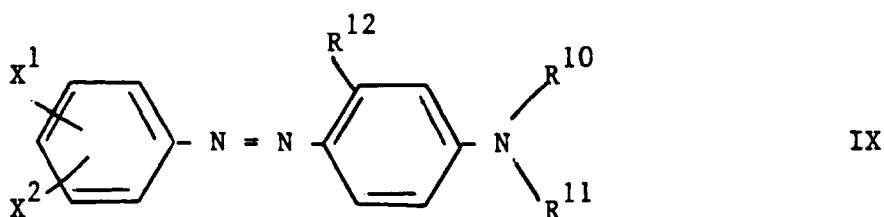
For the aniline of formula V the radical E is formed by loss of the H atom para to the amino group.

For the tetrahydroquinoline of formula VI the radical E is formed by loss of the H atom in the 7-position on the tetrahydroquinoline nucleus.

For the lilioine or julolidine of formula VII the radical E is formed by loss the H-atom on the benzene ring situated in the para position to the N atom.

Examples of suitable coupling components in accordance with Formulae V, VI and VII are: lilolidine julolidine N-benzylaniline N-ethyl-N-(2-acetoxyethyl)aniline N,N-diethylaniline N-ethyl-N-(2-phthalimidoethyl)aniline N,N-bis(2-acetoxyethyl)aniline N,N-bis(2-ethoxycarbonyl)ethyl)aniline N-ethyl-N-(2-cyanoethyl)aniline N-ethyl-N-(n-butyl)aniline N,N-di(n-propyl)aniline N-ethyl-N-(2-ethoxyethyl)aniline N,N-bis (2-methoxycarbonyl)ethyl)aniline N-ethyl-N-(2-ethoxycarbonyl)ethyl) aniline N,N-bis(2-methoxycarbonyloxyethyl)aniline N-(2-cyanoethyl)-N-(2-acetoxyethyl)aniline N-ethyl-N-(2-[phenoxyacetoxy]ethyl)aniline N-(2-cyanoethyl)-N-(2-[phenoxyacetoxy]ethyl)aniline N-(2-cyanoethyl)-N-(2-[i-propoxy-carbonyloxy]ethyl)aniline N-(2-cyanoethyl)-N-(2-methoxy-3-phenoxy-n-propyl)aniline N-(2-cyanoethyl)-N-(2-[n-butylaminocarbonyloxy]-ethyl)aniline 1-(2-acetoxyethyl)-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline and the 3-methyl, 3-acetyl-amino, 3-chloro and 3-methylsulphonylamino analogues thereof.

Preferred dyes of Formula I, giving orange to violet shades, are of the formula:



wherein

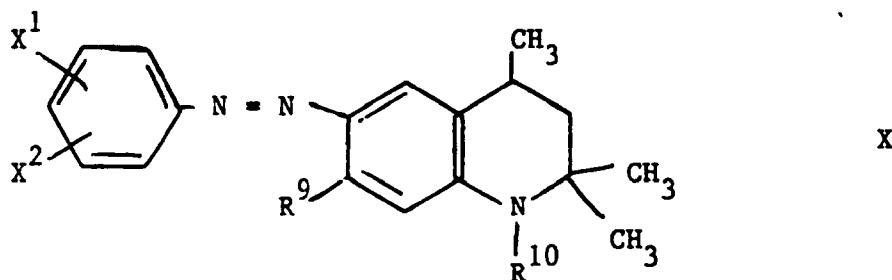
X¹ is NO<sub>2</sub> or CN,

X² is selected from NO<sub>2</sub>, CN, -SO<sub>2</sub>CH<sub>3</sub>

R¹⁰ & R¹¹ are each independently selected from C<sub>1-4</sub>-alkyl, -C<sub>2</sub>H<sub>4</sub>CN, C<sub>1-4</sub>-alkylene-OCO-C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkylene-COO-C<sub>1-4</sub>-alkyl and

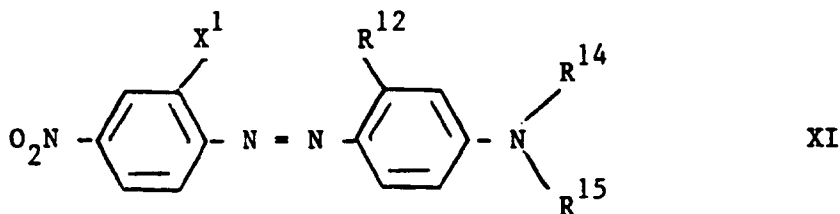
R¹² is H, CH<sub>3</sub> or -NHCOCH<sub>3</sub>;

or of the formula:



wherein X¹, X², R⁹ & R¹⁰ are as hereinbefore defined.

In the dyes of Formula IX and X, it is preferred that X² is NO<sub>2</sub>, CN or -SO<sub>2</sub>CH<sub>3</sub>. An especially preferred class of dyes in accordance with Formula IX, giving a magenta shade, has the formula:

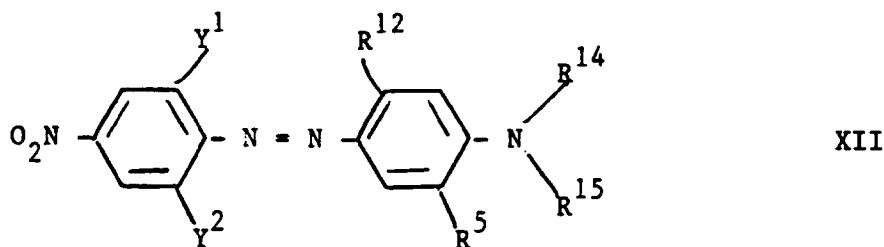


10  
wherein

15  $X^1$  &  $R^{12}$  are as hereinbefore defined; and  
 $R^{14}$  &  $R^{15}$  are each independently selected from  $C_{2-4}$ -alkyl,  $C_{1-4}$ -alkylene-OCO- $C_{1-4}$ -alkyl and  $C_2H_4CN$ .

Within this class of dyes it is especially preferred that  $X^1$  is CN,  $R^{12}$  is methyl,  $R^{14}$  is ethyl, n-propyl, n-butyl or - $C_2H_4OCOCH_3$ , and  $R^{15}$  is - $C_2H_4OCOCH_3$ .

Preferred dyes of Formula I, giving a blue shade, are of the formula:



25  
30  
wherein

35  $Y^1$  represents  $NO_2$  or CN,  
 $Y^2$  represents CN, and  
 $R^{14}$  &  $R^{15}$  are each independently selected from  $C_{2-4}$ -alkyl and  $C_{1-4}$ -alkylene-OCO- $C_{1-4}$ -alkyl;  
 $R^5$  is H,  $C_{1-4}$ -alkyl or  $C_{1-4}$ -alkoxy; and  
 $R^{12}$  is H,  $CH_3$  or - $NHCOCH_3$ .

40 In the dye of Formula XII it is especially preferred that  $Y^1$  and  $Y^2$  are both CN or that  $Y^1$  is CN and  $Y^2$  is  $NO_2$  and that  $R^5$  is H,  $R^{12}$  is - $NHCOCH_3$  and  $R^{14}$  &  $R^{15}$  are  $C_{2-4}$ -alkyl.

Thermal transfer printing sheets carrying a compound of Formula I in which the coupling component is a substituted aniline of Formula V, wherein one or both of  $R^3$  and  $R^4$  is an alkyl group, especially ethyl or propyl, carrying an electron withdrawing group, especially CN, OCO- $C_{1-4}$ -alkyl or COO- $C_{1-4}$ -alkyl, are especially preferred species of the present invention because of their very good stability. Stability of a dye on the transfer sheet is an important property because dyes with poor stability (i) tend to crystallise on the sheet and as a result do not transfer evenly onto the receiver sheet during the TTP process and/or (ii) tend to transfer under pressure alone so that (a) the receiver sheet becomes coloured in areas to which no heat is applied, while it is in contact, under pressure, with the transfer sheet during the TTP process and (b) dye is transferred from the front to the back of the transfer sheet when the transfer sheet is rolled up.

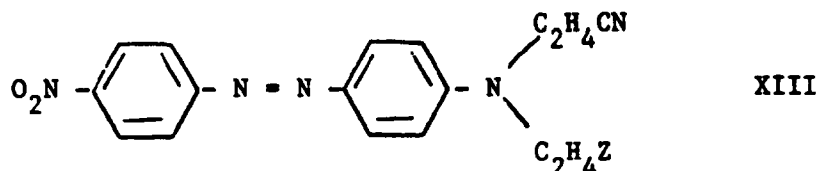
A dye of Formula I generally has good thermal properties giving rise to even prints on the receiver sheet, whose depth of shade is related to the quantity of applied heat so that a good gradation of colour density can be obtained.

A dye of Formula I also generally has strong coloristic properties and good solubility in a wide range of solvents, especially those solvents which are widely used and accepted in the printing industry, such as alkanols, e.g. ethanol, isopropanol & butanol, aromatic hydrocarbons, such as toluene and ketones such as MEK, MIBK and cyclohexanone. This facilitates the application of the dye to the substrate from a solution and thus aids in the achievement of bright, glossy prints on the receiver sheet. The combination of strong coloristic properties and good solubility in the preferred solvents allows the achievement of deep and even shades of good light fastness.

The blue dye of Formula XII in which  $Y^1$  &  $Y^2$  are both CN,  $R^5$  is H,  $R^{12}$  is  $-NHCOCH_3$  and  $R^{14}$  &  $R^{15}$  are both  $C_2H_5$  allows the achievement of a strong bright greenish-blue print on the receiver sheet of moderate lightfastness and high optical density. The related dye in which  $Y^2$  is  $NO_2$  allows the achievement of a strong bright mid-blue shade print of good lightfastness and high optical density.

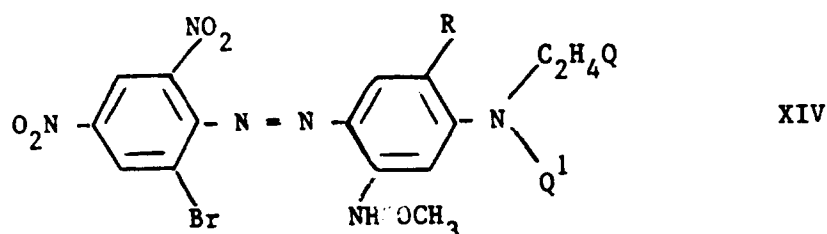
The dyes of Formula I give orange to blue shades. However, another important shade in trichromatic printing is black and mixtures of the present dyes, especially of dyes giving orange shades and dyes giving reddish blue shades, can be used to give good strong black shades.

Preferred orange dyes for use in such mixtures are of the formula:



wherein Z is H or  $-OCOCH_3$ .

Preferred blue dyes for use in such mixtures are of the formula:



wherein

R is H or  $-OCH_3$ ;

Q is selected from H,  $-OCOCH_3$  and  $-COOC_2H_4OCH_3$ ; and

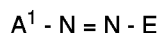
$Q^1$  is selected from H,  $-C_2H_5$  and  $-C_2H_4OCOCH_3$ .

Especially preferred blue dyes are those in which:

|       |                                 |                       |                        |
|-------|---------------------------------|-----------------------|------------------------|
| Dye 1 | R = $-OCH_3$ ;                  | Q = H;                | $Q^1 = -C_2H_5$        |
| Dye 2 | R = H;                          | Q = H;                | $Q^1 = -C_2H_5$        |
| Dye 3 | R = $-OCH_3$ ;                  | Q = $-OCOCH_3$ ;      | $Q^1 = -C_2H_4OCOCH_3$ |
| Dye 4 | R = $-OCH_3$ ;                  | Q = $-COOC_2H_4OCH_3$ | $Q^1 = H$              |
| Dye 5 | 3:1 mixture of Dye 2 and Dye 1. |                       |                        |

The relative proportions of the blue dye of Formula XII or XIV and the orange dye of Formula XIII required to produce a mixture giving a black shade depend on the shade of black required and the relative strengths of the component dyes. However the relative proportions generally range from 90:10 to 10:90 and more preferably from 70:30 to 30:70.

The coloristic properties and particularly the tinctorial strength of a dye of Formula I may be further improved by the addition of an azo dye containing a heterocyclic component. A suitable dye for use in admixture with one or more dyes of Formula I is one of the formula:



XV

wherein:

- A<sup>1</sup> is the radical of a diazotisable heteroaromatic amine, A<sup>1</sup>-NH<sub>2</sub>, in which A<sup>1</sup> is selected from imidazolyl, pyrazolyl, thiazolyl, benzothiazolyl, isothiazolyl, benzoisothiazolyl, pyridoisothiazolyl & thiophenyl; &  
 5 E is as hereinbefore defined.

The use of the dyes of Formula XV on TTP transfer sheets is described in European Patent Application No 86306158.6.

10 The radical, A<sup>1</sup>, of the heteroaromatic amine, A<sup>1</sup>-NH<sub>2</sub>, may be substituted by non-ionic groups, preferably those which are free from acidic hydrogen atoms, unless these are positioned so that they form intramolecular hydrogen bonds. Examples of such substituents are NO<sub>2</sub>; CN; CNS; halogen, especially F, Cl & Br; CF<sub>3</sub>; C<sub>1-4</sub>-alkyl; C<sub>1-4</sub>-alkoxy; C<sub>1-4</sub>-alkoxy-C<sub>1-4</sub>-alkyl; cyano-C<sub>1-4</sub>-alkyl; -SO<sub>2</sub>NH<sub>2</sub>; -SO<sub>2</sub>F; -SO<sub>2</sub>Cl; -CONH<sub>2</sub>; -COF; -COCl; C<sub>1-4</sub>-alkylthio; -SO<sub>2</sub>-C<sub>1-4</sub>-alkyl; -CON-(C<sub>1-4</sub>-alkyl)<sub>2</sub>; -SO<sub>2</sub>N(C<sub>1-4</sub>-alkyl)<sub>2</sub>; -COO-C<sub>1-4</sub>-alkyl and -CO-C<sub>1-4</sub>-alkyl.

15 Examples of suitable heteroaromatic residues, A<sup>1</sup>, are: 2,3-dicyanoimidazol-5-yl, 1-ethyl-2,3-dicyanoimidazol-5-yl, 5-nitrothiazol-2-yl, 3-methyl-4-cyanoisothiazol-5-yl, 4-cyanoisothiazol-5-yl, 6-fluorosulphonylbenzothiazol-2-yl, 6-thio-cyanobenzothiazol-2-yl, 6-methylsulphonylbenzothiazol-2-yl, 6-methoxybenzothiazol-2-yl, 5-nitro-2,1-benzoisothiazol-3-yl, 6-nitrobenzothiazol-2-yl, 1-ethyl-3,4-dicyanopyrazol-5-yl, 3,5-dicyanothiophen-1-yl, 3-cyanomethyl-4-cyanopyrazol-5-yl, 3,5-dinitrothiophen-1-yl, 6-cyanopyrido[2,3-c]isothiazol-1-yl, 3-cyano-5-nitrothiophen-1-yl, 6-nitropyrido[2,3-c]isothiazol-1-yl, 3-formyl-5-nitrothiophen-1-yl, 3-carboxy-5-nitrothiophen-1-yl, 1-cyanomethyl-3,4-dicyanopyrazol-5-yl, 20 1-cyanomethyl-2,3-dicyanoimidazol-5-yl, 1,3-di(cyanomethyl)-4-cyanopyrazol-5-yl, 5-nitro-7-bromo-2,1-benzoisothiazol-3-yl, 5-methyl-6-cyanopyrido[2,3-c]isothiazol-1-yl, 5-methoxy-6-cyanopyrido[2,3-c]isothiazol-1-yl.

The radical E present in the dye of Formula XV is preferably derived from a coupling component of Formula V.

25 Preferred dyes of Formula XV are the magenta dyes where A<sup>1</sup> is 3-methyl-4-cyanoisothiazol-5-yl, 4-cyanoisothiazol-5-yl and 1-cyanomethyl-3,4-dicyanopyrazol-5-yl, and where E is the radical of an aniline of Formula V where R<sup>2</sup> is H, Cl or C<sub>1-4</sub>-alkyl, especially CH<sub>3</sub>; R<sup>5</sup> is H; and R<sup>3</sup> & R<sup>4</sup> are each independently selected from C<sub>2</sub>-C<sub>4</sub>-alkyl, optionally substituted by -OCO-C<sub>1-4</sub>-alkyl, and especially from C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, and C<sub>2</sub>H<sub>4</sub>OCOCH<sub>3</sub>.

30 The preferred dyes of Formula XV are preferably used in admixture with the preferred dyes of Formula XI to prepare transfer sheets which have good storage stability and which give rise to magenta-shade prints of moderate lightfastness, of brighter shade than those derived from dyes of Formula XI and of significantly higher strength than is achievable with dyes of Formula XI alone.

The dyes of Formula XV are usually, but not necessarily, the minor components of the mixture.

35 The substrate may be any convenient sheet material capable of withstanding the temperatures involved in TTP, up to 400°C over a period of up to 20 milliseconds (msec), yet thin enough to transmit heat applied on one side through to the dye on the other side to effect transfer to a receiver sheet within such short periods, typically from 1 to 10 msec. Examples of suitable materials are paper, especially high quality paper of even thickness, such as capacitor paper, polyester, polyacrylate, polyamide, cellulosic and polyalkylene films, metallised forms thereof, including co-polymer and laminated films, especially laminates incorporating a polyester layer on which the dye is deposited. Such laminates preferably comprise, in addition to the polyester, a backcoat of a heat-resistant material, such as a thermosetting resin, e.g. silicone or polyurethane, to separate the heat source from the polyester so that the latter is not melted. The thickness of the substrate may vary within wide limits depending upon its thermal characteristics but is preferably less than 50 µm and more preferably below 10 µm.

The coating preferably comprises a binder and one or more dyes of Formula I, optionally with one or more dyes of Formula XV. The ratio of binder to dye is preferably at least 1:1 and more preferably from 1.5:1 to 4:1 in order to provide good adhesion between the dye and the substrate and inhibit migration of the dye during storage.

45 The binder may be any resinous or polymeric material suitable for binding the dye to the substrate. Examples of suitable binders are cellulose derivatives, such as ethylhydroxyethylcellulose (EHEC), hydroxypropylcellulose (HPC), ethylcellulose, methylcellulose, cellulose acetate and cellulose acetate butyrate; carbohydrate derivatives, such as starch; alginic acid derivatives; alkyl resins; vinyl resins and derivatives, such as polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral and polyvinyl pyrrolidone; polymers and copolymers derived from acrylates and acrylate derivatives, 50 such as polyacrylic acid, polymethyl methacrylate and styrene-acrylate copolymers, polyester resins, polyamide resins, such as melamines; polyurea and polyurethane resins; organosilicones, such as polysiloxanes, epoxy resins and natural resins, such as gum tragacanth and gum arabic.

The coating may also contain other additives, such as curing agents, preservatives, etc., these and other ingredients being described more fully in EP 133011A, EP 133012A and EP 111004A.

55 According to a further feature of the present invention there is provided a transfer printing process which comprises contacting a transfer sheet coated with a dye of Formula I with a receiver sheet, so that the dye is adjacent to the receiver sheet, and selectively heating an area of the transfer sheet whereby dye in the heated area of the transfer sheet may be selectively transferred to the receiver sheet.

The transfer sheet is preferably heated to a temperature from 250°C to 400°C, more preferably 300°C to 400°C, for a period of from 0.5 to 30 msec, more preferably from 1 to 10 msec, while it is maintained in contact with the receiver sheet. The depth of shade of print on any area of the receiver sheet will vary with the time period for, and temperature at, which the transfer sheet is heated while in contact with the receiver sheet.

The receiver sheet conveniently comprises a white polyester sheet material, especially of polyethylene terephthalate (PET). Although the dye of Formula I is known for the colouration of textile materials made from PET, the colouration of textile materials, by dyeing or printing, is carried out under such conditions of time and temperature that the dye can penetrate the PET and become fixed therein. In thermal transfer printing, the time period is so short that penetration of the PET is less effective and the receiver sheet is preferably provided with a receptive layer on the side to which the dye is applied, into which the dye can more readily diffuse to form a stable image on the receiver sheet. Such a receptive coating may comprise a thin layer, applied to the receiver sheet by co-extrusion or solution coating techniques, of a modified polyester or a different polymeric material which is more permeable to the dye than PET. The nature of the receptive coating will affect to some extent the depth of shade and quality of the print obtained but it has been found that the present dyes give particularly strong and good quality prints compared with other dyes which have been previously proposed for thermal transfer printing on any specific receiver sheet. The design of receiver sheets with receptive layers is discussed in EP 133,011A & EP 133,012A.

The invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated.

#### Ink 1

A mixture of 0.1g by weight of 3-methyl-4-(2-cyano-4-nitrophenylazo)-N,N-bis(2-acetoxyethyl)aniline 5 ml of chloroform and 9.5 ml of a solution of 2.7% ethylhydroxyethyl cellulose (EHEC - low mol wt grade) in chloroform was shaken until a homogeneous solution was formed. The absorption maximum and the molar extinction coefficient was determined and is recorded in Table 1.

#### Inks 2 to 26

A further 25 inks were prepared by the same method as Ink 1 using each of the azo dyes or mixtures of azo dyes indicated in Table 1 below.

#### Example 1

A thermal transfer sheet was prepared by forming a 24 µm coating of Ink 1 (using a Mayer bar) on the precleaned (with dichloromethane) surface of a sheet of PET film (6 µm, MELINEX) having a thermally protected back-coat layer (2 µm). The coating was dried in hot air stream. The transfer sheet is hereinafter referred to as TS1.

#### Examples 2 to 26

A further 25 transfer sheets (TS2 to TS26) were prepared by the method of Example 1 using Inks 2 to 26 in place of Ink 1.

#### Example 27

Transfer sheet TS1 was sandwiched with a composite receiver sheet comprising a white PET substrate and a receptive layer on the side in contact with the printed surface of TS1. The sandwich was placed on the cylindrical drum of thermal transfer printing machine. On rotation of the drum, the sandwich passed over a matrix of closely spaced pixels which were selectively heated in accordance with a pattern information signal to a temperature of 350°C for periods from 1 to 10 msec, whereby a quantity of the dye, in proportion to the heating period, at the position on the transfer sheet in contact with a pixel while it was hot, was transferred from the transfer sheet to the receiver sheet. The pattern information signal was formulated so that the heating period of the pixels was increased at regular intervals as the sandwiched passed over the matrix so that the printed pattern was in the form of a scale composed of bands of colour of increasing depth of shade. After passage over the array of pixels the transfer sheet was separated from the receiver sheet. Superficial dye which had not penetrated the receptor layer on the receiver sheet was removed by the application and removal of a strip of self-adhesive tape. The printed receiver sheet is hereinafter referred to as RS1.

Examples 28 to 52

A further 25 receiver sheets (RS 2 to RS 26) were printed by the method of Example 27 using TS2 to TS 26 in place of TS1.

Assessment of Receiver Sheets

The reflectance optical density of the print on each receiver sheet was measured by examination of the band having the maximum depth of shade with a Sakura digital densitometer and the results of the measurements are given in Table 1. Magenta dyes were examined through a green filter and blue dyes were examined through a red filter.

Table 1

| <u>Ink/Ex</u> | <u>Dye</u>                                                                          | <u>Abs Max</u><br><u>(EtOAc)</u> | <u>Molar</u><br><u>Extinct</u><br><u>Coeff</u> | <u>Reflectance</u><br><u>Optical</u><br><u>Density</u> |
|---------------|-------------------------------------------------------------------------------------|----------------------------------|------------------------------------------------|--------------------------------------------------------|
| 1/27          | 3-methyl-4-(2-cyano-4-nitrophenylazo)-N,N-bis-(2-acetoxyethyl)-aniline              | 516                              | 37,647                                         | 1.08                                                   |
| 2/28          | 4-(2-cyano-4-nitrophenylazo)-N,N-bis-(2-acetoxyethyl)aniline                        | 503                              | 34,188                                         | 1.40                                                   |
| 3/29          | 4-(2-cyano-4-nitrophenylazo)-N,N-diethylaniline                                     | 529                              | 43,397                                         | 1.68                                                   |
| 4/30          | 4-(2-cyano-4-nitrophenylazo)-N-(2-acetoxyethyl)-N-ethylaniline                      | 518                              | 37,361                                         | 1.20                                                   |
| 5/31          | 4-(2-cyano-4-nitrophenylazo)-N-(2-ethoxyethyl)-N-ethylaniline                       | 526                              | 39,170                                         | 1.52                                                   |
| 6/32          | 4-(2-cyano-4-nitrophenylazo)-3-acetylamino-N,N-bis-(2-methoxycarbonyl-ethyl)aniline | 534                              | 48,405                                         | 1.40                                                   |
| 7/33          | 4-(2,4-dicyanophenylazo)-3-acetylamino-N,N-diethylaniline                           | 525                              | 55,800                                         | 1.77                                                   |
| 8/34          | 4-(2,4-dinitrophenylazo)-3-acetylamino-N,N-bis-(2-methoxycarbonyl-ethyl)-aniline    | 530                              | 48,784                                         | 1.19                                                   |

| <u>Example</u> | <u>Dye</u>                                                                                                                                                           | <u>Abs Max</u><br>(EtOAc) | <u>Molar</u><br><u>Extinct</u><br><u>Coeff</u> | <u>Reflectance</u><br><u>Optical</u><br><u>Density</u> |
|----------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------|------------------------------------------------|--------------------------------------------------------|
| 9/35           | 6-(3,4-dicyanophenylazo)-<br>1-(2-acetoxyethyl)-<br>1,2,3,4-tetrahydro-<br>2,2,4,7-tetramethyl-<br>quinoline                                                         | 501                       | 39,128                                         | 1.00                                                   |
| 10/36          | 3-methyl-4-(2,4-dinitro-<br>phenylazo)-N,N-bis-(2-ethoxy-<br>carbonylethyl)-aniline                                                                                  | 514                       | 35,427                                         | 1.10                                                   |
| 11/37          | 3-methyl-4-(2,4-dinitro-<br>phenylazo)-N-(2-acetoxy-<br>ethyl)-N-ethyl-aniline                                                                                       | 523                       | 36,225                                         | 1.20                                                   |
| 12/38          | 3-methyl-4-(2,4-dinitro-<br>phenylazo)-N,N-bis-<br>(2-acetoxyethyl) aniline                                                                                          | 507                       | 35,232                                         | 1.10                                                   |
| 13/39          | 3-methyl-4-(2-cyano-<br>4-nitrophenylazo)-<br>N,N-diethylaniline                                                                                                     | 541                       | 42,542                                         | 1.60                                                   |
| 14/40          | 3-methyl-4-(2-cyano-<br>4-nitrophenylazo)-N-ethyl<br>N-(2-acetoxyethyl) aniline                                                                                      | 529                       | 41,223                                         | 1.50                                                   |
| 15/41          | 3-methyl-4-(2-cyano-<br>4-nitrophenylazo)-<br>N,N-bis-(2-acetoxy-<br>ethyl) aniline<br>+<br>3-methyl-4-(3-methyl-<br>4-cyano-isothiazol-5-yl)-<br>N,N-diethylaniline | -                         | -                                              | 1.80                                                   |
| 16/42          | 3-methyl-4-(2-cyano-<br>4-nitrophenylazo)-<br>N,N-bis-(2-acetoxy-<br>ethyl) aniline<br>+<br>4-(3-methyl-4-cyano-<br>isothiazol-5-yl)-<br>N,N-diethylaniline          | -                         | -                                              | 2.10                                                   |

| <u>Example</u> | <u>Dye</u>                                                        | <u>Abs Max</u><br><u>(EtOAc)</u> | <u>Molar</u><br><u>Extinct</u><br><u>Coeff</u> | <u>Reflectance</u><br><u>Optical</u><br><u>Density</u> |
|----------------|-------------------------------------------------------------------|----------------------------------|------------------------------------------------|--------------------------------------------------------|
| 26/52          | 3-acetylamino-4-(2,4-dinitro-6-cyanophenylazo)-N,N-diethylaniline | 605                              | 67,366                                         | 1.58                                                   |

#### Example 53

Three black dye mixtures were prepared from the following dyes:

- Dye A: 3-acetylamino-4-(2,4-dinitro-6-bromophenylazo)-N,N-diethylaniline  
Dye B: 5-acetylamino-4-(2,4-dinitro-6-bromophenylazo)-2-methoxy-N,N-diethylaniline  
Dye C: 4-(4-nitrophenylazo)-N-(2-cyanoethyl)-N-(2-acetoxyethyl)aniline  
Dye D: 1-ethyl-3-cyan-4-methyl-5-(4-[2-(2-methoxyethoxy)ethoxy]carbonylphenylazo)-pyrid-2,6-dione  
Dye E: 1-ethyl-3-cyan-4-methyl-5-(2-nitrophenylazo)-pyrid-2,6-dione

- Black 1 0.43g Dye A + 0.16g Dye B + 0.42g Dye C  
Black 2 0.43g Dye A + 0.16g Dye B + 0.31g Dye C + 0.11g Dye D  
Black 3 0.43g Dye A + 0.16g Dye B + 0.31g Dye C + 0.11g Dye E

Each of these mixtures was formed into an ink by the method for Ink 1 and the ink used to prepare a transfer sheet by the method of Example 1. Each black mixture was transferred by the method of Example 27 to produce a receiver sheet having an even black shade.

Other dyes which are suitable for the preparation of thermal transfer sheets by the methods hereinbefore described are:

4-(2-cyan-4-nitrophenylazo)-N-(2-cyanoethyl)-N-(2-acetoxyethyl)aniline 4-(2-cyano-4-nitrophenylazo)-N-(2-cyanoethyl)-N-(2-methoxycarbonyl)ethyl)aniline 4-(2-cyan-4-nitrophenylazo)-N-(2-cyanoethyl)-N-(2-methoxycarbonyloxyethyl)aniline 4-(2-cyan-4-nitrophenylazo)-N-(2-cyanoethyl)-N-(2-[phenoxyethyl]carbonyloxy)ethyl)aniline 4-(2-cyano-4-nitrophenylazo)-N-(2-cyanoethyl)-N-(2-[propoxycarbonyloxy]ethyl)aniline 4-(2-cyano-4-nitrophenylazo)-N-(2-cyanoethyl)-N-(2-methoxy-3-phenoxypropyl)aniline 4-(2-cyano-4-nitrophenylazo)-N-(2-cyanoethyl)-N-(2-[n-butylaminocarbonyloxy]ethyl)aniline 4-(2-cyano-4-nitrophenylazo)-N,N-bis(2-methoxycarbonyloxyethyl)-aniline 4-(2-methylsulphonyl-4-nitrophenylazo)-N-ethyl-N-(2-acetoxyethyl)-aniline 4-(2-methylsulphonyl-4-nitrophenylazo)-N-ethyl-N-(2-[phenoxyethyl]carbonyloxy)ethyl)aniline 3-methyl-4-(2-cyano-4-nitrophenylazo)-N,N-bis(2-methoxycarbonyloxyethyl)aniline 3-methyl-4-(2-methylsulphonyl-4-nitrophenylazo)-N,N-bis(2-acetoxyethyl)aniline 3-chloro-4-(2-cyano-4-nitrophenylazo)-N-ethyl-N-(2-ethoxycarbonyl)ethyl)aniline 3-acetylamino-4-(2-cyan-4-nitrophenylazo)-N-ethyl-N-(2-phthalimidoethyl)aniline 3-acetylamino-4-(2-cyano-4-nitrophenylazo)-N-benzylaniline 3-acetylamino-4-(2-cyano-4-nitrophenylazo)-N,N-bis(2-methoxyethyl)-aniline 3-methylsulphonylamino-4-(2,6-dicyano-4-nitrophenylazo)-N,N-diethylaniline 3-methylsulphonylamino-4-(2,6-dicyano-4-nitrophenylazo)-N,N-bis(n-propyl)aniline and compound shades such as brown, grey and black, by mixing these dyes in appropriate proportions.

#### Comparative Example

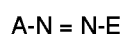
An ink (Ink A) was made according to the procedure of Ink 1 using the same weight of 1-amino-2-phenoxy-4-hydroxyanthraquinone in place of Dye 1. A transfer sheet (TSA) was prepared according to Example 1 using Ink A in place of Ink 1. A printed receiver sheet (RSA) was prepared by the method of Example 27 using TSA in place of TS1. The reflectance optical density of RSA was measured by examination of the band having maximum depth of shade with a Sakura digital densitometer under the same conditions as the assessment of receiver sheets RS1 to RS26. The result of the measurement is shown below in comparison with that of RS1 (taken from Example 27 in Table 1)

| Receiver Sheet | Reflectance Optical Density |
|----------------|-----------------------------|
| RSA            | 0.63                        |
| RS1            | 1.08                        |

## Claims

Claims for the following Contracting States : DE, FR, GB, IT, NL

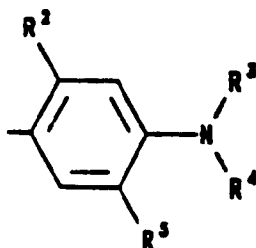
1. A thermal transfer printing sheet comprising a substrate having a coating comprising a dye of the formula:



wherein:

A is a phenyl group substituted by two or three groups selected from NO<sub>2</sub>, CN and -SO<sub>2</sub>C<sub>1-4</sub>-alkyl and optionally by one or more groups selected from C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkoxy; and  
E is selected from,

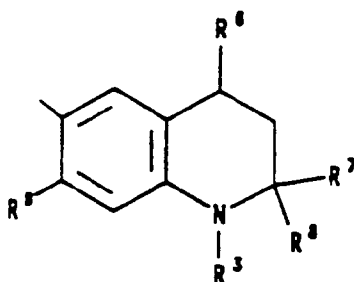
(i) an amino group of the formula:



wherein:

R<sup>2</sup> is selected from H, C<sub>1-4</sub>-alkyl, C<sub>1-4</sub>-alkoxy, C<sub>1-4</sub>-alkylthio, NH<sub>2</sub>-CO-NH-, HCONH-, phenyl-CONH-, C<sub>1-4</sub>-alkyl-CO-NH-, C<sub>1-4</sub>-alkyl-SO<sub>2</sub>-NH-, CN, CF<sub>3</sub>, and halogen;  
R<sup>3</sup> & R<sup>4</sup> are independently selected from H; C<sub>1-6</sub>-alkyl and C<sub>4-8</sub>-cycloalkyl, each of which is unsubstituted or substituted by a group independently selected from halogen, CN, phenyl, mono- or bicyclic heteroaryl, -OCO-C<sub>1-4</sub>-alkyl, -COO-C<sub>1-4</sub>-alkyl, C<sub>2-4</sub>-alkenyl, and C<sub>1-4</sub>-alkoxy; or together with the nitrogen atom to which they are attached form a heterocyclic ring, such as morpholine, piperazine or thiomorpholine; and  
R<sup>5</sup> is selected from H, C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkoxy;

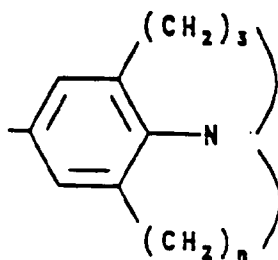
(ii) a tetrahydroquinoliny group of the formula:



wherein:

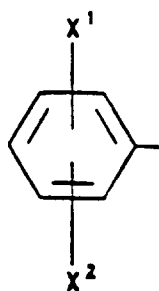
$R^3$  is selected from H;  $C_{1-6}$ -alkyl and  $C_{4-8}$ -cycloalkyl, each of which is independently unsubstituted or substituted by a group selected from halogen, CN, phenyl, mono- or bicyclic heteroaryl, -OCO- $C_{1-4}$ -alkyl, -COO- $C_{1-4}$ -alkyl,  $C_{2-4}$ -alkenyl, and  $C_{1-4}$ -alkoxy; and  $R^6$  to  $R^9$  are independently selected from H and  $C_{1-4}$ -alkyl; and

(iii) lilolidiny or julolidiny of the formula:



wherein:  $n = 2$  (lilolidine) or  $3$  (julolidine) provided that the dye is not C.I. Disperse Blue 165, C.I. Disperse Blue 287 and C.I. Disperse Red 73 or that the substrate does not have a good heat conductive powder or that the substrate is not paper.

2. A thermal transfer printing sheet according to Claim 1 wherein A is of the formula:

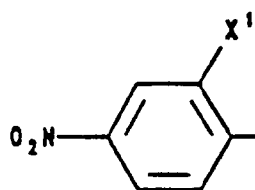


wherein:

$X^1$  is  $NO_2$ , CN or  $-SO_2CH_3$ ; and  
 $X^2$  is  $NO_2$ , CN,  $-SO_2CH_3$

provided that the dye is not C.I. Disperse Red 73 or that the substrate does not have a good heat conductive powder.

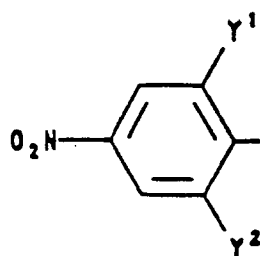
3. A thermal transfer printing sheet according to Claim 1 where A is of the formula:



wherein:

$X^1$  is  $\text{NO}_2$ , CN or  $-\text{SO}_2\text{CH}_3$  provided that the dye is not C.I. Disperse Red 73 or that the substrate does not have a good heat conductive powder.

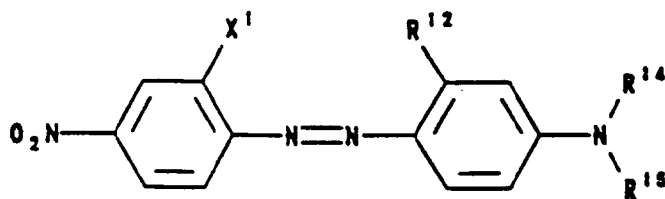
4. A thermal transfer printing sheet according to Claim 1 wherein A is of the formula:



wherein:

$Y^1$  &  $Y^2$  are independently selected from CN,  $\text{NO}_2$  provided that they are not both  $\text{NO}_2$  provided that the dye is not C.I. Disperse Blue 165 and C.I. Disperse Blue 287 or that the substrates does not have a good heat conductive powder.

5. A thermal transfer printing sheet according to Claim 1 wherein the dye is of the formula:



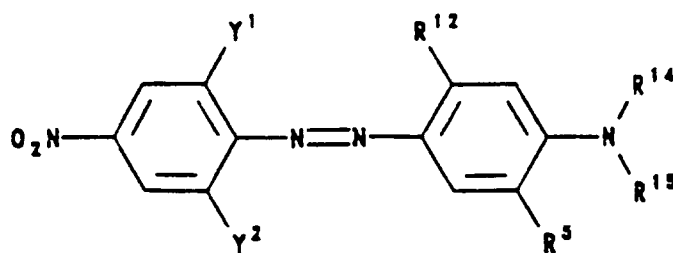
wherein:

$X^1$  is  $\text{NO}_2$  or CN;

$R^{12}$  is selected from H,  $\text{CH}_3$  and  $-\text{NHCOCH}_3$ ; and

$R^{14}$  &  $R^{15}$  are each independently selected from  $\text{C}_{2-4}$ -alkyl,  $\text{C}_{1-4}$ -alkylene-OCO- $\text{C}_{1-4}$ -alkyl and  $\text{C}_2\text{H}_4\text{CN}$  provided that the dye is not C.I. Disperse Red 73 or that the substrate does not have a good heat conductive powder.

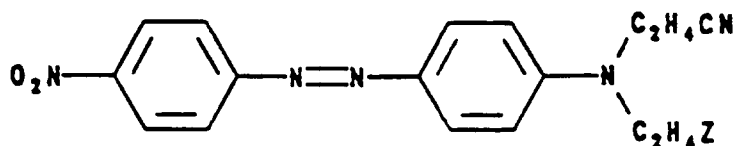
6. A thermal transfer printing sheet according to Claim 1 wherein the dye is of the formula:



wherein:

- Y<sup>1</sup> is NO<sub>2</sub> or CN;  
 Y<sup>2</sup> is CN;  
 R<sup>14</sup> & R<sup>15</sup> are each independently selected from C<sub>2-4</sub>-alkyl and C<sub>1-4</sub>-alkylene-OCO-C<sub>1-4</sub>-alkyl;  
 R<sup>5</sup> is selected from H, C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkoxy; and  
 R<sup>12</sup> is selected from H, CH<sub>3</sub> or -NHCOCH<sub>3</sub> provided that the dye is not C.I. Disperse Blue 165 and C.I. Disperse Blue 287 or that the substrate does not have a good heat conductive powder.

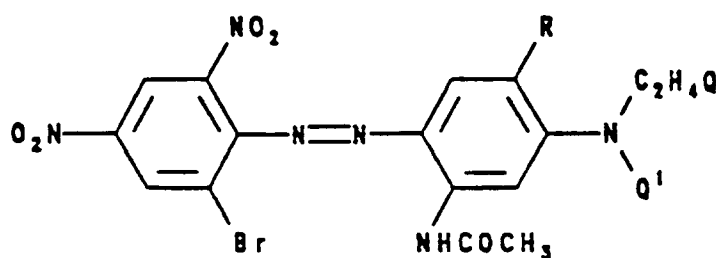
7. A thermal transfer printing sheet according to Claim 1 wherein the coating comprises a dye of the formula:



wherein:

- Z is H or -OCOCH<sub>3</sub>;

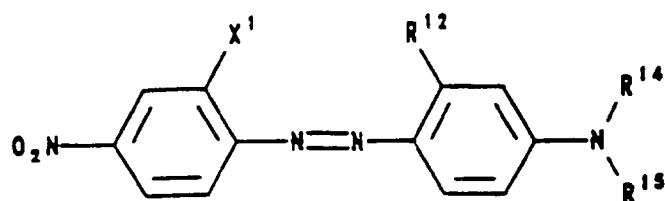
in admixture with a dye of the formula:



wherein:

- R is H or -OCH<sub>3</sub>;  
 Q is selected from H, -OCOCH<sub>3</sub> and -COOC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub>; and  
 Q<sup>1</sup> is selected from H, -C<sub>2</sub>H<sub>5</sub> and -C<sub>2</sub>H<sub>4</sub>OCOCH<sub>3</sub>.

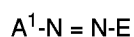
8. A thermal transfer printing sheet according to Claim 1 wherein the coating comprises a dye of the formula:



wherein:

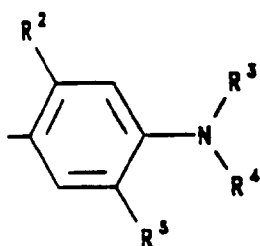
- $X^1$  is  $\text{NO}_2$  or  $\text{CN}$ ;  
 $R^{12}$  is selected from H,  $\text{CH}_3$  and  $-\text{NHCOCH}_3$ ; and  
 $R^{14}$  &  $R^{15}$  are each independently selected from  $\text{C}_{2-4}$ -alkyl,  $\text{C}_{1-4}$ -alkylene-OCO- $\text{C}_{1-4}$ -alkyl and  $\text{C}_2\text{H}_4\text{CN}$ ;

in admixture with a dye of the formula:



wherein:

- $\text{A}^1$  is selected from 3-methyl-4-cyanoisothiazol-5-yl, 4-cyanoisothiazol-5-yl and 1-cyanomethyl-3,4-dicyanopyrazol-5-yl; and  
 E is of the formula:



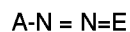
wherein:

- $R^2$  is selected from H, chlorine and  $\text{C}_{1-4}$ -alkyl;  
 $R^3$  &  $R^4$  are each independently  $\text{C}_{2-4}$ alkylene-OCO- $\text{C}_{1-4}$ -alkyl or  $\text{C}_{2-4}$ -alkyl; and  
 $R^5$  is H.

9. A thermal transfer printing process which comprises contacting a transfer sheet according to Claim 1 coated with a dye of Formula I with a receiver sheet, so that the dye is adjacent to the receiver sheet, and selectively heating an area of the transfer sheet to a temperature from  $250^\circ\text{C}$  to  $400^\circ\text{C}$  for a period of from 0.5 to 30 msec whereby dye in the heated area of the transfer sheet is selectively transferred to the receiver sheet.

Claims for the following Contracting States : AT, BE, CH, LI, SE

1. A thermal transfer printing sheet comprising a substrate having a coating comprising a dye of the formula:

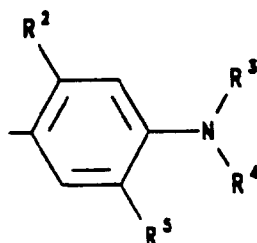


I

wherein:

- A is a phenyl group substituted by two or three groups selected from NO<sub>2</sub>, CN and -SO<sub>2</sub>C<sub>1-4</sub>-alkyl and optionally by one or more groups selected from C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkoxy; and  
 E is selected from,

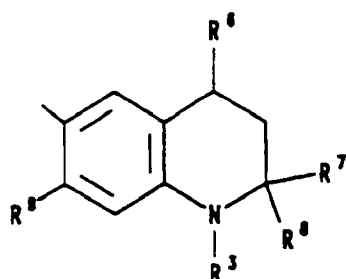
(i) an anilino group of the formula:



wherein:

- R<sup>2</sup> is selected from H, C<sub>1-4</sub>-alkyl, C<sub>1-4</sub>-alkoxy, C<sub>1-4</sub>-alkylthio, NH<sub>2</sub>-CO-NH-, HCONH-, phenyl-CONH-, C<sub>1-4</sub>-alkyl-CO-NH-, C<sub>1-4</sub>-alkyl-SO<sub>2</sub>-NH-, CN, CF<sub>3</sub>, and halogen;  
 R<sup>3</sup> & R<sup>4</sup> are independently selected from H; C<sub>1-6</sub>-alkyl and C<sub>4-8</sub>-cycloalkyl, each of which is unsubstituted or substituted by a group independently selected from halogen, CN, phenyl, mono- or bicyclic heteroaryl, -OCO-C<sub>1-4</sub>-alkyl, -COO-C<sub>1-4</sub>-alkyl, C<sub>2-4</sub>-alkenyl, and C<sub>1-4</sub>-alkoxy; or  
 R<sup>3</sup> & R<sup>4</sup> together with the nitrogen atom to which they are attached form a heterocyclic ring, such as morpholine piperazine or thiomorpholine; and  
 R<sup>5</sup> is selected from H, C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkoxy;

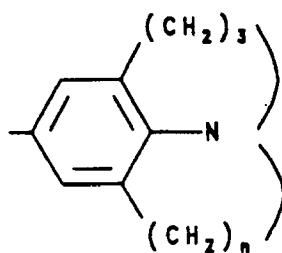
(ii) a tetrahydroquinolinyl group of the formula:



wherein:

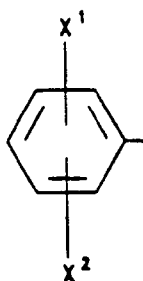
- R<sup>3</sup> is selected from H; C<sub>1-6</sub>-alkyl and C<sub>4-8</sub>-cycloalkyl, each of which is independently unsubstituted or substituted by a group selected from halogen, CN, phenyl, mono- or bicyclic heteroaryl, -OCO-C<sub>1-4</sub>-alkyl, -COO-C<sub>1-4</sub>-alkyl, C<sub>2-4</sub>-alkenyl, and C<sub>1-4</sub>-alkoxy; and  
 R<sup>6</sup> to R<sup>9</sup> are independently selected from H and C<sub>1-4</sub>-alkyl; and

(iii) lilolidinyl or julolidinyl of the formula:



wherein:  $n = 2$  (lilolidine) or  $3$  (julolidine) provided that the substrate does not have a good heat conductive powder or that the substrate is not paper.

2. A thermal transfer printing sheet according to Claim 1 wherein A is of the formula:

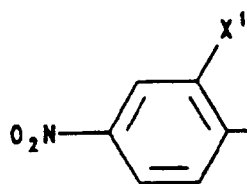


wherein:

$X^1$  is  $\text{NO}_2$ ,  $\text{CN}$  or  $-\text{SO}_2\text{CH}_3$ ; and

$X^2$  is  $\text{NO}_2$ ,  $\text{CN}$ ,  $-\text{SO}_2\text{CH}_3$  provided that the substrate does not have a good heat conductive powder or that the substrate is not paper.

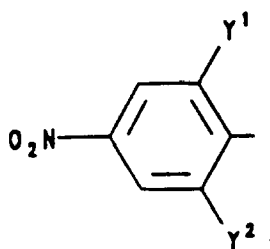
3. A thermal transfer printing sheet according to Claim 1 where A is of the formula:



wherein:

$X^1$  is  $\text{NO}_2$ ,  $\text{CN}$  or  $-\text{SO}_2\text{CH}_3$  provided that the substrate does not have a good heat conductive powder or that the substrate is not paper.

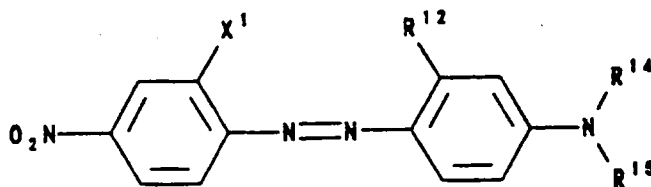
4. A thermal transfer printing sheet according to Claim 1 wherein A is of the formula:



wherein:

$\text{Y}^1$  &  $\text{Y}^2$  are independently selected from CN,  $\text{NO}_2$  provided that they are not both  $\text{NO}_2$  provided that the substrate does not have a good heat conductive powder.

5. A thermal transfer printing sheet according to Claim 1 wherein the dye is of the formula:



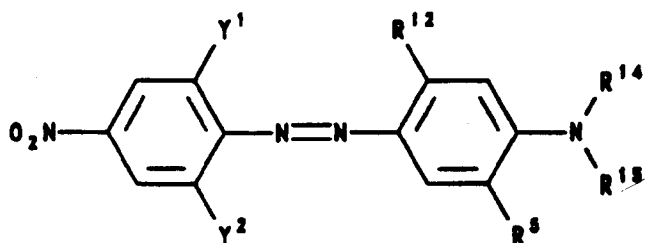
wherein:

$\text{X}^1$  is  $\text{NO}_2$  or CN;

$\text{R}^{12}$  is selected from H,  $\text{CH}_3$  and  $\text{-NHCOCH}_3$ ; and

$\text{R}^{14}$  &  $\text{R}^{15}$  are each independently selected from  $\text{C}_{2-4}$ -alkyl,  $\text{C}_{1-4}$ -alkylene-OCO- $\text{C}_{1-4}$ -alkyl and  $\text{C}_2\text{H}_4\text{CN}$  provided that the substrate does not have a good heat conductive powder or that the substrate is not paper.

6. A thermal transfer printing sheet according to Claim 1 wherein the dye is of the formula:



wherein:

$\text{Y}^1$  is  $\text{NO}_2$  or CN;

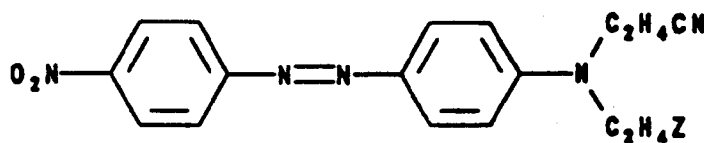
$\text{Y}^2$  is CN;

$\text{R}^{14}$  &  $\text{R}^{15}$  are each independently selected from  $\text{C}_{2-4}$ -alkyl and  $\text{C}_{1-4}$ -alkylene-OCO- $\text{C}_{1-4}$ -alkyl;

$\text{R}^5$  is selected from H,  $\text{C}_{1-4}$ -alkyl and  $\text{C}_{1-4}$ -alkoxy; and

$\text{R}^{12}$  is selected from H,  $\text{CH}_3$  or  $\text{-NHCOCH}_3$  provided that the substrate does not have a good heat conductive powder.

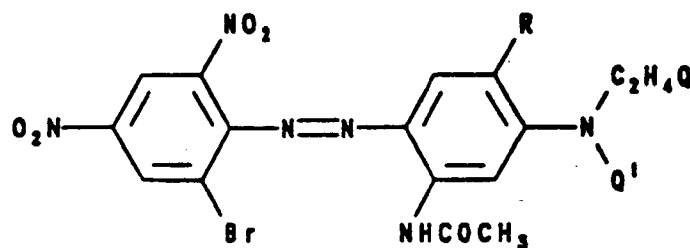
7. A thermal transfer printing sheet according to Claim 1 wherein the coating comprises a dye of the formula:



wherein:

Z is H or -OCOCH<sub>3</sub>;

in admixture with a dye of the formula:



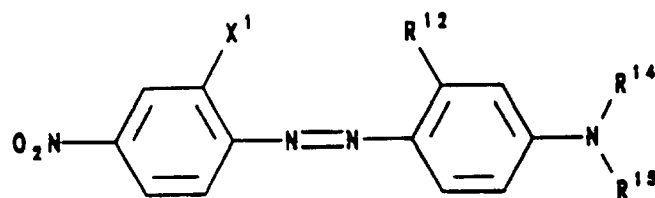
wherein:

R is H or -OCH<sub>3</sub>;

Q is selected from H, -OCOCH<sub>3</sub> and -COOC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub>; and

Q' is selected from H, -C<sub>2</sub>H<sub>5</sub> and -C<sub>2</sub>H<sub>4</sub>OCOCH<sub>3</sub>.

8. A thermal transfer printing sheet according to Claim 1 wherein the coating comprises a dye of the formula:



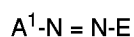
wherein:

X<sup>1</sup> is NO<sub>2</sub> or CN;

R<sup>12</sup> is selected from H, CH<sub>3</sub> and -NHCOCH<sub>3</sub>; and

R<sup>14</sup> & R<sup>15</sup> are each independently selected from C<sub>2-4</sub>-alkyl, C<sub>1-4</sub>-alkylene-OCO-C<sub>1-4</sub>-alkyl and C<sub>2</sub>H<sub>4</sub>CN;

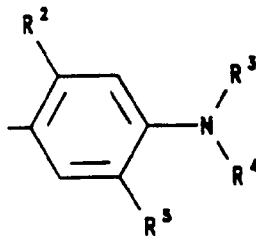
in admixture with a dye of the formula:



wherein:

A<sup>1</sup> is selected from 3-methyl-4-cyanoisothiazol-5-yl, 4-cyanoisothiazol-5-yl and 1-cyanomethyl-3,4-dicyano-pyrazol-5-yl; and

E is of the formula:



wherein:

$R^2$  is selected from H, chlorine and  $C_{1-4}$ -alkyl;  
 $R^3$  &  $R^4$  are each independently  $C_{2-4}$ alkylene-OCO- $C_{1-4}$ -alkyl or  $C_{2-4}$ -alkyl;  
 and  
 $R^5$  is H.

9. A thermal transfer printing process which comprises contacting a transfer sheet according to Claim 1 coated with a dye of Formula I with a receiver sheet, so that the dye is adjacent to the receiver sheet, and selectively heating an area of the transfer sheet to a temperature from 250°C to 400°C for a period of from 0.5 to 30 msec whereby dye in the heated area of the transfer sheet is selectively transferred to the receiver sheet.

#### Patentansprüche

Patentansprüche für folgende Vertragsstaaten : DE, FR, GB, IT, NL

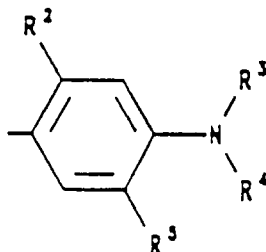
1. Thermotransferdruckblatt, welches aus einem Substrat mit einem Belag besteht, der einen Farbstoff der Formel



enthält, worin

A für ein Phenyl-Gruppe steht, die durch zwei oder drei Gruppen, welche ausgewählt sind aus  $NO_2$ , CN und  $SO_2C_{1-4}$ -Alkyl, und gegebenenfalls durch eine oder mehrere Gruppen, welche ausgewählt sind aus  $C_{1-4}$ -Alkyl und  $C_{1-4}$ -Alkoxy, substituiert ist; und  
 E ausgewählt ist aus

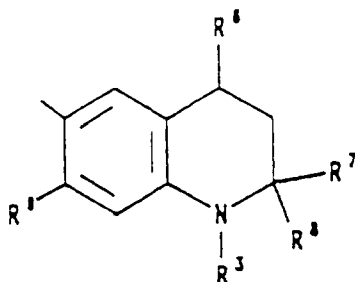
(i) Anilino-Gruppen der Formel



wobei

$R^2$  ausgewählt ist aus H,  $C_{1-4}$ -Alkyl,  $C_{1-4}$ -Alkoxy,  $C_{1-4}$ -Alkylthio,  $NH_2-CO-NH-$ ,  $HCONH-$ , Phenyl-  
 $CONH-$ ,  $C_{1-4}$ -Alkyl- $CO-NH-$ ,  $C_{1-4}$ -Alkyl- $SO_2-NH-$ , CN,  $CF_3$  und Halogen,  
 $R^3$  und  $R^4$  unabhängig ausgewählt sind aus H,  $C_{1-6}$ -Alkyl und  $C_{4-8}$ -Cycloalkyl, welches jeweils unsubstitu-  
 iert oder durch eine Gruppe substituiert ist, die unabhängig ausgewählt ist aus Halogen, CN,  
 Phenyl, mono- oder bicyclischem Heteroaryl,  $-OCO-C_{1-4}$ -Alkyl,  $-COO-C_{1-4}$ -Alkyl,  $C_{2-4}$ -Alkenyl  
 und  $C_{1-4}$ -Alkoxy, oder  
 $R^3$  und  $R^4$  zusammen mit dem Stickstoffatom, an welches sie gebunden sind, einen heterocyclischen Ring,  
 wie z.B. Morpholin, Piperazin oder Thiomorpholin, bilden, und  
 $R^5$  ausgewählt ist aus H,  $C_{1-4}$ -Alkyl und  $C_{1-4}$ -Alkoxy;

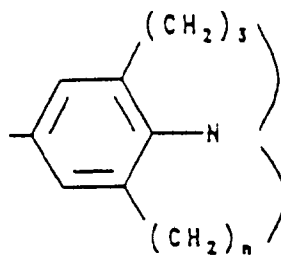
(ii) Tetrahydrochinoliny-Gruppen der Formel,



wobei

$R^3$  ausgewählt ist aus H,  $C_{1-6}$ -Alkyl und  $C_{4-8}$ -Cycloalkyl, welches jeweils unsubstituiert oder  
 durch eine Gruppe substituiert ist, die unabhängig ausgewählt ist aus Halogen, CN, Phenyl,  
 mono- oder bicyclischem Heteroaryl,  $-OCO-C_{1-4}$ -Alkyl,  $-COO-C_{1-4}$ -Alkyl,  $C_{2-4}$ -Alkenyl und  $C_{1-4}$ -  
 Alkoxy, und  
 $R^6$  bis  $R^9$  unabhängig ausgewählt sind aus H und  $C_{1-4}$ -Alkyl; und

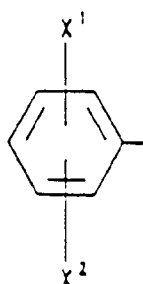
(iii) Lilolidinyl oder Julolidinyl der Formel,



wobei:

$n$  für 2 (Lilolidin) oder 3 (Julolidin) steht, mit der Maßgabe, daß der Farbstoff nicht C.I. Disperse Blue 165, C.I.  
 Disperse Blue 287 und C.I. Disperse Red 73 ist oder das Substrat kein die Wärme gut leitendes Pulver auf-  
 weist oder das Substrat kein Papier ist.

2. Thermotransferdruckblatt nach Anspruch 1, bei welchem A die Formel

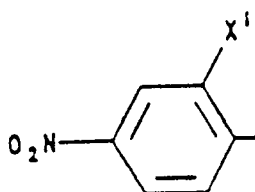


aufweist, worin

X¹ für NO<sub>2</sub>, CN oder -SO<sub>2</sub>CH<sub>3</sub> steht und

X² für NO<sub>2</sub>, CN oder -SO<sub>2</sub>CH<sub>3</sub> steht, mit der Maßgabe, daß der Farbstoff nicht C.I. Disperse Red 73 ist oder das Substrat kein die Wärme gut leitendes Pulver aufweist.

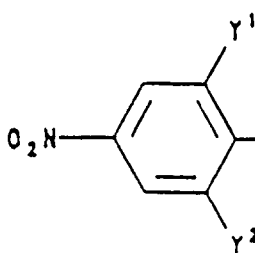
3. Thermotransferdruckblatt nach Anspruch 1, bei welchem A die Formel



aufweist, worin

X¹ für NO<sub>2</sub>, CN oder -SO<sub>2</sub>CH<sub>3</sub> steht, mit der Maßgabe, daß der Farbstoff nicht C.I. Disperse Red 73 ist oder das Substrat kein die Wärme gut leitendes Pulver aufweist.

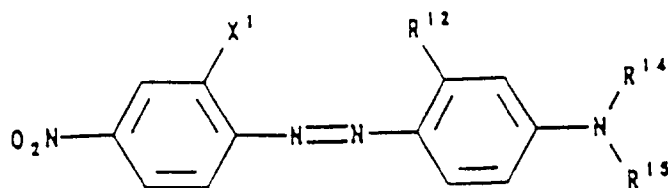
4. Thermotransferdruckblatt nach Anspruch 1, bei welchem A die Formel



aufweist, worin

Y¹ und Y² unabhängig ausgewählt sind CN und NO<sub>2</sub>, mit der Maßgabe, daß nicht beide für NO<sub>2</sub> stehen, und mit der Maßgabe, daß der Farbstoff nicht C.I. Disperse Blue 165 und C.I. Disperse Blue 287 ist oder das Substrat kein die Wärme gut leitendes Pulver aufweist.

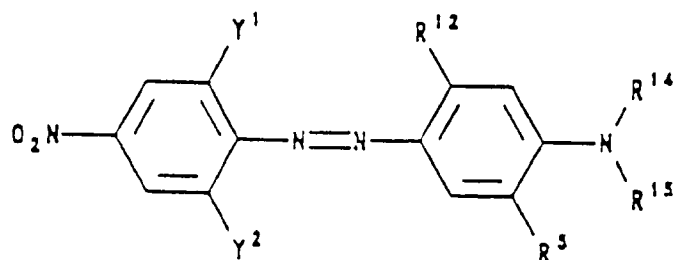
5. Thermotransferdruckblatt nach Anspruch 1, bei welchem der Farbstoff die Formel



aufweist, worin

$X^1$  für  $\text{NO}_2$  oder  $\text{CN}$  steht,  
 $R^{12}$  ausgewählt ist aus  $\text{H}$ ,  $\text{CH}_3$  und  $-\text{NHCOCH}_3$  und  
 $R^{14}$  und  $R^{15}$  jeweils unabhängig ausgewählt sind aus  $\text{C}_{2-4}$ -Alkyl,  $\text{C}_{1-4}$ -Alkylen-OCO- $\text{C}_{1-4}$ -Alkyl und  $\text{C}_2\text{H}_4\text{CN}$ , mit der Maßgabe, daß der Farbstoff nicht C.I. Disperse Red 73 ist oder das Substrat kein die Wärme gut leitendes Pulver aufweist.

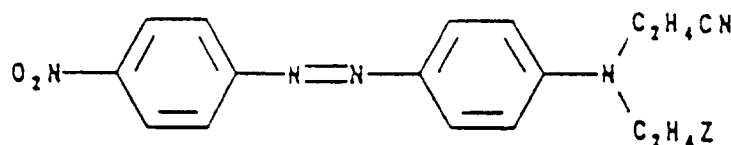
6. Thermotransferdruckblatt nach Anspruch 1, bei welchem der Farbstoff die Formel



aufweist, worin

$Y^1$  für  $\text{NO}_2$  oder  $\text{CN}$  steht,  
 $Y^2$  für  $\text{CN}$  steht,  
 $R^{14}$  und  $R^{15}$  jeweils ausgewählt sind aus  $\text{C}_{2-4}$ -Alkyl und  $\text{C}_{1-4}$ -Alkylen-OCO- $\text{C}_{1-4}$ -alkyl,  
 $R^5$  ausgewählt ist aus  $\text{H}$ ,  $\text{C}_{1-4}$ -Alkyl und  $\text{C}_{1-4}$ -Alkoxy und  
 $R^{12}$  ausgewählt ist aus  $\text{H}$ ,  $\text{CH}_3$  und  $-\text{NHCOCH}_3$ , mit der Maßgabe, daß der Farbstoff nicht C.I. Disperse Blue 165 und C.I. Disperse Blue 287 ist oder das Substrat kein die Wärme gut leitendes Pulver aufweist.

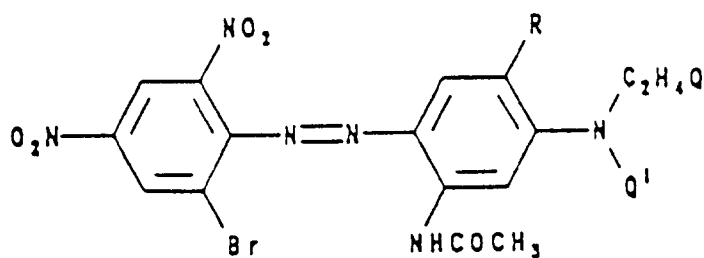
7. Thermotransferdruckblatt nach Anspruch 1, bei welchem die Beschichtung einen Farbstoff der Formel,



worin

$Z$  für  $\text{H}$  oder  $-\text{OCOCH}_3$  steht,

in Mischung mit einem Farbstoff der Formel,

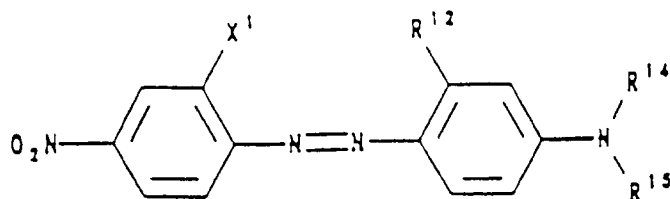


worin

R für H oder  $-\text{OCH}_3$  steht,  
 Q ausgewählt ist aus H,  $-\text{OCOCH}_3$  und  $-\text{COOC}_2\text{H}_4\text{OCH}_3$  und  
 Q<sup>1</sup> ausgewählt ist aus H,  $-\text{C}_2\text{H}_5$  und  $-\text{C}_2\text{H}_4\text{OCOCH}_3$ ,

enthält.

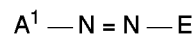
8. Thermotransferdruckblatt nach Anspruch, bei welchem die Beschichtung einen Farbstoff der Formel,



worin

X<sup>1</sup> für  $\text{NO}_2$  oder CN steht,  
 R<sup>12</sup> ausgewählt ist aus H,  $\text{CH}_3$  und  $-\text{NHCOCH}_3$  und  
 R<sup>14</sup> und R<sup>15</sup> unabhängig ausgewählt sind aus  $\text{C}_{2-4}$ -Alkyl,  $\text{C}_{1-4}$ -Alkyl-OCO- $\text{C}_{1-4}$ -alkyl und  $\text{C}_2\text{H}_4\text{CN}$ ,

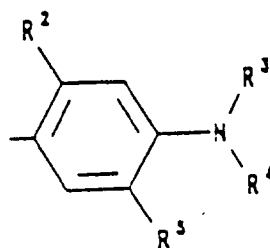
in Mischung mit einem Farbstoff der Formel



worin

A<sup>1</sup> ausgewählt ist aus 3-Methyl-4-cyanoisothiazol-5-yl, 4-Cyano-isothiazol-5-yl und 1-Cyanomethyl-3,4-dicyanopyrazol-5-yl und

E die Formel



aufweist, wobei

$R^2$  ausgewählt ist aus H, Chlor und  $C_{1-4}$ -Alkyl,  
 $R^3$  und  $R^4$  jeweils unabhängig für  $C_{2-4}$ -Alkylen-OCO- $C_{1-4}$ -alkyl oder  $C_{2-4}$ -Alkyl stehen und  
 $R^5$  für H steht,

enthält.

9. Thermotransferdruckverfahren, bei welchem ein mit einem Farbstoff der Formel I beschichtetes Transferblatt nach Anspruch 1 mit einem Aufnahmeblatt derart zusammengebracht wird, daß der Farbstoff dem Aufnahmeblatt benachbart ist, und selektiv ein Bereich des Transferblatts während einer Zeit von 0,5 bis 30 ms auf eine Temperatur von 250 bis 400°C erhitzt wird, wodurch Farbstoff im erhitzten Bereich des Transferblatts selektiv auf das Aufnahmeblatt übertragen wird.

**Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, LI, SE**

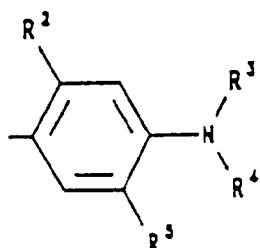
1. Thermotransferdruckblatt, welches aus einem Substrat mit einem Belag besteht, der einen Farbstoff der Formel



enthält, worin

A für ein Phenyl-Gruppe steht, die durch zwei oder drei Gruppen, welche ausgewählt sind aus  $NO_2$ , CN und  $-SO_2C_{1-4}$ -Alkyl, und gegebenenfalls durch eine oder mehrere Gruppen, welche ausgewählt sind aus  $C_{1-4}$ -Alkyl und  $C_{1-4}$ -Alkoxy, substituiert ist; und  
 E ausgewählt ist aus

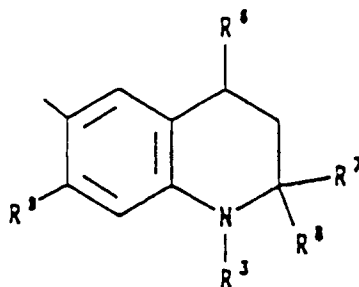
(i) Anilino-Gruppen der Formel



wobei

$R^2$  ausgewählt ist aus H,  $C_{1-4}$ -Alkyl,  $C_{1-4}$ -Alkoxy,  $C_{1-4}$ -Alkylthio,  $NH_2-CO-NH-$ ,  $HCONH-$ , Phenyl-  
 $CONH-$ ,  $C_{1-4}$ -Alkyl- $CO-NH-$ ,  $C_{1-4}$ -Alkyl- $SO_2-NH-$ , CN,  $CF_3$  und Halogen,  
 $R^3$  und  $R^4$  unabhängig ausgewählt sind aus H,  $C_{1-6}$ -Alkyl und  $C_{4-8}$ -Cycloalkyl, welches jeweils unsubstitu-  
 5 iert oder durch eine Gruppe substituiert ist, die unabhängig ausgewählt ist aus Halogen, CN, Phenyl, mono- oder bicyclischem Heteroaryl,  $-OCO-C_{1-4}$ -Alkyl,  $-COO-C_{1-4}$ -Alkyl,  $C_{2-4}$ -Alkenyl  
 und  $C_{1-4}$ -Alkoxy, oder  
 $R^3$  und  $R^4$  zusammen mit dem Stickstoffatom, an welches sie gebunden sind, einen heterocyclischen Ring,  
 wie z.B. Morpholin, Piperazin oder Thiomorpholin, bilden, und  
 $R^5$  ausgewählt ist aus H,  $C_{1-4}$ -Alkyl und  $C_{1-4}$ -Alkoxy;

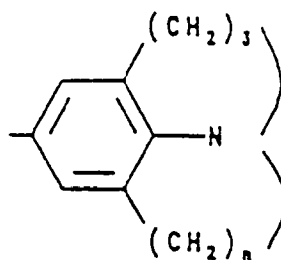
(ii) Tetrahydrochinoliny-Gruppen der Formel,



wobei

$R^3$  ausgewählt ist aus H,  $C_{1-6}$ -Alkyl und  $C_{4-8}$ -Cycloalkyl, welches jeweils unsubstituiert oder  
 durch eine Gruppe substituiert ist, die unabhängig ausgewählt ist aus Halogen, CN, Phenyl,  
 mono- oder bicyclischem Heteroaryl,  $-OCO-C_{1-4}$ -Alkyl,  $-COO-C_{1-4}$ -Alkyl,  $C_{2-4}$ -Alkenyl und  $C_{1-4}$ -  
 30 Alkoxy, und  
 $R^6$  bis  $R^9$  unabhängig ausgewählt sind aus H und  $C_{1-4}$ -Alkyl; und

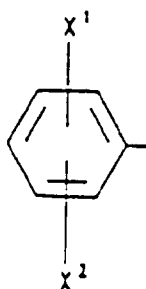
(iii) Lilolidinyl oder Julolidinyl der Formel,



wobei:

n für 2 (Lilolidin) oder 3 (Julolidin) steht, mit der Maßgabe, daß das Substrat kein die Wärme gut leitendes Pul-  
 55 ver aufweist oder das Substrat kein Papier ist.

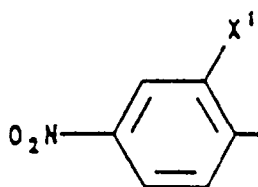
2. Thermotransferdruckblatt nach Anspruch 1, bei welchem A die Formel



aufweist, worin

X¹ für NO<sub>2</sub>, CN oder -SO<sub>2</sub>CH<sub>3</sub> steht und  
 X² für NO<sub>2</sub>, CN oder -SO<sub>2</sub>CH<sub>3</sub> steht, mit der Maßgabe, daß das Substrat kein die Wärme gut leitendes Pulver aufweist oder das Substrat kein Papier ist.

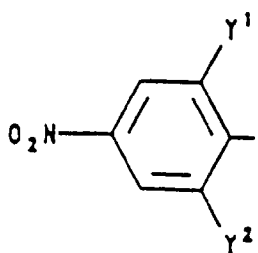
3. Thermotransferdruckblatt nach Anspruch 1, bei welchem A die Formel



aufweist, worin

X¹ für NO<sub>2</sub>, CN oder -SO<sub>2</sub>CH<sub>3</sub> steht, mit der Maßgabe, daß das Substrat kein die Wärme gut leitendes Pulver aufweist oder das Substrat kein Papier ist.

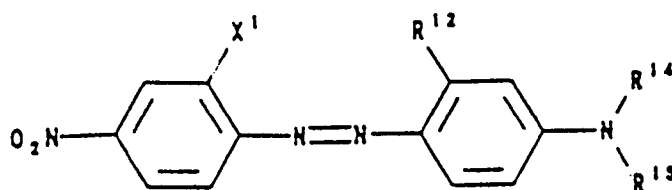
4. Thermotransferdruckblatt nach Anspruch 1, bei welchem A die Formel



aufweist, worin

Y¹ und Y² unabhängig ausgewählt sind CN und NO<sub>2</sub>, mit der Maßgabe, daß nicht beide für NO<sub>2</sub> stehen, und mit der Maßgabe, daß das Substrat kein die Wärme gut leitendes Pulver aufweist.

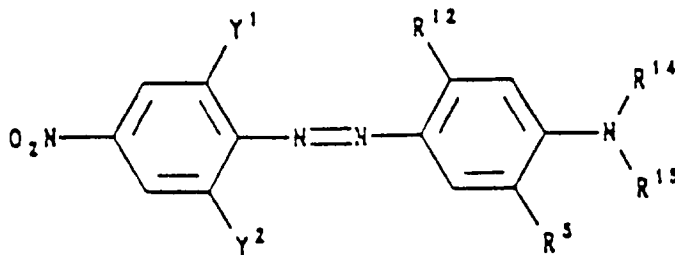
5. Thermotransferdruckblatt nach Anspruch 1, bei welchem der Farbstoff die Formel



aufweist, worin

$X^1$  für  $\text{NO}_2$  oder  $\text{CN}$  steht,  
 $R^{12}$  ausgewählt ist aus  $\text{H}$ ,  $\text{CH}_3$  und  $-\text{NHCOCH}_3$  und  
 $R^{14}$  und  $R^{15}$  jeweils unabhängig ausgewählt sind aus  $\text{C}_{2-4}$ -Alkyl,  $\text{C}_{1-4}$ -Alkylen- $\text{OCO-C}_{1-4}$ -Alkyl und  $\text{C}_2\text{H}_4\text{CN}$ , mit der Maßgabe, daß das Substrat kein die Wärme gut leitendes Pulver aufweist oder das Substrat kein Papier ist.

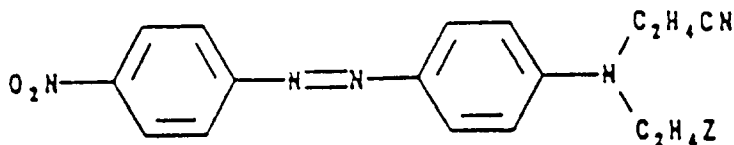
6. Thermotransferdruckblatt nach Anspruch 1, bei welchem der Farbstoff die Formel



aufweist, worin

$Y^1$  für  $\text{NO}_2$  oder  $\text{CN}$  steht,  
 $Y^2$  für  $\text{CN}$  steht,  
 $R^{14}$  und  $R^{15}$  jeweils ausgewählt sind aus  $\text{C}_{2-4}$ -Alkyl und  $\text{C}_{1-4}$ -Alkylen- $\text{OCO-C}_{1-4}$ -alkyl,  
 $R^5$  ausgewählt ist aus  $\text{H}$ ,  $\text{C}_{1-4}$ -Alkyl und  $\text{C}_{1-4}$ -Alkoxy und  
 $R^{12}$  ausgewählt ist aus  $\text{H}$ ,  $\text{CH}_3$  und  $-\text{NHCOCH}_3$ , mit der Maßgabe, daß das Substrat kein die Wärme gut leitendes Pulver aufweist.

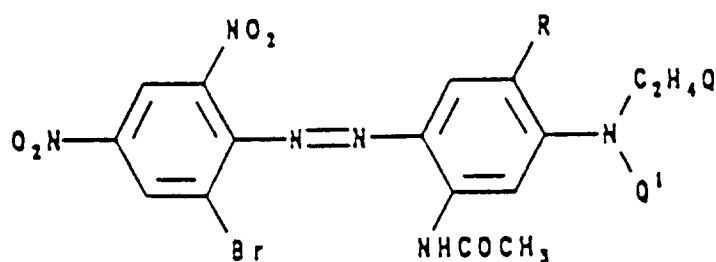
7. Thermotransferdruckblatt nach Anspruch 1, bei welchem die Beschichtung einen Farbstoff der Formel,



worin

$Z$  für  $\text{H}$  oder  $-\text{OCOCH}_3$  steht,

in Mischung mit einem Farbstoff der Formel,

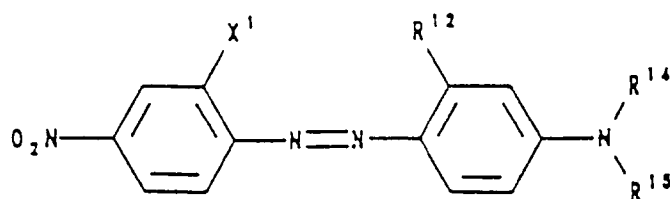


worin

R für H oder -OCH<sub>3</sub> steht,  
 Q ausgewählt ist aus H, -OCOCH<sub>3</sub> und -COOC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub> und  
 Q<sup>1</sup> ausgewählt ist aus H, -C<sub>2</sub>H<sub>5</sub> und -C<sub>2</sub>H<sub>4</sub>OCOCH<sub>3</sub>,

enthält.

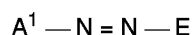
8. Thermotransferdruckblatt nach Anspruch, bei welchem die Beschichtung einen Farbstoff der Formel,



worin

X<sup>1</sup> für NO<sub>2</sub> oder CN steht,  
 R<sup>12</sup> ausgewählt ist aus H, CH<sub>3</sub> und -NHCOCH<sub>3</sub> und  
 R<sup>14</sup> und R<sup>15</sup> unabhängig ausgewählt sind aus C<sub>2-4</sub>-Alkyl, C<sub>1-4</sub>-Alkylen-OCO-C<sub>1-4</sub>-alkyl und C<sub>2</sub>H<sub>4</sub>CN,

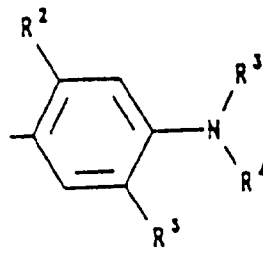
in Mischung mit einem Farbstoff der Formel



worin

A<sup>1</sup> ausgewählt ist aus 3-Methyl-4-cyanoisothiazol-5-yl, 4-Cyano-isothiazol-5-yl und 1-Cyanomethyl-3,4-dicyanopyrazol-5-yl und

E die Formel



aufweist, wobei

$R^2$  ausgewählt ist aus H, Chlor und  $C_{1-4}$ -Alkyl,  
 $R^3$  und  $R^4$  jeweils unabhängig für  $C_{2-4}$ -Alkylen-OCO- $C_{1-4}$ -alkyl oder  $C_{2-4}$ -Alkyl stehen und  
 $R^5$  für H steht,

enthält.

9. Thermotransferdruckverfahren, bei welchem ein mit einem Farbstoff der Formel I beschichtetes Transferblatt nach Anspruch 1 mit einem Aufnahmeblatt derart zusammengebracht wird, daß der Farbstoff dem Aufnahmeblatt benachbart ist, und selektiv ein Bereich des Transferblatts während einer Zeit von 0,5 bis 30 ms auf eine Temperatur von 250 bis 400°C erhitzt wird, wodurch Farbstoff im erhitzten Bereich des Transferblatts selektiv auf das Aufnahmeblatt übertragen wird.

## Revendications

Revendications pour les Etats contractants suivants : DE, FR, GB, IT, NL

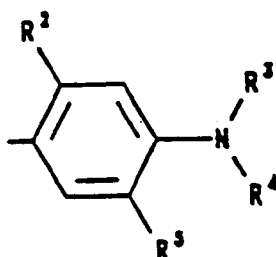
1. Feuille d'impression par transfert thermique comprenant un substrat portant un revêtement comprenant un colorant de formule :



dans laquelle :

- A représente un groupe phényle substitué avec deux ou trois groupes choisis entre des groupes  $NO_2$ , CN et  $-SO_2-$  (alkyle en  $C_1$  à  $C_4$ ), et facultativement avec un ou plusieurs groupes choisis entre des groupes alkyle en  $C_1$  à  $C_4$  et alkoxy en  $C_1$  à  $C_4$  ; et  
 E est choisi entre

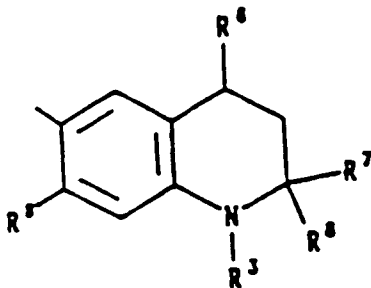
(i) un groupe anilino de formule :



dans laquelle :

- $R^2$  est choisi entre H, des groupes alkyle en  $C_1$  à  $C_4$ , alkoxy en  $C_1$  à  $C_4$ , alkylthio en  $C_1$  à  $C_4$ ,  $NH_2$ -CO-NH-, HCONH-, phényl-CONH-, (alkyle en  $C_1$  à  $C_4$ )-CO-NH-, (alkyle en  $C_1$  à  $C_4$ )-SO<sub>2</sub>-NH-, CN, CF<sub>3</sub> et halogéno ;
- $R^3$  et  $R^4$  sont choisis indépendamment entre H, des groupes alkyle en  $C_1$  à  $C_6$  et cycloalkyle en  $C_4$  à  $C_8$ , chacun de ces groupes étant non substitué ou substitué avec un groupe choisi indépendamment entre des groupes halogéno, CN, phényle, hétéroaryle mono- ou bicyclique, -OCO-(alkyle en  $C_1$  à  $C_4$ ), -COO-(alkyle en  $C_1$  à  $C_4$ ), alcényle en  $C_2$  à  $C_4$  et alkoxy en  $C_1$  à  $C_4$  ; ou bien
- $R^3$  et  $R^4$  conjointement avec l'atome d'azote auquel ils sont fixés, forment un noyau hétérocyclique, tel qu'un noyau morpholine, pipérazine ou thiomorpholine ; et
- $R^5$  est choisi entre H, des groupes alkyle en  $C_1$  à  $C_4$  et alkoxy en  $C_1$  à  $C_4$  ;

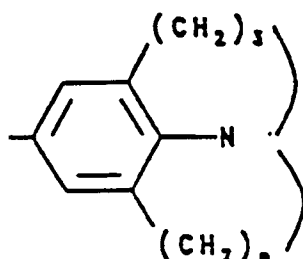
(ii) un groupe tétrahydroquinolinyle, de formule :



dans laquelle :

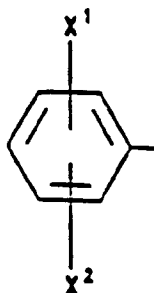
- $R^3$  est choisi entre H, des groupes alkyle en  $C_1$  à  $C_6$  et cycloalkyle en  $C_4$  à  $C_8$ , chacun de ces groupes étant indépendamment non substitué ou substitué avec un groupe choisi entre des groupes halogéno, CN, phényle, hétéroaryle mono- ou bicyclique, -OCO-(alkyle en  $C_1$  à  $C_4$ ), -COO-(alkyle en  $C_1$  à  $C_4$ ), alcényle en  $C_2$  à  $C_4$  et alkoxy en  $C_1$  à  $C_4$ , et
- $R^6$  à  $R^9$  sont choisis indépendamment entre H et un groupe alkyle en  $C_1$  à  $C_4$  ; et

(iii) un groupe lilolidinyle ou julolidinyle, de formule :



dans laquelle : n est égal à 2 (lilolidine) ou à 3 (julolidine) , sous réserve que le colorant ne consiste pas en les colorants bleus C.I. Disperse Blue 165 et C.I. Disperse Blue 287 et le colorant rouge C.I. Disperse Red 73 ou que le substrat ne présente pas une bonne capacité de conduction de chaleur ou bien que le substrat ne consiste pas en papier.

2. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle A répond à la formule :

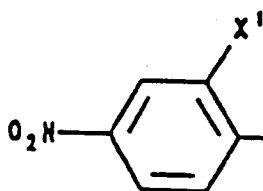


dans laquelle :

X<sup>1</sup> représente un groupe NO<sub>2</sub>, CN ou -SO<sub>2</sub>CH<sub>3</sub> ; et  
X<sup>2</sup> représente un groupe NO<sub>2</sub>, CN, -SO<sub>2</sub>CH<sub>3</sub>,

sous réserve que le colorant ne consiste pas en le colorant rouge C.I. Disperse Red 73 ou que le substrat ne présente pas une bonne capacité de conduction de chaleur.

3. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle A répond à la formule :

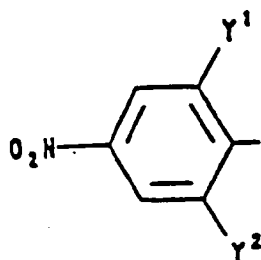


dans laquelle :

X<sup>1</sup> représente un groupe NO<sub>2</sub>, CN ou -SO<sub>2</sub>CH<sub>3</sub>,

sous réserve que le colorant ne consiste pas en le colorant rouge C.I. Disperse Red 73 ou que le substrat ne présente pas une bonne capacité de conduction de chaleur.

4. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle A répond à la formule :

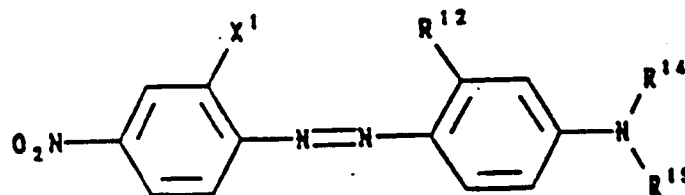


dans laquelle :

$Y^1$  et  $Y^2$  sont choisis indépendamment entre des groupes CN et  $NO_2$ ,

sous réserve qu'ils ne représentent pas l'un et l'autre un groupe  $NO_2$ , sous réserve que le colorant ne consiste pas en l'un des colorants bleus C.I. Disperse Blue 165 et C.I. Disperse Blue 287 ou que le substrat ne présente pas une bonne capacité de conduction de chaleur.

5. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle le colorant répond à la formule :



dans laquelle :

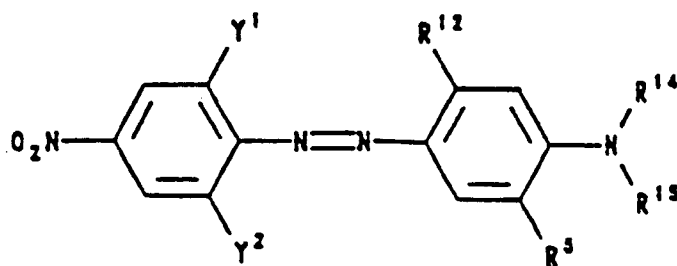
$X^1$  représente un groupe  $NO_2$  ou CN ;

$R^{12}$  est choisi entre H, un groupe  $CH_3$  et un groupe  $-NHCOCH_3$  ; et

$R^{14}$  et  $R^{15}$  sont choisis chacun indépendamment entre des groupes alkyle en  $C_2$  à  $C_4$ , (alkylène en  $C_1$  à  $C_4$ )-OCO-(alkyle en  $C_1$  à  $C_4$ ) et  $C_2H_4CN$ ,

sous réserve que le colorant ne consiste pas en le colorant rouge C.I. Disperse Red 73 ou que le substrat ne présente pas une bonne capacité de conduction de chaleur.

6. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle le colorant répond à la formule :

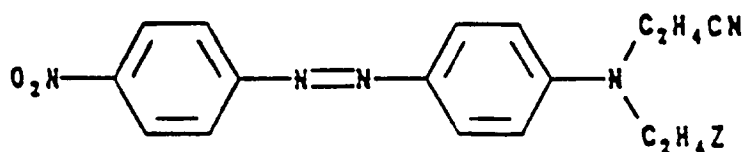


dans laquelle :

- Y<sup>1</sup> représente NO<sub>2</sub> ou CN ;  
 Y<sup>2</sup> représente un groupe CN ;  
 R<sup>14</sup> et R<sup>15</sup> sont choisis chacun indépendamment entre des groupes alkyle en C<sub>2</sub> à C<sub>4</sub> et (alkylène en C<sub>1</sub> à C<sub>4</sub>)-OCO-(alkyle en C<sub>1</sub> à C<sub>4</sub>) ;  
 R<sup>5</sup> est choisi entre H, un groupe alkyle en C<sub>1</sub> à C<sub>4</sub> et un groupe alkoxy en C<sub>1</sub> à C<sub>4</sub> ; et  
 R<sup>12</sup> est choisi entre H, un groupe CH<sub>3</sub> et un groupe -NHCOCH<sub>3</sub>,

sous réserve que le colorant ne consiste pas en l'un des colorants bleus C.I. Disperse Blue 165 et C.I. Disperse Blue 287 ou que le substrat ne présente pas une bonne capacité de conduction de chaleur.

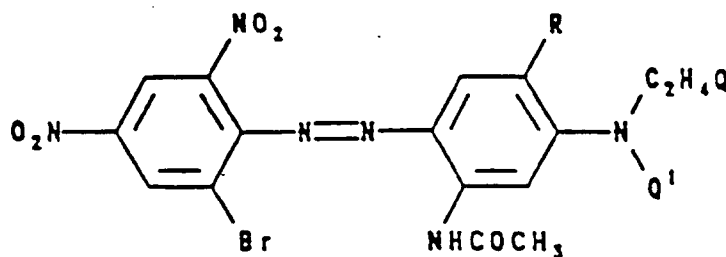
7. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle le revêtement comprend un colorant de formule :



dans laquelle :

Z représente H ou un groupe -OCOCH<sub>3</sub> ;

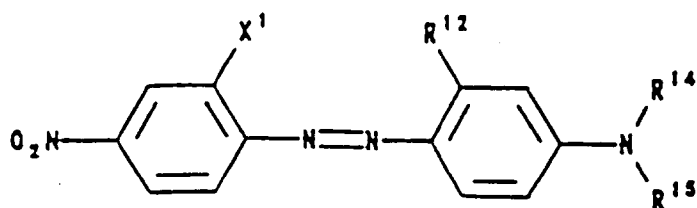
en mélange avec un colorant de formule :



dans laquelle

- R représente H ou un groupe -OCH<sub>3</sub> ;  
 Q est choisi entre H, un groupe -OCOCH<sub>3</sub> et un groupe -COOC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub> ;  
 Q<sup>1</sup> est choisi entre H, un groupe -C<sub>2</sub>H<sub>5</sub> et un groupe -C<sub>2</sub>H<sub>4</sub>OCOCH<sub>3</sub>.

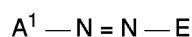
8. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle le revêtement comprend un colorant de formule :



dans laquelle :

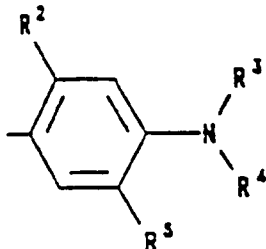
$X^1$  représente un groupe  $\text{NO}_2$  ou  $\text{CN}$  ;  
 $R^{12}$  est choisi entre H, un groupe  $\text{CH}_3$  et un groupe  $-\text{NHCOCH}_3$  ; et  
 $R^{14}$  et  $R^{15}$  sont choisis chacun indépendamment entre des groupes alkyle en  $\text{C}_2$  à  $\text{C}_4$ , (alkylène en  $\text{C}_1$  à  $\text{C}_4$ )- $\text{OCO}$ -(alkyle en  $\text{C}_1$  à  $\text{C}_4$ ) et  $\text{C}_2\text{H}_4\text{CN}$  ;

en mélange avec un colorant de formule :



dans laquelle :

$A^1$  est choisi entre les groupes 3-méthyl-4-cyanoisothiazole-5-yle, 4-cyanoisothiazole-5-yle et 1-cyanométhyl-3,4-dicyanopyrazole-5-yle ; et  
 $E$  répond à la formule :



dans laquelle :

$R^2$  est choisi entre H, le chlore et un groupe alkyle en  $\text{C}_1$  à  $\text{C}_4$  ;  
 $R^3$  et  $R^4$  représentent chacun indépendamment un groupe (alkylène en  $\text{C}_2$  à  $\text{C}_4$ )- $\text{OCO}$ -(alkyle en  $\text{C}_1$  à  $\text{C}_4$ ) ; ou un groupe alkyle en  $\text{C}_2$  à  $\text{C}_4$  ; et  
 $R^5$  représente H.

9. Procédé d'impression par transfert thermique, qui comprend la mise en contact d'une feuille de transfert suivant la revendication 1 revêtue d'un colorant de formule I avec une feuille réceptrice, de telle sorte que le colorant soit adjacent à la feuille réceptrice, et le chauffage sélectif d'une zone de la feuille de transfert à une température de  $250^\circ\text{C}$  à  $400^\circ\text{C}$  pendant un temps de 0,5 à 30 ms, ce qui provoque le transfert sélectif à la feuille réceptrice du colorant présent dans la zone chauffée de la feuille de transfert.

## Revendications pour les Etats contractants suivants : AT, BE, CH, LI, SE

1. Feuille d'impression par transfert thermique comprenant un substrat portant un revêtement comprenant un colorant de formule :

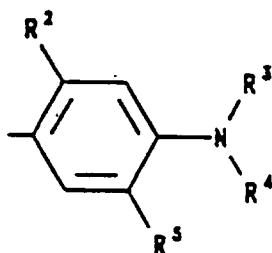


dans laquelle :

A représente un groupe phényle substitué avec deux ou trois groupes choisis entre des groupes  $\text{NO}_2$ , CN et  $-\text{SO}_2$ -(alkyle en  $\text{C}_1$  à  $\text{C}_4$ ), et facultativement avec un ou plusieurs groupes choisis entre des groupes alkyle en  $\text{C}_1$  à  $\text{C}_4$  et alkoxy en  $\text{C}_1$  à  $\text{C}_4$  ; et

E est choisi entre

(i) un groupe anilino de formule :



dans laquelle :

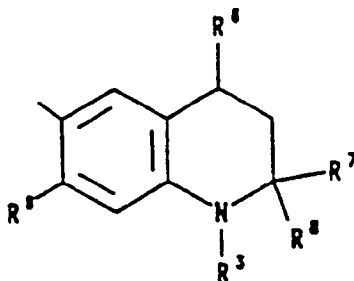
$\text{R}^2$  est choisi entre H, des groupes alkyle en  $\text{C}_1$  à  $\text{C}_4$ , alkoxy en  $\text{C}_1$  à  $\text{C}_4$ , alkylthio en  $\text{C}_1$  à  $\text{C}_4$ ,  $\text{NH}_2$ -CO-NH-, HCONH-, phényl-CONH-, (alkyle en  $\text{C}_1$  à  $\text{C}_4$ )-CO-NH-, (alkyle en  $\text{C}_1$  à  $\text{C}_4$ )- $\text{SO}_2$ -NH-, CN,  $\text{CF}_3$  et halogéno ;

$\text{R}^3$  et  $\text{R}^4$  sont choisis indépendamment entre H, des groupes alkyle en  $\text{C}_1$  à  $\text{C}_6$  et cycloalkyle en  $\text{C}_4$  à  $\text{C}_8$ , dont chacun est non substitué ou substitué avec un groupe choisi indépendamment entre des groupes halogéno, CN, phényle, hétéroaryle mono- ou bicyclique,  $-\text{OCO}$ -(alkyle en  $\text{C}_1$  à  $\text{C}_4$ ),  $-\text{COO}$ -(alkyle en  $\text{C}_1$  à  $\text{C}_4$ ), alcényle en  $\text{C}_2$  à  $\text{C}_4$  et alkoxy en  $\text{C}_1$  à  $\text{C}_4$  ; ou bien

$\text{R}^3$  et  $\text{R}^4$  conjointement avec l'atome d'azote auquel ils sont fixés, forment un noyau hétérocyclique, tel qu'un noyau morpholine, pipérazine ou thiomorpholine ; et

$\text{R}^5$  est choisi entre H, des groupes alkyle en  $\text{C}_1$  à  $\text{C}_4$  et alkoxy en  $\text{C}_1$  à  $\text{C}_4$  ;

(ii) un groupe tétrahydroquinolinyle, de formule :

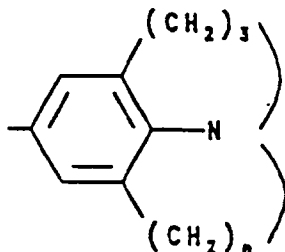


dans laquelle :

$R^3$  est choisi entre H, des groupes alkyle en  $C_1$  à  $C_6$  et cycloalkyle en  $C_4$  à  $C_8$ , dont chacun est indépendamment non substitué ou substitué avec un groupe choisi entre des groupes halogéno, CN, phényle, hétéroaryle mono- ou bicyclique, -OCO-(alkyle en  $C_1$  à  $C_4$ ), -COO-(alkyle en  $C_1$  à  $C_4$ ), alcényle en  $C_2$  à  $C_4$  et alkoxy en  $C_1$  à  $C_4$  ; et

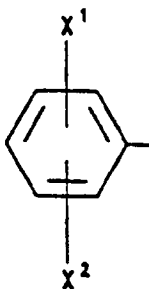
$R^6$  à  $R^9$  sont choisis indépendamment entre H et un groupe alkyle en  $C_1$  à  $C_4$  ; et

(iii) un groupe lilolidinyle ou julolidinyle, de formule :



dans laquelle : n est égal à 2 (lilolidine) ou à 3 (julolidine), sous réserve que le substrat ne présente pas une bonne capacité de conduction de chaleur ou bien que le substrat ne consiste pas en papier.

2. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle A répond à la formule :

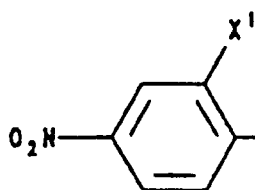


dans laquelle :

$X^1$  représente un groupe  $NO_2$ , CN ou  $-SO_2CH_3$  ; et  
 $X^2$  représente un groupe  $NO_2$ , CN ou  $-SO_2CH_3$ ,

sous réserve que le substrat ne présente pas une bonne capacité de conduction de chaleur ou bien que le substrat ne consiste pas en papier.

3. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle A répond à la formule :

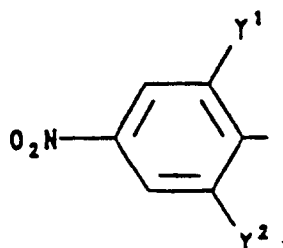


dans laquelle :

$X^1$  représente un groupe  $\text{NO}_2$ , CN ou  $-\text{SO}_2\text{CH}_3$ ,

sous réserve que le substrat ne présente pas une bonne capacité de conduction de chaleur ou bien que le substrat ne consiste pas en papier.

4. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle A répond à la formule :

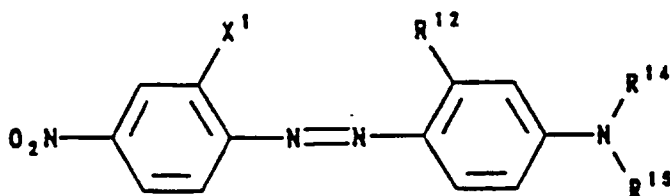


dans laquelle :

$Y^1$  et  $Y^2$  sont choisis indépendamment entre des groupes CN et  $\text{NO}_2$ ,

sous réserve qu'ils ne représentent l'un et l'autre un groupe  $\text{NO}_2$ , sous réserve que le substrat ne présente pas une bonne capacité de conduction de chaleur.

5. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle le colorant répond à la formule :

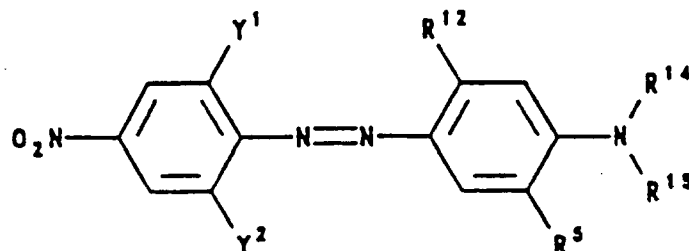


dans laquelle :

$X^1$  représente un groupe  $\text{NO}_2$  ou CN ;  
 $R^{12}$  est choisi entre H, un groupe  $\text{CH}_3$  et un groupe  $-\text{NHCOCH}_3$  ;  
 $R^{14}$  et  $R^{15}$  sont choisis chacun indépendamment entre des groupes alkyle en  $\text{C}_2$  à  $\text{C}_4$ , (alkylène en  $\text{C}_1$  à  $\text{C}_4$ )-OCO-(alkyle en  $\text{C}_1$  à  $\text{C}_4$ ) et  $\text{C}_2\text{H}_4\text{CN}$ ,

sous réserve que le substrat ne présente pas une bonne capacité de conduction de chaleur ou bien que le substrat ne consiste pas en papier.

6. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle le colorant répond à la formule :

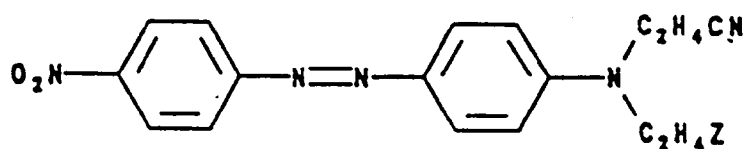


dans laquelle :

- Y<sup>1</sup> représente un groupe NO<sub>2</sub> ou CN ;  
 Y<sup>2</sup> représente un groupe CN ;  
 R<sup>14</sup> et R<sup>15</sup> sont choisis chacun indépendamment entre des groupes alkyle en C<sub>2</sub> à C<sub>4</sub> et (alkylène en C<sub>1</sub> à C<sub>4</sub>)-OCO-(alkyle en C<sub>1</sub> à C<sub>4</sub>) ;  
 R<sup>5</sup> est choisi entre H, des groupes alkyle en C<sub>1</sub> à C<sub>4</sub> et alkoxy en C<sub>1</sub> à C<sub>4</sub> ; et  
 R<sup>12</sup> est choisi entre H, un groupe CH<sub>3</sub> et un groupe -NHCOCH<sub>3</sub>,

sous réserve que le substrat ne présente pas une bonne capacité de conduction de chaleur.

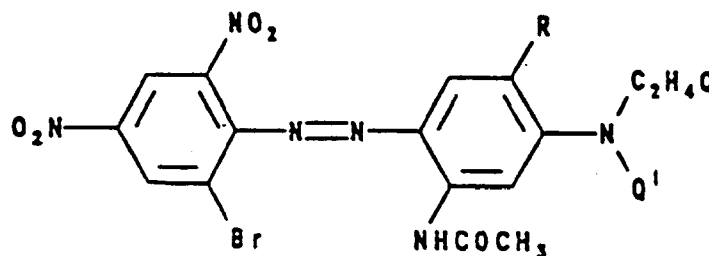
7. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle le revêtement comprend un colorant de formule :



dans laquelle :

Z représente H ou un groupe -OCOCH<sub>3</sub> ;

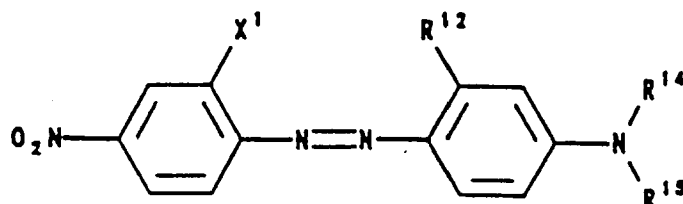
en mélange avec un colorant de formule :



dans laquelle :

- R représente H ou un groupe  $-\text{OCH}_3$  ;  
 Q est choisi entre H, un groupe  $-\text{OCOCH}_3$  et un groupe  $-\text{COOC}_2\text{H}_4\text{OCH}_3$  ; et  
 Q<sup>1</sup> est choisi entre H, un groupe  $-\text{C}_2\text{H}_5$  et un groupe  $-\text{C}_2\text{H}_4\text{OCOCH}_3$ .

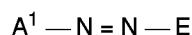
- 5 8. Feuille d'impression par transfert thermique suivant la revendication 1, dans laquelle le revêtement comprend un colorant de formule :



dans laquelle :

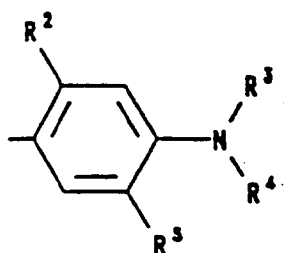
- X<sup>1</sup> représente un groupe  $\text{NO}_2$  ou  $\text{CN}$  ;  
 R<sup>12</sup> est choisi entre H, un groupe  $\text{CH}_3$  et un groupe  $-\text{NHCOCH}_3$  ; et  
 R<sup>14</sup> et R<sup>15</sup> sont choisis chacun indépendamment entre des groupes alkyle en C<sub>2</sub> à C<sub>4</sub>, (alkylène en C<sub>1</sub> à C<sub>4</sub>)-OCO-(alkyle en C<sub>1</sub> à C<sub>4</sub>) et  $\text{C}_2\text{H}_4\text{CN}$  ;

en mélange avec un colorant de formule :



dans laquelle :

- A<sup>1</sup> est choisi entre les groupes 3-méthyl-4-cyanoisothiazole-5-yle, 4-cyanoisothiazole-5-yle et 1-cyanométhyl-3,4-dicyanopyrazole-5-yle ; et  
 E répond à la formule :



dans laquelle :

- R<sup>2</sup> est choisi entre H, le chlore et un groupe alkyle en C<sub>1</sub> à C<sub>4</sub> ;  
 R<sup>3</sup> et R<sup>4</sup> représentent chacun indépendamment un groupe (alkylène en C<sub>2</sub> à C<sub>4</sub>)-OCO-(alkyle en C<sub>1</sub> à C<sub>4</sub>) ;  
 R<sup>5</sup> représente H.

- 55 9. Procédé d'impression par transfert thermique, qui comprend la mise en contact d'une feuille de transfert suivant la revendication 1 revêtue d'un colorant de formule I avec une feuille réceptrice, de telle sorte que le colorant soit adjacent à la feuille réceptrice, et le chauffage sélectif d'une zone de la feuille de transfert à une température de 250°C à 400°C pendant un temps de 0,5 à 30 ms, ce qui provoque le transfert sélectif à la feuille réceptrice du colorant présent dans la zone chauffée de la feuille de transfert.