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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C09D 11/00, C08G 18/28, 18/80, C07C 271/24, 271/28

A1

(11) International Publication Number: WO 94/14902

(43) International Publication Date: 7 July 1994 (07.07.94)

(21) International Application Number: PCT/GB93/02629

(22) International Filing Date: 22 December 1993 (22.12.93)

(30) Priority Data:
9226772.3 23 December 1992 (23.12.92) GB

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(81) Designated States: JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: HOT MELT INK JET PRINTING

(57) Abstract

A material suitable for use in a hot melt ink, having a melting point of at least 65 °C and obtainable by reacting an aliphatic or aromatic diisocyanate with an at least stoichiometric amount of: (i) a monohydric alcohol component; or (ii) a monohydric alcohol component followed by another different monohydric alcohol component; or (iii) a monohydric alcohol component, followed by a dihydric alcohol component followed by a monohydric alcohol component; the monohydric alcohol component(s) comprising a monohydric aliphatic alcohol or an etherified or esterified dihydric aliphatic alcohol or dihydric polyalkylene glycol; as the dihydric alcohol component comprising a dihydric aliphatic alcohol or a dihydric polyalkylene glycol and being used in an amount of not more than 50 % of the stoichiometric amount of hydroxyl groups required to react with the isocyanate groups on the diisocyanate.

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Hot Melt Ink Jet Printing

This invention is concerned with improvements in and relating to materials of compositions for use in hot melt ink jet printing processes.

Ink jet printing generally comprises forming a patterned array of droplets of an ink upon a substrate to form the desired indicia on the substrate. In a hot melt ink jet printing process, the ink is one which is normally solid at ambient temperatures and which is applied to the substrate in molten form so that the droplets solidify on cooling on the substrate.

Typically, the ink employed in hot melt ink jet printing comprises a fusible carrier together with a colourant, i.e. a pigment or dyestuff. Suitable materials for use as or in the vehicles for inks for hot melt ink jet printing (hereinafter, simply, "hot melt inks") should be relatively hard and non-tacky at ambient temperatures whilst being capable of melted to form inks. Suitably, they have a melting point of at least 65°C. A wide variety of materials have been proposed for use as vehicles in hot melt inks but there still remains a need for a good, thermally stable material having a relatively sharp melting point.

It has now been found, in accordance with the present invention, that there may be used as hot melt ink vehicles reaction products obtained by reacting a diisocyanate with one or more monohydric alcohols, optionally in combination with a dihydric alcohol.

According to one embodiment of the invention, therefore, there is provided a material suitable for use as a vehicle in a hot melt ink, having a melting point of at least 65°C and obtainable by reacting an aliphatic or aromatic diisocyanate with an at least stoichiometric amount of:

(i) a monohydric alcohol component; or
(ii) a monohydric alcohol component followed by another different monohydric alcohol component; or
(iii) a monohydric alcohol component, followed by a dihydric alcohol component, followed by a monohydric alcohol component;

the monohydric alcohol component(s) comprising a monohydric aliphatic alcohol or an etherified or esterified dihydric aliphatic alcohol or dihydric polyalkylene glycol; and the dihydric alcohol component comprising a dihydric aliphatic alcohol or a dihydric polyalkylene glycol and being used in an amount not more than 50% of the stoichiometric amount of hydroxyl groups required to react with the isocyanate groups on the diisocyanate.

As noted above, it is a requirement of the present invention that the material obtained (hereinafter simply referred to as an "oligourethane") have a melting point of at least 65°C (The term 'melting point' as used herein means the melting point as determined by the ball and ring method). It should be noted that by no means all materials obtainable in accordance with the process outlined above will have melting points of at least 65°C. Our experiments have shown that there is wide variation in melting point and attempts to predict whether a particular reaction product will have the desired melting point, for example having regard to the molecular weight of the component reactants or the possible molecular weight of the final product, simply do not yield meaningful results. However, of course, to determine the melting point of any particular material is a matter for simple routine experiment and trial.

Suitable diisocyanates for use in the preparation of the oligourethane include toluene diisocyanate, diphenylmethane-4,4'-diisocyanate (MDI), hexamethylene-1,6-diisocyanate, napthylene-1,5-diisocyanate, 3,3'-dimethoxy-4,4'-biphenyldiisocyanate, 3,3'-dimethyl-4,4'-biphenyldiisocyanate, phenylene diisocyanate, 4,4'-biphenyldiisocyanate, isophorone diisocyanate (IPDI), trimethylhexamethylene diisocyanate,and tetramethylene xylene diisocyanate. Of these diisocyanates, the aromatic diisocyanates are generally preferred and, in particular, isophorone diisocyanate has been found to give particularly useful oligourethanes.

A wide variety of monohydric aliphatic alcohols may be used to produce the oligourethanes, e.g. C_1 to C_{22} alcohols. Typical etherified dihydric alcoholic materials which may be used as monohydric alcoholic component include propylene glycol methyl ether (PGME), dipropylene glycol methyl ether (DPGME), ethylene glycol butyl ether (EGBE), diethylene glycol butyl ether (DPGBE), tripropylene glycol butyl ether (TPGBE) and propylene glycol phenyl ether (PPL). When the monohydric alcohol component is an esterified dihydric alcohol, the esterifying acid may be an ethylenically unsaturated acid (such as acrylic acid or methacrylic acid), thereby introducing ethylenic unsaturation into the oligourethane and rendering it suitable for eventual further addition polymerisation (curing) after having been applied to a substrate by hot melt printing. Dihydric alcohols may be used include, for example, alcohols, ethylene glycol, polyethylene glycol (PEG 1500), polypropylene glycol (PPG 750, 1000 and 1500), trimethylene glycol, dipropylene glycol,methyl-propanediol and 1,6-hexanediol.

The reaction between diurethane and monohydric/dihydric alcohol component is suitably carried out in the presence of a catalyst such as cobalt benzoate, lithium acetate, stannous octoate, ethylamine and dibutyl tin dilaurate.

The molecular weight of the final oligourethane is suitably from 250 to 2000,preferably from 250-750.

For some applications of hot melt inks, it is desirable that the vehicles, the oligourethanes, be clear. Again, it is virtually impossible to predict whether any particular oligourethane produced in accordance with the invention will, or will not, have the desired optical properties in this respect. However, here again it is a matter of simple routine trial and experiment and many of the oligourethanes do have the desired optical properties. Similarly, it is generally desirable that the oligourethanes should have relatively low viscosities (e.g. less than 50 cp at 125°C) and, here again, it is difficult to make predictions as to the viscosity of any particular oligourethane material.

The oligourethanes of the invention are used as vehicles, or components of the vehicles, of hot melt inks and, in addition to the oligourethanes, such inks will generally comprise colourants such as pigments or dyestuffs. Further, other conventional additives such as antioxidants etc, may also be present. Generally the vehicle (oligourethane) will form from 80 to 95% by weight, especially 90 to 95% by weight of any ink with viscosity and compatibility improving additives forming the bulk of the remainder and the other additives (colorants, etc.) being present in relatively small amounts, e.g. to a total of not more than 10% by weight of the ink.

In order that the invention may be well understood the following Examples are given by way of illustration only.

EXAMPLE 1

442 g of isophorone diisocyanate (IPDI) and 1 g of dibutyl tin dilaurate were charged to a dry, round bottomed reaction flask fitted with a stirrer and thermometer and heated, under an inert atmosphere, to 40°C. 240 g of isopropanol were slowly added to the mixture over a period of 3 hours, the reaction mixture being cooled to 60°C during this addition. Once a stable temperature of 60°C had been reached, the

reaction mixture was heated to 110°C and maintained at this temperature until the residual isocyanate value had dropped to less than 30 PPM. The molten di-urethane was then discharged and allowed to cool. The material produced was a transparent, water white and tack-free solid with a ball and ring melting point of 71°C and a viscosity of 40 centipoise at 125°C (measured on an REL cone and plate viscometer). The material displayed excellent stablity under hot conditions, remaining unchanged in clarity or viscosity after storage at 150°C for seven days.

EXAMPLE 2

250 g of diphenyl methane-4,4'-diisocyanate and 0.1 g of stannous octoate were charged to a dry, round-bottomed reaction flask fitted with a stirrer and thermometer. The flask was heated to 40°C under an inert atmosphere and 74 g of dipropylene glycol methyl ether (DPGME) were carefully added over 30 minutes, the temperature being controlled to 55°C by cooling. Once all the DPMGE had been added, 0.49 g of hydroquinone was added and the reaction mixture was aerated with air at a rate of 1 liter/min as a 130 g of hydroxyethyl acrylate were charged over one hour. The reaction mixture was maintained at a temperature of 70°C by cooling. Once a steady temperature had been attained, 162 g of octadecanol were added and the batch carefully heated to

100°C. This temperature was then maintained until the residual isocyanate value had fallen below 30 ppm. The molten material was then discharged onto a tray to cool.

The acrylate functional diurethane obtained was an opaque, tack-free solid with a ball and ring melting point of 95°C and a viscosity of 30 centipoise at 125°C (measured as an in Example 1).

EXAMPLE 3

250 g of diphenylmethane, 4,4'-diisocyanate and 0.1 g of colbalt benzoate were charged to a dry, round-bottomed flask fitted with a stirrer, thermometer and nitrogen spurge and heated to 40°C. 195 g of octadecanol were then charged to the flask over a period of 30 min., the temperature being controlled to below 60°C by cooling. Once the exotherm had abated, 26 g of dipropylene glycol were added over 30 min and the temperature controlled was 70°C until a steady temperature was obtained. Finally, 148 g of DPGME were charged to the reaction mixture whose temperature was then allowed to rise to 110°C. The reaction mixture was held at this temperature until the residual isocyanate value had fallen below 30 ppm. The molten oligourethane was discharged to a tray to cool.

The material produced was a transparent, water-white, tack-free solid with a melting point of 102°C and a viscosity of 50 centipoise at 125°C.

EXAMPLE 4

Following the procedure of Example 1, 442 g of isophorone diisocyanate were reacted with 128 g of methanol to give a diurethane which was a transparent, colourless solid with a ball and ring melting point of 75°C and a viscosity of 75 centipoise of 125°C.

Following the general procedure of Examples 1-3, a variety of oligourethanes have been produced. Listed below are examples of combinations which proved successful, i.e. gave products having a melting point above 65°C. The combinations are listed in terms of the isocyanate, followed by the alcohol(s), the numbers in brackets after the alcohol(s) being the number of moles of alcohol per mole of diisocyanate.

MDI/octadecanol (0.65)/dipropylene glycol (0.15)/TPGBE (1.05);
MDI/octadecanol (0.60)/DPGME (1.40);
MDI/octadecanol (0.40)/dipropylene glycol (0.26)/PGME (1.1);
MDI/octadecanol (1.00)/triethylene glycol (0.50);

MDI/hexadecanol (1.00)/triethylene glycol (0.50);

MDI/octadecanol (0.60)/dipropylene glycol (0.20)/DPGME (1.00);

MDI/octadecanol (0.50)/dipropylene glcyol (0.25)/PGME (1.00);

MDI/PPh (2.0);

IPDI/t-butanol (1.50)/octadecanol (0.50);

IPDE/PPh (2.00);

IPDEI/t-butanol (2.00).

Listed below, in similar fashion, are examples of combinations which did not prove successful, that is gave products having melting points below 65°C.

MDI/PGME (2.00);

MDI/DPGBE (2.00);

MDI/Methanol (1.00)/PPh (1.00);

MDI/Octadecanol (0.25)/PPh (1.75);

MDI/butanol (1.25)/triethylene glycol (0.375);

IPDI/isopropanol (1.00)/octadecanol (1.00);

IPDI/methanol (1.50)/octadecanol (0.50);

IPDI/isopropanol (1.30)/hexanediol (0.20)/octadecanol (0.30);

IPDI/isobutanol (2.00).

Example 5

The reaction product of one equivalent of isophorone di-isocynate with an equivalent of isopropanol (as described in Example 1) was melted at 140°C and 10% w/w of a monoamide (the reaction product of n-butylamide and stearic acid) stirred into it, until a clear homogenous fluid was formed. Waxoline red YP FW dye (ICI colours and fine chemicals), 0.02% w/w, was then added and dispersed using a Silverson high speed stirrer; the resulting red liquid was filtered through a 5 micron filter. The ink produced was a transparent red solid, with a viscosity of 13.7 centipoise at 125°C. When applied using a thermal ink jet printer, or by heated drawn down bar onto polyester overhead projection film (Mylar) the ink showed good colour homogenity, transparency to back-lighting and excellent adhesion to the substrate coupled with good resistance to flexing.

Example 6

The reaction product of one equivalent of diphenyl methane-4,4'-di-siocyanate with half equivalent of dipropylene glycol methyl ether (DAGME) and half equivalent of hydroxyethyl acrylate (as per Example 2) was melted at 140°C and 6% w/w of benzophenone (a photoinitiator), 10% w/w of erucamide (crodamide ER, Croda Ltd) and 0.02% w/w macrolex yellow 3g dye (Bayer

Ltd) were added with stirring. The material was kept hot while being thoroughly dispersed using a Silverson high speed stirrer. The resulting clear yellow fluid was filtered through a 5 micron filter when cooled a translucent yellow solid with a viscosity of 55 centipoise at 1250°C was produced. When applied by thermal ink jet printing and by heated drawdown bar onto polyester (Mylar) sheet the ink showed excellent adhesion and resistance to flexing, but was slightly tacky. When the ink was passed through a UV cure unit (to give it a cure of 1500 mJ/cm^2) the surface became tack free, with improved rub resistance. The cured film was translucent.

Example 7

The oligourethane produced by the method described in Example 3 was heated to 140°C and mixed, using a silverson high speed stirrer, with stearamide (crodamide SR, Croda Ltd), 5% w/w, stearone (5% w/w) and methylene blue dye (0.05% w/w) until a homogenous blue liquid was produced. This liquid was filtered through a 5 micron filter and cooled to give a clear blue solid ink with a viscosity of 25 centipoise at 125°C. This ink, when applied to a polyester film substrate using a hot ink jet printer or a heated draw down bar coater gave a transparent blue film with good light transparency, adhesion and crease resistance.

CLAIMS:

1. A material suitable for use in a hot melt ink, having a melting point of at least 65°C and obtainable by reacting an aliphatic or aromatic diisocyanate with an at least stoichiometric amount of:

(i) a monohydric alcohol component; or
(ii) a monohydric alcohol component followed by another different monohydric alcohol component; or
(iii) a monohydric alcohol component, followed by a dihydric alcohol component followed by a monohydric alcohol component;

the monohydric alcohol component(s) comprising a monohydric aliphatic alcohol or an etherified or esterified dihydric aliphatic alcohol or dihydric polyalkylene glycol; as the dihydric alcohol component comprising a dihydric aliphatic alcohol or a dihydric polyalkylene glycol and being used in an amount of not more than 50% of the stoichiometric amount of hydroxyl groups required to react with the isocyanate groups on the diisocyanate.

2. A hot melt ink containing, as vehicle, a material as claimed in claim 1 together with a colorant.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 93/02629

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C09D11/00 C08G18/28 C08G18/80 C07C271/24 C07C271/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C09D C08G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,36 06 478 (BASF) 3 September 1987 ---	1
X	GB,A,575 652 (WINGFOOT CORP.) 27 February 1946 ---	1
X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 28 (C-471)(2875) 27 January 1988 & JP,A,62 179 580 (ASAHI CHEM IND CO LTD) 6 August 1987 see abstract ---	1
A	EP,A,0 154 678 (BYK-CHEMIE) 18 September 1985 ---	1
A	EP,A,0 404 493 (XEROX CORP.) 27 December 1990 -----	2

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 15 March 1994	Date of mailing of the international search report 18. 04. 94
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/GB 93/02629

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