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(54) Title: COLOURED INK AND USES THEREOF

(57) Abstract: A coloured ink, the ink comprising: at least 51 wt% of a slow drying liquid carrier, having a boiling point of at least 161° C (at 760mm Hg) and a relative evaporation rate of less than 0.25 (relative to that of N-butyl acetate); at least 2.5 wt% of a colourant; and wherein the total solids content of the ink is at least 4.0 wt% and which is substantially free of cyclohexanone and derivatives thereof.



Coloured Ink and Uses thereof

Technical Field

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The present invention relates to a coloured ink composition, to a method of printing using the coloured ink, and to a printing apparatus provided with the coloured ink.

Background and Prior Art

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Analogue printing, via a contact printing process, typically prints each ink layer onto a dry (or at least highly viscous) preceding layer, thereby maintaining the integrity of the preceding ink layer when the subsequent ink layer is applied. Using a non-impact digital printing process, of which inkjet printing is a common type, it is possible to print one wet ink layer on top of a previously printed wet ink layer. However, printing a thick layer of wet ink with inkjet printing is undesirable, especially on non-porous or semi-porous substrates, as the ink is prone to spread excessively on the surface (feather), bleed between colours and even flow or run. Also, inkjet printing inks are typically less viscous than analogue printing inks as low viscosity is a requirement of the inkjet print heads to be able to eject the ink.

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Accordingly a high speed, single pass industrial production inkjet printing process would therefore typically involve printing one or two layers with drying (or in the case of UV inks, UV curing) in between to stabilize the deposited ink layer(s) before the next layer was applied. In "single pass" printing, the print head remains essentially static during printing, whilst the material to be printed on, usually a roll or reel of flexible substrate, is fed past the print head.

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Inkjet inks that are based on pigments for the colourant are typically made by obtaining a pigment "chip" which is a 50:50 blend of pigment and a dispersant. The pigment chip is then stirred with cyclohexanone or a derivative thereof. It is believed that the cyclohexanone provides a particularly effective stabilising effect on the pigment particles via chemical mechanism, believed to be akin to the formation of a complex of cyclohexanone molecules around a pigment particle. However,

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cyclohexanone is undesirable for other reasons such as its relatively high toxicity and flammability rating.

An example of an ink prepared in this way is given in US 7,950,794.

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Surprisingly, the inventors have found that, by use of coloured inks of novel and inventive formulation, it is possible to use inkjet printing in a single pass industrial process without needing to allow each colour of ink to dry completely before printing the next colour ink. Furthermore, the formulation allows the omission of

10 cyclohexanone, providing a further benefit regarding toxicity and flammability of the printed images.

Summary of the Invention

15 In a first aspect, the invention provides a coloured ink, the ink comprising: at least 51 wt% of a slow drying liquid carrier (as herein defined); at least 2.5 wt% of a colourant; and wherein the total solids content of the ink is at least 4.0 wt% and which is substantially free of cyclohexanone and derivatives thereof.

20 By “substantially free” is meant that the ink comprises less than 2 wt% cyclohexanone or derivatives thereof, preferably less than 1 wt% and more preferably is completely free of any cyclohexanone or derivatives thereof.

For present purposes a liquid carrier is liquid at 20°C and 760mm Hg pressure. A

25 liquid carrier is “slow drying” if it has a boiling point of at least 161°C (at 760mm Hg) and has a relative evaporation rate of less than 0.25 (relative to that of N-butyl acetate).

Preferably the liquid carrier has a boiling point of at least 162°C. More preferably the

30 liquid carrier has a boiling point of at least 163°C. Most preferably the liquid carrier has a boiling point of at least 164°C. Preferred liquid carriers may have a boiling point of 165°C, 166°C, 167°C, 168°C, 169°C, 170°C, 171°C, 172°C, 175°C or higher. A maximum boiling point for the liquid carrier may be 300°C. A preferred range for the boiling point of the liquid carrier is 161-260°C, more preferably 162-250°C and most

35 preferably 165-250°C.

Preferably the coloured ink comprises at least 70 wt% of the slow drying liquid carrier.

- 5 The liquid carrier may be a single compound or may be a mixture of two or more compounds. Methods of empirically determining the boiling point of a mixture of compounds are well known to those skilled in the art.

10 The relative evaporation rate of the slow drying liquid carrier (relative to that of N-butyl acetate) is less than 0.25, preferably less than 0.20, more preferably less than 0.15, and most preferably less than 0.10. A preferred range for the relative evaporation rate of the liquid carrier is in the range 0.001-0.20, more preferably 0.001-0.19, and most preferably 0.001-0.18.

- 15 The method of determining the relative rate of evaporation of a liquid carrier or mixture of liquid carriers is described by Hofmann, Harry E. "Evaporation rates of Organic Liquids"; Ind. Eng. Chem. 1932 **24**, 135.

20 Generally the slow drying liquid carrier may consist of, substantially comprise, or contain, one or more humectants. Examples of slow drying liquid carriers which may be suitable for use in the present invention include glycol acetates, especially alkyl glycol acetates. A preferred alkyl glycol acetate is butyl glycol acetate. Other slow drying liquid carriers which may be suitable for use in the invention include lactates, especially alkyl lactates such as butyl lactate.

25 Table 1 below shows a non-exhaustive list of some compounds that may be useful in a liquid carrier for an ink in accordance with the invention. From n-pentyl propionate onwards, the compounds all have boiling points in excess of 161°C.

- 30 The preceding compounds have a boiling point which is below 161°C. However, these solvents may still be useful when present at low concentration in a liquid carrier formulation together with other compounds having higher boiling points (and typically also lower evaporation rates).

However, the inks of the present invention are substantially free of cyclohexanone and derivatives thereof. This is because this material represents an unacceptably high level of toxicity and flammability, rendering it unacceptable for many uses, especially in the printing of material which may come into contact with people or children, such as e.g. wallpaper.

The inventors have found that inks in accordance with the invention not only provide acceptable image quality when used in inkjet printing, but they also confer good latency time and good decap time.

Latency time (or dwell time) is the time that inkjet nozzles can be left uncovered and idle before there is noticeable reduction in performance, for instance a reduction in drop velocity that will noticeably affect the image quality.

Decap time (or open time) is the time that nozzles can be uncovered and idle before they will no longer print (and need to be recovered by purging).

Table 1

	Boiling point [C] (1.010.8 hPa)	Evaporation rate (n- Butylacetate = 1)
ethylglycol acetate	156.3	0.19
cyclohexanone	156.7	0.31
Ethoxy Propyl Acetate	159	0.21
Diglyme	160.16	0.36
cyclohexanol	160.6	0.05
n-pentyl propionate	165	0.18
diacetonolcohol	169.2	0.12
diisobutyl Ketone	169.4	0.19
UCAR ester EEP	169.7	0.12
ethylene glycol n-butyl ether	170.7	0.079
propylene glycol n-butyl ether	171	0.093
butylglycol	171.2	0.07
cyclohexyl acetate	173	0.11
Proglyme	175	0.13
dipropylene glycol dimethyl ether	175	0.13
Diisobutyl Carbinol	178	0.06
Isopentanoic acid	183.1	0.04

2-ethylhexanol	184.8	0.02
Valeric acid	185.5	0.02
butyl lactate	187	0.03
Polypropylene	187.3	0.01
Dipropylene glycol methyl ether	188.3	0.02
Ethyl Diglyme	188.9	0.04
ethylene glycol diacetate	190.9	0.026
propylene glycol diacetate	191	0.039
butylglycol acetate	191.6	0.037
ethylene glycol n-butyl ether acetate	192	0.04
diethylene glycol methyl ether	194.1	0.019
methyldiglycol	194.2	0.02
Hexyleneglycol	197.1	0.01
ethylene glycol	197.6	0.01
2-ethylhexyl acetate	199	0.034
diethylene glycol ethyl ether	202	0.013
ethyldiglycol	202.7	0.01
Gamma Butyrolactone	204	0.03
ethylene glycol hexyl ether	208	0.0082
dipropylene glycol methyl ether acetate	209	0.015
dipropylene glycol n-propyl ether	213	0.014
Isophorone	215.2	0.02
Triglyme	216.25	0.001
ethyl diglycol acetate	217.4	0.01
trimethylnonanol	225	0.01
2-ethylhexoic acid	227.8	0.01
dipropylene glycol n-butyl ether	230	0.006
diethylene glycol n-butyl ether	230.4	0.004
butyldiglycol	230.6	0.01
Dipropyleneglycol	232.8	0.001
Tripropylene glycol methyl ether	243	0.0026
propylene glycol phenyl ether	243	0.002
ethylene glycol phenyl ether	244	0.001
diethylene glycol n-butyl ether acetate	245.3	0.0017
Diethyleneglycol	245.8	0.001
butyl diglycol acetate	246	0.01
triethylene glycol methyl ether	249.2	0.002
Butyl Diglyme	251.31	0.001
ethylene glycol phenyl ether (major)	254	0.0001
triethylene glycol ethyl ether	256.3	0.002
diethylene glycol hexyl ether	259.1	0.0006

tripropylene glycol n-butyl ether	274	0.0004
Polyglyme (High Mol weight glymes)	275	0.001
Higlyme	275	0.001
Tetraglyme	276.49	0.001
triethylene glycol n-butyl ether	279.7	0.0004
dipropylene glycol phenyl ether	280	0.0002
diethylene glycol phenyl ether	282	0.0002
Poly(oxy-1,2-ethanediyl), alpha-phenyl-omega-hydroxy	350	0.0001

The coloured ink of the invention is preferably suitable, and preferably adapted and configured, for use in a non-impact printing technique, especially inkjet printing.

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The ink formulation of the present invention comprises a concentration of colourant which is at least 2.5 wt%, typically more than 3.0 wt%. This is higher than that typical for an ink designed for use in an inkjet printer. Preferably the colourant is present in a concentration at least 3.5 wt%, more preferably at least 3.8 wt%, and most preferably at least 4.0 wt%.

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The use of a high concentration of colourant in the ink of the invention allows a coloured image to be formed on a substrate using a small volume or thickness of ink on the substrate which, as explained elsewhere, is desirable.

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The colourant is preferably present in the composition at a concentration of less than 10 wt%. Whilst it is desirable in the present invention to have a relatively high concentration of colourant, the total solid content of the ink may be limited by the effect of the solid content on the physical properties of the ink including, in particular, the viscosity thereof. More preferably the colourant concentration in the ink is less than 8.0 wt% and most preferably less than 6.0 wt%. Thus, for example, a preferred concentration range for the colourant in the ink of the invention is 3.5-10.0 wt%, more preferably 3.8-8.0 wt%, and most preferably 4.0-6.0 wt%.

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The colourants used in the present invention are preferably highly transparent (i.e. have a mean particle diameter of 1µm or less). In such embodiments, the coloured ink may be printed on top of another substance without obscuring it. In particular, as described elsewhere, the coloured ink may be printed on top of a metallic or other

'special effect' layer on a substrate without significantly detrimentally scattering or attenuating the light illuminating the special effect layer.

Desirably the ink will comprise a cyan, magenta, yellow or black colourant. Suitable colourants are commercially available from a number of sources and include, for example, Hostaprint® Blue B2G32, Hostaprint™ Magenta E5B32, Hostaprint™ Yellow HG32 (all available from Clariant), and Microlith™ 0066K (available from BASF).

The ink of the invention may further comprise a dispersant. The function of the dispersant is to improve the homogeneity of the ink (e.g. by improving the separation of the particles and to inhibit settling). Generally dispersants attach to the surface of particles of the colourant. Typically, commercially available colourants are supplied by the manufacturer with an amount of dispersant already present. The ratio of dispersant to colourant (wt) is typically about 50:50, but could be higher than this. For example an acceptable ratio of dispersant to colourant could be in the range 1:1 to 6:1. Any conventional dispersant may be used in the ink of the invention, and suitable examples are well known to those skilled in the art. A typical dispersant comprises a vinyl acetate/vinyl chloride ("VAVC") copolymer, or acrylic. Other suitable dispersants may comprise a copolymer of styrene acrylic acid and methacrylic acid or styrene maleic acid, or a styrene-acrylic polymer. The dispersant can advantageously be selected for compatibility with the intended substrate, e.g. acrylic is suitable for printing onto an ABS substrate. The ink may also optionally comprise other components, such as a binder resin or polymer (although the dispersant may be sufficient binder itself). The fine details of the ink composition may be adjusted for compatibility with the intended substrate.

The total solids content of the ink is at least 4.0 wt%. This is required to offset the slow drying nature of the liquid carrier. However it is preferred that the total solids content of the ink is as low as possible whilst being consistent with the need to allow the ink to dry in a reasonable time.

The use of the minimum desirable total solids content allows for a very thin layer of ink to be formed on the substrate once dry. Typically the thickness of the dried ink

layer on the substrate will be less than 5µm, preferably less than 3µm, and more preferably 1.5µm, as described and explained elsewhere.

Desirably therefore the total solids content of the ink is less than 20 wt%, preferably less than 18 wt%, more preferably less than 16 wt%, and most preferably less than 14 wt%. In preferred embodiments, the total solids content of the ink is in the range 4.0-20.0 wt%, more preferably in the range 4.0-16.0 wt%, and most preferably in the range 4.0-10.0 wt%.

The solid component of the ink, in addition to the colourant, may comprise for example a resin or other binder substance. Suitable binders for use in the ink include, but are not limited to, methyl methacrylate/n-butyl methacrylate copolymer (e.g. available under the trade name Elvacite® 2614, molecular weight 56,000). Other suitable acrylate resins are MMA resins; MMA copolymers; EMA resins; and BMA resins.

Other suitable binders comprise vinyl copolymers such as copolymers of vinyl chloride and vinyl acetate; terpolymers of vinyl chloride, vinyl acetate and dicarboxylic acids; copolymers of vinyl chloride & hydroxy acrylate; terpolymers of vinyl chloride, hydroxy acrylate and dicarboxylic acid ester; and terpolymers of vinyl chloride, vinyl acetate and vinyl alcohol.

Another suitable binder is cellulose acetate butyrate.

The ink of the invention preferably comprises a single colourant, but in principle, the ink may comprise a mixture of colourants, which together make up at least 2.5 wt% of the ink. The preferred colourants are solid pigments (i.e. substantially insoluble in any liquid carrier) but may, in some embodiments be “dispersed dyes” having very limited solubility in the liquid carrier.

The person skilled in the art will appreciate that the average molecular weight of the solid is also relevant. Accordingly a relatively high solids content (e.g. up to 20 wt%) may be tolerated where the average molecular weight is small (say, less than 500), whilst polymeric solids with an average molecular weight of 10kD, for example, may be present at low concentration (4.0 wt%).

The physical properties of the ink will desirably be such that the ink is especially suitable for use in inkjet printing. For example, the ink will typically have a viscosity in the range 7-20cP (as measured at 25°C, at 30 RPM using a Brookfield DV II+ viscometer).

In a second aspect, the invention provides a method of printing onto a substrate, the method comprising the step of applying an ink in accordance with the first aspect onto a surface of the substrate, in sufficient amount to form a visible image.

The ink is preferably applied via a non-impact printing technique, more especially by means of inkjet printing.

The substrate is typically flexible and conveniently may be formed into a roll.

Desirably a roll of substrate is fed into a printing apparatus which performs the method of the invention and prints onto the substrate in a substantially continuous, automated process.

As defined above, the substrate in the method of the invention is preferably wallpaper. Wallpaper, for present purposes may be defined as follows: a flexible material adapted and configured for application to a wall for use as a decorative wall covering complying with BS EN 12956:1999, the flexible material comprising a paper or non-woven substrate having a weight in the range 60-130gm per m² of substrate, the substrate being coated on one side with a coating of a thermoplastic material, the coating having a maximum thickness in the range 0.05-1.0mm, the coating further comprising one or more of a blowing agent, plasticizer, dispersing agent, thinner, filler, pigment or stabiliser, the coating being applied to the substrate in an amount in the range 150-250gm coating per m² of substrate over the entire upper surface of the substrate.

The method of the invention preferably comprises a "single pass" inkjet printing technique. In "single pass" inkjet printing, the inkjet printing head is essentially static, and the substrate is fed past the printing head.

Typically the printing method for the invention involves the application of two or more different coloured inks to the substrate. More typically the method may involve feeding the substrate through an inkjet printing apparatus provided with each of a cyan, magenta, yellow and black ink, with the image being formed by application of one or more the selected inks in selected amounts.

Surprisingly it has been found that the inkjet printing process of the invention can print multiple layers of inkjet ink "wet-on-wet" and yield an acceptable high quality image incorporating colour print. Furthermore this has the additional advantages of reducing the size of the carriage containing the print heads, improving the accuracy with which one printed layer is registered to the next, and thus improving the resultant image quality.

To achieve the best results when printing wet-on-wet it is desirable to control the maximum wet layer thickness. The maximum thickness of the total of all wet ink layers should be less than 50µm), preferably less than 30µm and most preferably 15µm. In other terms the total of all wet ink layers should be less than 50 g/m², preferably less than 30 g/m² and most preferably less than 15 g/m².

As well as the application of a coloured ink of the first aspect of the invention, the method of the second aspect may further comprise the application of a "special effect" ink.

Special effects may comprise additional decorative features to enhance a printed colour image and include but are not limited to metallic, pearlescent, luminescent, fluorescent, phosphorescent, glitter, sparkle, pearl, gloss and matt effects. To create these effects, special effects inks often contain particulate pigment materials that are difficult to inkjet print due to their size.

A preferred metallic ink contains metallic (flake) pigments and creates a metallic effect directly on printing, thus requiring no pre or post treatment to realise the metallic effect. Typically the metallic pigments are aluminium or mica-flakes which give a silver metallic effect. Overprinting the silver metallic effect with (transparent) colour inks enables a wide range of metallic colours to be produced.

In a typical embodiment, the printing method of the invention comprises at least 4 colour image printing, typically using CMYK (cyan, magenta, yellow and black) colours and optionally may also include additional process colours (such as orange and purple or light cyan and light magenta) or spot colours (such as white, red and/or green), and/or at least one or two special effects inks.

The special effects may be printed in any order with the colour printing, though preferably are arranged with at least one special effect printed before the colour printing and at least one special effect printed after the colour printing. Most preferably the special effect occurring before the colour printing is a metallic effect and the special effect occurring after the colour printing is a gloss effect.

To achieve acceptable image quality and colour strength it is desirable to at least maximise the concentration of the colorants within the colour inks, but also preferably to minimise the layer thickness, and this can be achieved by using coloured inks in accordance with the first aspect of the invention.

In order to help minimise the thickness of the dried ink layer, it is desirable to optimize the ink dot size (D in microns) on the substrate, such that the smallest possible ink dots are applied to the surface (the ink dots need to be of a size and density such that they just touch a closest neighbor dot on the substrate and can coalesce). The ink dots are at least equal to $D = \frac{25,400\sqrt{2}}{R}$, preferably at least

equal to $D = \frac{25,400\sqrt{2}}{R} + 10$, or most preferably at least equal to

$D = \frac{25,400\sqrt{2}}{R} + 20$ where R is the resolution (in dpi) perpendicular to the printing

direction. Preferred values for R are 300-600dpi, preferably 300-600dp. A typical dot size is about 50 or 60 μ m.

Substrates to which the printing method of the invention may be applied include, *inter alia*, wall coverings (e.g. wallpaper), laminate flooring (e.g. vinyl floor coverings), packaging (especially paper board packaging), greetings cards, labels, self-adhesive labels, fine art reproductions, banners, promotional literature, POP and

POS items, posters etc. Typically the substrate may comprise a surface, onto which the ink is applied, which is semi-permeable to the ink.

The substrate is desirably pre-heated before printing, to raise the substrate
5 temperature above the ambient temperature. The temperature of the substrate will be such as to aid evaporation of the volatile components of the ink but not sufficient to compromise the integrity or stability of the substrate itself. The substrate pre-heat temperature is at least 25°C, preferably at least 35°C and most preferably at least 45°C. The pre-heating is desirably accomplished with a system comprising a plurality
10 of infrared lamps.

The substrate temperature is desirably maintained at a temperature above ambient temperature in the printing area. The temperature maintained in the printing area may be the same as the pre-heat temperature or may be different, with the substrate
15 temperature preferably being at least 25°C, preferably at least 35°C and most preferably at least 45°C. The substrate heating in the printing area is desirably accomplished using a heated platen (e.g. electrically powered) which warms the reverse (non-printed) side of the substrate.

20 The printed ink(s) and substrate are then typically further heated to dry the ink once clear of the printing area. The post-print heating must be sufficient to dry the printed image sufficiently well before it reaches the first roller or other object that comes into contact with the printed surface of the substrate. The post-print temperature is at least 50°C, preferably at least 80°C and most preferably at least 110°C. The post-
25 print heating is conveniently effected by means of a cartridge of infra-red light lamps.

Using the ink of the first aspect of the present invention, the inventors have found that it is possible, in the method of the second aspect, to achieve a print speed onto a reel of substrate in excess of 24 metres/minute, and even up to 48 metres/minute,
30 which speeds render feasible an industrial process utilising the method of the invention.

In a third aspect, the invention provides inkjet printing apparatus comprising a plurality of print heads and at least one ink reservoir comprising an ink in accordance
35 with the first aspect of the invention.

The print heads used to print the colour inks are preferably recirculating piezo drop on demand print heads as the recirculation reduces the rate of the ink drying in the print head nozzles and displaces any debris, bubbles or particles that can prevent the drop being produced correctly. This reduces the maintenance required and improves the reliability and productivity of the printing system, as well as enabling more volatile solvents to be used which make drying the printed image faster and easier. A major part of special effects are produced with particulated inks generally denser than the fluid they are incorporated in, so the print heads are preferably recirculating.

The printing apparatus is preferably of the single pass type, with static print heads and the substrate to be printed being fed through the apparatus. The printing apparatus of the third aspect of the invention may be largely conventional, save for the presence of the ink composition of the first aspect of the invention. Digital inkjet printing devices which may be adapted for the present invention include those disclosed in, *inter alia*, WO2010/150012, WO2010/125129, WO2008/065411 and EP2055490.

The printing apparatus of the third aspect of the invention is preferably adapted and configured to perform the printing method of the second aspect of the invention. The various aspects of the invention will now be further described by way of illustrative example and with reference to the accompanying drawings, in which:

Examples

Example 1

Table 2 below gives sample formulations of four coloured inks (C, M, Y, K) in accordance with the invention, and also the formulation of a metallic silver effect ink and a gloss effect ink. The numbers are the wt% of the ingredients. The bottom three rows of the table also show the viscosity (at 25 or 45°C) of the inks and their surface tension.

Table 2

Ingredients (wt%)	Colour				Effects	
	Cyan	Magenta	Yellow	Black	Silver	Gloss
Microlith 0066K (Pigment Black 7)	-	-	-	9	-	-
Hostaprint Blue B2532 (Pigment Blue 15:3)	9.5	-	-	-	-	-
Hostaprint Magenta (Pigment Violet 19)	-	9	-	-	-	-
Hostaprint Yellow HG32 (Pigment Yellow 180)	-	-	8.5	-	-	-
Joncryl 586	-	-	-	-	-	25
Butyl Lactate	-	-	-	-	78.75	75
Butyl Glycol Acetate	90.5	91	91.5	91	-	-
Dianal PB-204	-	-	-	-	8.75	-
Metasheen RD215	-	-	-	-	12.5	-
Viscosity at 25°C (30 RPM cp)	9.9	11.7	7.9	9.5	6.7	-
Viscosity at 45°C (30 RPM cp)	-	-	-	-	-	15.0
Surface tension (dynes/cm)	30.0	30.5	28.0	31.0	31.5	33

The pigments noted above are provided as a 1:1 mixture with a dispersant. Thus, for example, where the Table shows the pigment Microlith™ 0066K (Pigment Black 7) as present at 9 wt%, the actual black pigment concentration in the ink is 4.5 wt%, and the ink comprises 4.5 wt% dispersant and 91 wt% slow drying liquid carrier (butyl glycol acetate). Microlith™ 0066K is available from BASF. The Hostaprint™ pigments are available from Clariant.

Dianal PB-204 is a low molecular weight, high acid number resin available from Dianal America, Inc. Joncryl™ 586 is a styrene-based polymer available from BASF. Metasheen RD215 is an aluminium-containing pigment; similar products are available from BASF.

Example 2

An inkjet printing apparatus in accordance with the invention comprises a substrate feed section, a fixed array (single pass) inkjet print section and a post-print processing section.

5 The apparatus is designed to print on an elongate web of flexible substrate supplied on a substrate supply roll. In the feed section, the leading edge of the substrate passes over tension rollers. The substrate also passes through an alignment station via a humidification treatment arrangement that functions to impart a desired, uniform level of humidity to the substrate.

10 The alignment station is arranged to detect the lateral positioning of the substrate and makes any necessary translational adjustment of the substrate for correct alignment. The alignment station incorporates an arrangement for detecting any surface roughness or irregularity greater than a predetermined level (typically 0.3 mm) above the print surface that might damage the printer, and for halting substrate
15 feed in this event.

The substrate then passes to the print section which comprises a pre-printing heating zone, a printing zone and a post-printing heating zone, with the two heating zones being isolated from the printing zone. The pre-heating zone has an array of infrared
20 lamps arranged to bring the substrate to a desired temperature, typically at least 25°C, preferably at least 35°C and more preferably at least 45°C, prior to printing. The pre-heating temperature of the substrate should be sufficient to aid evaporation of volatile components from the inks without compromising the integrity or stability of the substrate.

25 The printing zone comprises a vacuum bed located below a print carriage. The print carriage comprises an array of twelve print bars, each bar being elongate and extending across the width of the vacuum bed. Each print bar comprises ten recirculating piezoelectric drop-on-demand inkjet printheads arranged in two side-by-side staggered arrays extending across the length of the bar, the printheads of one
30 array overlapping those of the other array to provide coverage across the length of the bar. There are 120 printheads in total.

Typically two adjacent print bars will be used for a particular type of ink, and in a
35 typical embodiment capable of printing full colour images with special effects, the first

two print bars (in the direction of printing) are for a special effect metallic ink, the next pair of print bars for black (K) ink, the next pair for cyan (C) ink, the next pair for yellow (Y) ink, the next pair for magenta (M) ink and the last pair for a special effect gloss ink. The C, Y, M and K coloured inks are each in accordance with the first aspect of the invention defined above. Optionally additional print bars may be provided for additional process colours (such as orange and purple or light cyan and light magenta) or spot colours (such as white, red and/or green). Each printhead preferably has a minimum drop volume of 6 pL-12 pL. The print bars are stationary during printing, with the substrate passing thereunder, but can be moved laterally with respect to the vacuum bed, when not printing, e.g. for maintenance.

The vacuum bed includes a planar, horizontally oriented rigid metal platen that has an array of apertures extending therethrough. The upper surface of platen is heated to maintain the temperature of the substrate during printing at the level attained by the pre-heating.

A vacuum chamber is connected to the underside of the platen to apply a vacuum to the backing surface of the substrate (i.e. the non-printed surface) via the apertures on the platen to urge the substrate into contact with the platen and maintain the substrate in the correct lateral position with respect to the printheads and also at the correct spacing from the printheads on passage of the substrate below the stationary printheads during printing. Printing is controlled by a PC or other programmable digital electronic control device.

After printing the substrate is conveyed from the printing zone to the post-printing heating zone which is located below and isolated from the printing zone for drying of the printed image, being conveyed over rollers to pass over a first dryer comprising a cartridge of infrared lamps arranged to produce a temperature of the atmosphere in the vicinity of the substrate of at least 50°C, preferably at least 80°C and more preferably at least 110°C, with the temperature used in the heat treatment typically being between about 110°C and about 160°C. Drying is assisted by an air knife with an air velocity of at least 10 m/s, preferably at least 20 m/s, more preferably at least 30 m/s.

Drying is such that the printed image is sufficiently dry before the contact surface of the substrate passes over transport rollers so that no damage occurs to the printing. The substrate then passes through second dryer in the form of oven.

5 The substrate with the dry printed image then passes to the post-print processing section, passing over rollers through an alignment mechanism that detects the lateral positioning of the substrate and makes any necessary translational adjustment, and then to an edge trimmer assembly that trims the edges to produce a substrate of desired width, typically with a printed image extending across the full width.

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The substrate is then typically subjected to further downstream processing such as being cut to length, with cut lengths being rolled up along their length to obtain a roll.

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Movement of the substrate through the equipment is produced by applying a tensile force to a downstream portion of the substrate, with the tension preferably being about 5-25 Newtons.

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The speed of movement of the substrate with respect to the printheads is typically 12 m/s, 24 m/s or 48 m/s depending on the type of image and resolution required.

After printing, the substrate was edge trimmed to produce a desired width and cut into desired lengths.

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Using this apparatus and method, printed wallpaper was produced with a print pattern having a resolution of 300x600 dpi. After the production of the printed product, samples of the same production batch and from different production batches comprising a similar colour print pattern were compared and examined for potential colour differences.

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Colour can be determined in an objective manner, for example through aid of a spectrophotometer or a tristimulus colorimeter, whereby light is directed at a sample and the reflected light is detected and analyzed for its intensity. Using a spectrophotometer, the light which is directed at the sample usually originates from a polychromatic light source whereby the reflected light is measured at a range of wavelengths at a distance of 5, 10 or 20 nm throughout the whole visible spectrum

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(380-730 nm or 400-700 nm). A Tungsten light bulb of a Xenon lamp may be used as a light source. To evaluate the colour differences, the samples are preferably measured using various light sources, both in the presence of daylight as well as in the presence of e.g. the light of a fluorescent lamp.

5

When measuring colour differences, a threshold value should be taken into account, under which value colour differences are not generally capable of being distinguished by the human eye: $dE_{CMC} \geq 1.0$.

10 Colour differences within the same production batch and between different batches of the product comprising a similar colour print pattern were measured using a spectrophotometer and the values obtained for each sample were compared to each other.

15 The printed product which was produced according to the method as described above displayed a dE_{CMC} value below 0.4 for samples from the same production batch comprising a same colour print pattern and below 0.7 for samples obtained from different production batches comprising a same colour print pattern, and in both cases thus were below the threshold value of 1.0.

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Claims

1. A coloured ink, the ink comprising: at least 51 wt% of a slow drying liquid carrier, having a boiling point of at least 161°C (at 760mm Hg) and a relative evaporation rate of less than 0.25 (relative to that of N-butyl acetate)); at least 2.5 wt% of a colourant; and wherein the total solids content of the ink is at least 4.0 wt% and which is substantially free of cyclohexanone and derivatives thereof.
2. A coloured ink according to claim 1, which comprises colourant at a level of at least 3.0 wt%, preferably at least 3.5 wt%, more preferably at least 3.8 wt%, and most preferably at least 4.0 wt%.
3. A coloured ink according to claim 1 or claim 2, wherein the total solids content of the ink is less than 20 wt%, preferably less than 18 wt%, more preferably less than 16 wt%, and most preferably less than 14 wt%.
4. A coloured ink according to any one of the preceding claims, which comprises at least 70 wt% of the slow drying liquid carrier.
5. A coloured ink according to any one of the preceding claims, which is suitable for use in inkjet printing.
6. A method of printing onto a substrate, the method comprising the step of applying an ink according to any one of the preceding claims onto a surface of the substrate, in a sufficient amount to form a visible image.
7. A method according to any one of claim 6, which comprises a "single pass" inkjet printing technique.
8. A method according to claim 6 or claim 7, wherein the substrate is a wall covering, preferably a wallpaper.
9. A method according to any one of claims 6 to 8, wherein the substrate is flexible and may be formed into a roll.

10. A method according to claim 9, wherein a roll of substrate is fed into a printing apparatus and prints onto the substrate in a substantially continuous, automated process.
- 5 11. A method according to any one of claims 6 to 10, wherein the substrate is pre-heated before printing, to raise the substrate temperature above the ambient temperature.
- 10 12. A method according to claim 11, wherein the pre-heat temperature is at least 25°C, preferably at least 35°C and most preferably at least 45°C.
13. A method according to any one of claims 7 to 12, wherein multiple layers of inkjet ink wet-on-wet are printed onto the substrate.
- 15 14. A method according to claim 13, wherein the total of all wet ink layers is less than 50µm, preferably less than 30µm and most preferably less than 15µm.
- 20 15. A method according to claim 13 or 14, wherein the total of all wet ink layers is less than 50 g/m², preferably less than 30 g/m² and most preferably less than 15 g/m².
- 25 16. A method according to any one of claims 6 to 15, wherein the thickness of the dried ink layer on the substrate is less than 5µm, preferably less than 3µm, and more preferably 1.5µm.
17. A method according to any one of claims 6 to 16, operated at a print speed onto a reel of substrate in excess of 24 metres/minute.
- 30 18. Inkjet printing apparatus comprising a plurality of print heads and at least one ink reservoir comprising an ink according to any one of claims 1 to 5.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2019/051981

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D11/36 C09D11/322 B41M3/18
ADD.

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)
C09D B41M

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 practicable, search terms used)

EPO-Internal, WPI Data

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Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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