(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 333 336**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **89301750.9**

(51) Int. Cl.[4]: **B41M 5/26**

(22) Date of filing: **23.02.89**

(30) Priority: **17.03.88 GB 8806315**
02.06.88 GB 8813040

(43) Date of publication of application:
20.09.89 Bulletin 89/38

(84) Designated Contracting States:
AT BE CH DE ES FR GB IT LI LU NL SE

(71) Applicant: **IMPERIAL CHEMICAL INDUSTRIES PLC**
Imperial Chemical House Millbank
London SW1P 3JF(GB)

(72) Inventor: **Gregory, Peter**
129 Armadale Road
Bolton BL3 4UN(GB)
Inventor: **McClelland, Robert David**
8 Four Lanes Way Wolstenholme Fold
Norden Rochdale Lancashire OL11 5TL(GB)
Inventor: **Parton, Brian**
11 Cleadon Drive South
Bury Lancashire BL8 1EJ(GB)
Inventor: **Price, Roger Vernon**
17 Pickmere Drive Sutton Park
Runcorn Cheshire(GB)

(74) Representative: **Stephenson, Kenneth et al**
Imperial Chemical Industries PLC Legal Department: Patents PO Box 6 Bessemer Road
Welwyn Garden City Herts, AL7 1HD(GB)

(54) Thermal transfer material.

(57) A thermal transfer sheet comprising a substrate having thereon a coating comprising a transferable medium containing an organic dye in which the transferable medium comprises a halogenated hydrocarbon.

EP 0 333 336 A2

THERMAL TRANSFER MATERIAL

This invention relates to thermal transfer material useful in a thermal transfer process.

In the thermal wax transfer process, a transfer sheet or film made of paper or a plastics material has on one side a coating comprising a pigment and a wax, for example carnauba wax, paraffin wax, montan wax or beeswax. When a thermal head, activated by input colour signals corresponding to the coloration of a coloured original, generates heat on the other side of the sheet or film, the wax coating is melted and transferred to an image-receiving material or copy sheet reproducing thereon an image of the coloured original. A process of this type has been described in, for example, GB 2069160.

Because of deficiencies exhibited by the waxes normally used, especially some paraffin waxes which cause a progressive deterioration in recording properties, it has been proposed in Japanese Kokai JP 58-162678 to use a pigment in conjunction with a chlorinated paraffin wax. An ink composition containing carbon black and equal weights of a chlorinated paraffin (m.p. 50-53 °C) and carnauba wax is specifically described.

Unfortunately, pigments, when used in conjunction with the waxes described in the prior art for this purpose, generally give coatings having inadequate transparency for some applications. It has now been found that when certain dyes, rather than pigments, are used in conjunction with certain halogenated hydrocarbons, transparent films suitable for overhead transparency projection can be obtained by virtue of the non-crystalline nature of the halogenated hydrocarbon heat transferable media.

Accordingly, the invention provides a thermal transfer sheet comprising a substrate having thereon a coating comprising a transferable medium containing an organic dye in which the transferable medium comprises a halogenated hydrocarbon.

The substrates employed in preparing the transfer sheets of the invention are suitably plastic films or paper having a thickness of from 3μ to 25μ. As specific examples of such substrates, there may be mentioned polyethylene terephthalate film, polyethylene film, polypropylene film, polystyrene film, glassine paper, synthetic paper and laminated paper.

The coating preferably has a thickness from 1μ to 10μ and preferably contains from 2% to 30%, by weight, of dye.

The transferable medium preferably contains at least 80%, more preferably at least 90% and especially from 95% to 100%, by weight of the halogenated hydrocarbon. The remaining portion of the transfer medium may consist of waxes such as carnauba wax, paraffin wax and softening agents such as stearic acid, chlorostearic acid and oleic acid.

The halogenated hydrocarbon preferably has a softening point of at least 50 °C and more preferably from 50 °C to 100 °C. It is preferably a chlorinated paraffin having a chlorine content of from 65% to 72% by weight obtained by chlorinating a paraffin or mixture of paraffins containing from 18 to 35 carbon atoms.

As indicated above, the chlorinated paraffin may be based on a single paraffin or on a mixture of paraffins. However, although chlorinated single paraffins can be made and are known, the common commercially available products comprise mixtures obtained by chlorinating mixed paraffins having a range of carbon chain lengths. It will be appreciated that, for example, a nominal C_{18-26}-paraffin fraction, such as might be used to prepare a chlorinated paraffin for use according to the invention, may contain small amounts of paraffins of chain length outside the specified range.

The chlorinated paraffins may be produced by chlorination of a suitable paraffin feedstock to the desired chlorine content in known manner. Any of the known methods for the production of chlorinated paraffins may be employed, these methods generally comprising passing chlorine gas into the liquid paraffins at a temperature above about 80 °C.

The chlorinated paraffins or the coatings present in the transfer sheets of the invention may contain any of the additives such as stabilisers and modifying agents normally incorporated in chlorinated paraffin compositions. Commercially available chlorinated paraffins usually contain a stabiliser or mixture of stabiliser to impart light-stability, high-temperature stability and storage stability to the compositions. A common stabiliser is an epoxide such as epoxidised soya bean oil.

The dyes present in the transfer sheets of the invention are preferably soluble in the halogenated hydrocarbon. This solubility characteristic distinguishes dyes from pigments which, in general, are substantially insoluble in the medium in which they are used.

Suitable dyes will generally contain no water-solubilising groups, that is to say no ionic groups such as sulphonate groups. As examples of suitable classes of dyes, there may be mentioned dyes classified in the Colour Index as Disperse dyes or Solvent dyes. Provided the preferred dyes have suitable solubility characteristics, the chemical class is not important except for the consideration that certain colours may be

associated with particular chromophores. Most of the dyes will be members of the azo, anthraquinone, triarylmethane or benzdifuranone series.

If desired, a pigment may be included in the transferable medium together with the dye in order to achieve desirable combinations of high light fastness, high transparency and excellent visual yields. Suitable pigments may be inorganic but the preferred pigments are organic.

Examples of suitable organic pigments are those in the azo, disazo, thioindigo, anthraquinone, anthanthrone, isobenzanthrone or triphendioxazine series, vat dye pigments, phthalocyanine pigments, such as copper phthalocyanine, its nuclear halogenated derivatives and copper tetraphenyl and octaphenyl phthalocyanines, quinacridone pigments, lakes of acid, basic and mordant dyestuffs and especially alpha and beta form copper phthalocyanines and carbon black, which for dispersion purposes is more conveniently classified as an organic pigment.

Such pigments are described in, for example, Volume 2 of the Colour Index (Second Edition 1956 or Third Edition 1971) under the heading "Pigments" and in subsequent authorised amendments thereto.

As examples of suitable inorganic pigments, there may be mentioned the transparent iron oxides.

The pigments are preferably formulated as a dispersion by milling in a suitable organic solvent in conjunction with dispersants and/or fluidising agents, said dispersion being mixed with a solution of halogenated hydrocarbon and dye. It has been found that the use of a suitable dispersant is important in obtaining a good transfer sheet because chlorinated paraffins have minimal dispersing properties.

Any suitable dispersant known in pigment technology may be employed when pigments are used but preferred dispersants are polymeric dispersants in which the solvatable chain is derived from a hydroxyaliphatic acid, such as hydroxystearic acid, ricinoleic acid and caprolactone, or a mixture thereof. Especially preferred dispersants are those which also incorporate an alkylamine, especially a polyalkyleneimine, such as are described in GB 1,373,660, EP 158,406A and EP 208,041A.

Suitable fluidising agents are disclosed in GB 1,508,576 and GB 2,108,143. The fluidising agent of GB 1,508,576 is a substituted ammonium salt of a coloured acid wherein there are from 19 to 60 carbon atoms in at least 3 chains attached to the N atom of the substituted ammonium ion. In a preferred fluidising agent of this type for use with a phthalocyanine pigment, the coloured acid is a copper phthalocyanine sulphonic acid containing, on an average, from 1 to 2 sulphonic acid groups. The coloured acid, as opposed to the ammonium salt, may itself be used as a fluidising agent. The fluidising agent of GB 2,108,143 is a water-insoluble disazo compound comprising a central divalent group free from acidic and other ionic substituents linked, through azo groups, to two monovalent end groups, one end group being free from acidic and other ionic substituents and the other carrying a single substituted ammonium salt group. Such fluidising agents are useful for enhancing the fluidity of the dispersion of the pigment and wax in the organic liquid so that it can be effectively milled and applied to the substrate.

Suitable dye/pigment combinations can contain up to 95% by weight of pigment, for example 10 to 90% by weight of pigment but preferred combinations contain from 40 to 60% by weight of pigment.

The coating may be applied to the substrate as a melt but is preferably applied as a solution or dispersion in an organic solvent, for example tetrahydrofuran, toluene or methyl isobutyl ketone.

When used in the thermal transfer process, a good grey-scale effect is observed, the amount of colour transferred from the substrate to the copy sheet increasing evenly with an increase in the applied thermal energy.

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight.

Example 1

CI Solvent Blue 36 (2g) was dissolved in a solution of a solid chlorinated C_{18-25}-paraffin (Cl content: 70-72%) (14g) in tetrahydrofuran (98g). The solution was applied to a 6μ thick film of polyester with a No.3 K-bar (0.001 inch wire bound) and dried to give a clear coloured film. When used in a thermal transfer printing process the images produced had excellent transparency and brightness.

Example 2

The dyestuff formed by coupling diazotised 5-amino-4-cyano-3-methylisothiazole with diethyl-m-toluidine (1g) was dissolved in a solution of a mixture of chlorinated paraffins (15g) in tetrahydrofuran (99g). The mixture of paraffins consisted of 90% of the chlorinated paraffin described in Example 1 and 10% of a

chlorinated C_{14-17}-paraffin (Cl content: 40%). This solution was applied to a 6μ thick film of polyester with a No.3 K-bar and dried to give a transparent coloured film, having a lower melting point than the film described in Example 1, which is suitable for use in transfer printing.

Example 3

The procedure of Example 2 was repeated except for the replacement of the chlorinated C_{14-17}-paraffin by the same weight of stearic acid. This solution was applied to a thin film of polyester with a No.3 K-bar (as in Example 1) and dried to give a transparent coloured film which is of lower melting point than the coating described in Example 1 and is suitable for use in transfer printing.

Example 4

CI Solvent Yellow 93 (2g) was dissolved in a solution of the mixture of chlorinated paraffins described in Example 2 (14g) in tetrahydrofuran (98g). This solution was applied to a 6μ thick film of polyester with a No.3 K-bar and dried to give a transparent coloured film which is suitable for use in transfer printing.

Example 5

The procedure of Example 4 was repeated except for the replacement of the chlorinated C_{14-17}-paraffin with chlorinated stearic acid (Cl content: 35%). This solution was applied to a thin film of polyester with a No.3 K-bar and dried to give a transparent coloured film which is suitable for use in transfer printing.

Example 6

The dyestuff formed by coupling diazotised p-chloroaniline with 3-cyano-6-hydroxy-4methyl-1-octylpyrid-2-one (3g) was dissolved in a solution of a solid chlorinated C_{18-26}-paraffin (Cl content: 70-72%) (13g) in tetrahydrofuran (97g). The solution was applied to a 6μ thick film of polyester with a No.3 K-bar (0.001 inch wire bound) and dried to give a clear coloured film. When used in a thermal transfer printing process the images produced had excellent transparency and brightness.

Examples 7-32

The procedure described in Example 3 was repeated except that the dye used was replaced in turn by the dyes identified in the following Table which also states the amount of dye used and the colour of the film obtained.

Ex.	Dye	Quantity	Colour
7	Product obtained by coupling diazotised 2-methoxy-5-nitroaniline with N,N-di(methoxycarbonylethyl)-m-aminoacetanilide	2g	Golden yellow
8	Product obtained by coupling diazotised 3,4-dicyanoaniline with N,N-diethyl-m-aminoacetanilide	2g	Bluish red
9	1-amino-4-hydroxy-2-phenoxy anthraquinone	4g	Bluish red
10	3-phenyl-7-(4-n-propoxyphenyl)-2,6-dioxo-2,6-dihydrobenzo-[1:2-b, 4:5-b']difuran	2g	Red
11	Product obtained by coupling diazotised 2,4-dinitroaniline with N,N-di(methoxycarbonylethyl)-m-aminoacetanilide	2g	Bluish red
12	50/50 2-(4-hydroxyphenoxy)- and 2-(4-methoxyphenoxy)-1,5-diamino-4,8-dihydroxyanthraquinone	3g	Blue
13	Product obtained by coupling diazotised 3-acetyl-5-nitro-2-aminothiophene with N,N-diethyl-m-aminoacetanilide	2g	Blue
14	Product obtained by coupling diazotised p-aminoacetanilide with p-cresol	3g	Greenish yellow
15	Product obtained by coupling diazotised 2-amino-6-thiocyanato-1,3-benzthiazole with N,N-di(2-acetoxyethyl)-m-toluidine	2g	Bluish red
16	Product obtained by coupling diazotised 2,5-dichloro-4-nitro-aniline with N,N-diethyl-m-amino-acetanilide	2g	Bluish red

Ex.	Dye	Quantity	Colour
17	Product obtained by coupling diazotised 2-cyano-4-nitroaniline with N,N-di(2-acetoxyethyl)-m-toluidine	3g	Bluish red
18	50/50 mixture of the methyl and ethyl esters of 1-amino-2-(4-carboxymethoxyphenoxy)-4-hydroxyanthraquinone	4g	Bluish red
19	Product obtained by coupling diazotised 2-cyano-4-nitroaniline with N,N-di(2-acetoxyethyl)aniline	3g	Red
20	4-hydroxy-4'-nitrodiphenylamine	4g	Yellow
21	Product obtained by coupling diazotised 4-chloroaniline with 1-n-butyl-5-cyano-4-methyl-6-hydroxypyrid-2-one	2g	Yellow
22	Product obtained by coupling diazotised 2-nitroaniline with 1-ethyl-4-methyl-6-hydroxypyrid-2-one	2g	Yellow
23	Product obtained by coupling diazotised 2-nitroaniline with 1-(2-ethylhexyl)-5-cyano-4-methyl-6-hydroxypyrid-2-one	3g	Yellow
24	Product obtained by coupling diazotised 4-methoxyethoxyethoxy carbonylaniline with 1-ethyl-5-cyano-4-methyl-6-hydroxypyrid-2-one	3g	Yellow
25	Product obtained by coupling diazotised 4-(N-2-ethylhexyl-sulphamoyl)aniline with 1-n-butyl-5-cyano-4-methyl-6-hydroxypyrid-2-one	3g	Yellow
26	1,5-diamino-4,8-dihydroxy-anthraquinone	3g	Blue

Ex.	Dye	Quantity	Colour
27	Product obtained by coupling diazotised 2-bromo-4,6-dinitro-aniline with N-ethyl-N-methoxy-ethoxycarbonylethyl-3-acetylamino-6-methoxyaniline	2g	Blue
28	1,5-bis-methoxyethoxycarbonyl-ethylamino-4-hydroxyanthraquinone	3g	Blue
29	Mixture of 1,4-bis-methylamino and 1,4-bis-hydroxyethylamino-5,8-dihydroxyanthraquinone	4g	Blue
30	1-(o-toluidino)-3-bromo-anthraquinone	4g	Blue
31	1-sec.butylamino-4-amino-5-nitro-8-hydroxyanthraquinone	3g	Turquoise blue
32	Product obtained by coupling diazotised 3,5-dinitro-2-amino-thiophene with N,N-diethyl-m-aminoacetanilide	2g	Bluish green

The stearic acid used in Examples 3 and 7-32 can be replaced by palmitic acid or carnauba wax. Any of these materials can suitably be used at a level of from 5 to 10% of the halogenated paraffins.

Example 33

A mixture of toluene (48g), Pigment Blue 15:3 (40g), Dispersant 8 described in EP 208041A (8g) and Fluidising Agent 1 described in EP 208041A (4g) was milled with 3mm glass beads on a flat bed shaker for 24 hours. The dispersion was diluted with a 10% solution of a C_{18-26} chlorinated aliphatic hydrocarbon having a chlorine content of 70% in toluene and also containing 10g of a blue dye (1036g) to give a finely divided fluid dispersion with a pigment/dye content of 4.4%. The dye used in this Example was 1 ,4-bis-isopropylaminoanthraquinone.

Example 34

A mixture of toluene (51g), Pigment Red 48:2 (35g) and Dispersant 8 described in EP 208041A (14g) was milled with 3mm glass beads on a flat bed shaker for 24 hours. The dispersion was diluted with a 10% solution of a C_{18-26} chlorinated aliphatic hydrocarbon having a chlorine content of 70% in toluene and also containing 8.75g of a magenta dye (894.3g) to give a finely divided fluid dispersion with a pigment/dye content of 4.4%.

The dye used in this Example was the product obtained by coupling diazotised 5-amino-4-cyano-3-methylisothiazole with N,N-diethyl-m-toluidine.

Example 35

A mixture of methyl isobutyl ketone (52g), Pigment Yellow 12 (30g), Dispersant 8 described in EP 208041A (12g) and SOLSPERSE 22000 (6g) was milled with 3mm glass beads on a flat bed shaker for 24

hours. The dispersion was diluted with a 10% solution of a C_{18-26} chlorinated aliphatic hydrocarbon having a chlorine content of 70% in methyl isobutyl ketone and also containing 7.5g of a yellow dye (752.2g) to give a finely divided fluid dispersion with a pigment/dye content of 4.4%.

The dye used in this Example was the product obtained by coupling diazotised 4-chloroaniline with 1-n-butyl-5-cyano-4-methyl-6-hydroxypyrid-2-one.

Claims

1. A thermal transfer sheet comprising a substrate having thereon a coating comprising a transferable medium containing an organic dye in which the transferable medium comprises a halogenated hydrocarbon.

2. A transfer sheet according to claim 1 wherein the coating contains from 2 to 30% by weight of dye.

3. A transfer sheet according to claim 1 or claim 2 wherein the transferable medium contains at least 80% by weight of the halogenated hydrocarbon.

4. A transfer sheet according to claim 3 wherein the transferable medium contains at least 90% by weight of the halogenated hydrocarbon.

5. A transfer sheet according to claim 4 wherein the transferable medium contains from 95 to 100% by weight of the halogenated hydrocarbon.

6. A transfer sheet according to any preceding claim wherein the halogenated hydrocarbon has a softening point of at least 50 °C.

7. A transfer sheet according to claim 6 wherein the halogenated hydrocarbon has a softening point in the range from 50 °C to 100 °C.

8. A transfer sheet according to any preceding claim wherein the halogenated hydrocarbon is a chlorinated paraffin having a chlorine content of from 65 to 72% by weight obtained by chlorinating a paraffin or mixture of paraffins containing from 18 to 35 carbon atoms.

9. A transfer sheet according to any preceding claim wherein the dye is soluble in the halogenated hydrocarbon.

10. A transfer sheet according to any preceding claim wherein the dye is a member of the azo, anthraquinone, triarylmethane or benzdifuranone series.

11. A transfer sheet according to any preceding claim wherein the transferable medium contains a dye and a pigment.

12. A transfer sheet according to claim 11 wherein the pigment is an organic pigment.

13. A transfer sheet according to claim 11 or claim 12 wherein the transferable medium contains a pigment dispersant and/or a fluidising agent.

14. A transfer sheet according to any of claims 11 to 13 wherein the dye and pigment are present in a weight ratio of from 90:10 to 10:90.

15. A transfer sheet according to claim 14 wherein the dye and pigment are present in a weight ratio of from 60:40 to 40:60.