

12 **EUROPEAN PATENT APPLICATION**

21 Application number: **89301749.1**

51 Int. Cl.4: **B41M 5/26**

22 Date of filing: **23.02.89**

30 Priority: **17.03.88 GB 8806314**  
**02.06.88 GB 8813041**

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: **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: **Schofield, John David**  
**Old oak house 482 Holcombe road**  
**Greenmount Bury Lancashire BL8 4HB(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 dispersion of a finely-divided pigment in a medium comprising at least 90% by weight of a halogenated hydrocarbon having a chlorine content of at least 65% by weight and a softening point of at least 50 °C.

**EP 0 333 335 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 which is readily miscible with the other waxes conventionally used in wax transfer printing. 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 pigments are used, in conjunction with certain halogenated hydrocarbons, transparent films having a high transmissivity can be prepared which are suitable for use in applications such as overhead transparency projection by virtue of the non-crystalline nature of the halogenated hydrocarbon.

Accordingly, the invention provides a thermal transfer sheet comprising a substrate having thereon a coating comprising a dispersion of a finely-divided pigment in a medium comprising at least 90% by weight of a halogenated hydrocarbon having a chlorine content of at least 65% by weight and a softening point of at least 50°C.

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 of about 1 to 10μ and desirably contains from 2 to 30%, by weight, of the pigment. The remainder of the coat-

ing preferably comprising the transferable medium.

The coating may be applied to the substrate as a melt but is preferably fluidised with an organic liquid in which the transfer medium is soluble and the pigment is dispersed, such as tetrahydrofuran.

The transferable medium preferably comprises more than 90%, more preferably at least 95% and especially 100%, by weight, of the halogenated hydrocarbon. The malleability of the halogenated hydrocarbon may be adjusted by the incorporation a small proportion, up to 10% but preferably not more than 5% by weight, of a softening agent, such as stearic acid, chlorostearic acid, oleic acid or a liquid chlorinated hydrocarbon based upon a hydrocarbon having a shorter carbon chain or a lower level of chlorination.

The halogenated hydrocarbon preferably has a softening point from 50°C to 100°C. It is preferably also a chlorinated hydrocarbon especially having a chlorine content from 65% to 72%, by weight. Such a product may be prepared by chlorinating a paraffin or mixture of paraffins containing from 18 to 35 carbon atoms and preferably from 18 to 26 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<sub>18-26</sub> paraffin fraction, such as might be used to prepare a chlorinated paraffin for use according to the invention, may contain a minor proportion 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 coating present in the transfer sheet 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 stabilisers 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 coating may also contain other conventional ingredients.

The pigment, or pigments, present in the trans-

fer sheet of the invention is preferably an organic pigment.

Examples of suitable organic pigments are those in the azo, disazo, thioindigo, anthraquinone, anthanthrone, isobenzanthrone or triphenldioxazine 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, especially the solvent in which the coating is to be applied to the such substrate, such as tetrahydrofuran, in conjunction with dispersants and/or fluidising agents. 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 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, for example poly C<sub>2-4</sub>-alkyleneimines carrying at least two mono- or poly-(carbonyl-C<sub>1-7</sub>-alkyleneoxy)groups.

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.

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 Example in which all parts and percentages are by weight.

#### Example 1

A mixture of tetrahydrofuran (54.5g), Pigment Blue 15.3 (35g), Dispersant 8 described in EP 208,041A (7g.) and Fluidising Agent 1 described in EP 208,041A (3.5g), 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<sub>18-26</sub>-chlorinated aliphatic hydrocarbon having a chlorine content of 70% in tetrahydrofuran (700g) to give a finely-divided, fluid dispersion with a pigment content of 4.4%.

The dispersion was applied to a sheet of 6μ polyester using a 24μ wire bound K-bar and dried to produce a clear blue transparent film on the polyester substrate, suitable for thermal transfer printing.

Further Examples are given below of formulations suitable for coating on to 6μ polyester film.

#### Example 2

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<sub>18-26</sub>-chlorinated aliphatic hydrocarbon having a chlorine content of 70% in toluene (809g) to give a finely divided fluid dispersion with a pigment content of 4.4%.

#### Examples 3-5

The toluene of Example 2 was replaced by the following solvents:

Example 3 Methyl ethyl ketone

Example 4 Methyl isobutyl ketone

Example 5 Xylene.

#### Example 6

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<sub>18-26</sub>-chlorinated aliphatic hydrocarbon having a chlorine content of 70% in toluene (700g) to give a finely divided fluid dispersion with a pigment content of 4.4%.

#### Example 7

The toluene of Example 6 was replaced by Xylene.

#### Example 8

The Pigment Red 48:2 of Example 6 was replaced by Pigment Red 57:1.

#### Examples 9-12

The toluene of Example 8 was replaced by the following solvents:

Example 9 Tetrahydrofuran

Example 10 Methyl ethyl ketone

Example 11 Methyl isobutyl ketone

Example 12 Xylene

#### Example 13

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<sub>18-26</sub>-chlorinated aliphatic hydrocarbon having a chlorine content of 70% in methyl isobutyl ketone (581.8g) to give a finely divided fluid dispersion with a pigment content of 4.4%.

#### Example 14

The Pigment Yellow 12 of Example 13 was replaced by Pigment Yellow 13.

### Claims

1. A thermal transfer sheet comprising a substrate having thereon a coating comprising a dispersion of a finely-divided pigment in a medium comprising at least 90% by weight of a halogenated hydrocarbon having a chlorine content of at least 65% by weight and a softening point of at least 50° C.

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

3. A transfer sheet according to claim 1 or claim 2 wherein the coating comprises a medium comprising at least 95% by weight of the halogenated hydrocarbon.

4. A transfer sheet according to claim 3 wherein the coating comprises a medium comprising 100% by weight of the halogenated hydrocarbon.

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

6. A transfer sheet according to any preceding claim wherein the halogenated hydrocarbon is a chlorinated hydrocarbon having a chlorine content in the range from 65 to 72% by weight.

7. A transfer sheet according to claim 6 wherein the chlorinated hydrocarbon is a product obtained by chlorinating a paraffin or mixture of paraffins containing from 18 to 35 carbon atoms.

8. A transfer sheet according to claim 7 wherein the halogenated hydrocarbon is a product obtained by chlorinating a paraffin or mixture of paraffins containing from 18 to 26 carbon atoms.

9. A transfer sheet according to any preceding claim wherein the pigment is an organic pigment.

10. A transfer sheet according to any preceding claim wherein the dispersion of pigment in the halogenated hydrocarbon includes a pigment dispersant and/or a fluidising agent.

11. A transfer sheet according to claim 10 wherein the dispersant is a polymeric dispersant having a solvatable chain derived from a hydroxylaliphatic acid.

12. A transfer sheet according to claim 10 or claim 11 wherein the dispersant contains a polyalkyleneimine residue.

13. A transfer sheet according to claim 12 wherein the dispersant is a poly(C<sub>2-4</sub>-alkyleneimine) carrying at least two mono-or poly-(carbonyl-C<sub>1-7</sub>-alkyleneoxy) groups.