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(54) Title: PROCESS FOR INK-JET PRINTING AND COMPOSITIONS FOR INK-JET PRINTING

(57) Abstract: A process for ink-jet printing an image on a substrate comprising applying thereto a composition comprising: (a) a water-dissipatable polyester comprising polyethylene oxide segment(s); (b) pigment; (c) water; and (d) water miscible solvent and a composition comprising a self dispersable pigment or a pigment coated with a dispersant.

PROCESS FOR INK-JET PRINTING AND COMPOSITIONS FOR INK-JET PRINTING

This invention relates to a process for ink-jet printing, compositions for ink-jet printing, substrates printed using the process or composition and to ink-jet printer cartridges.

Ink-jet printing involves printing an image onto a substrate using ink droplets ejected through a fine nozzle onto a substrate without bringing the fine nozzle into contact with the substrate.

There are many demanding performance requirements for colorants and inks used in ink-jet printing. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust which would block the tip of the fine nozzle and impede the printing process. The inks should also be stable to storage over time without decomposing or forming a precipitate which could also block the fine nozzle.

Thermal and piezoelectric ink-jet printers are widely used, thus there is a need for inks, suitable for use in both types of printers, having high colour strength and giving images having a high light-fastness and water-fastness when printed on a typical substrate.

A particular problem for photorealistic quality printing is that of light-fastness. Prints are often exposed to daylight for long periods and there is a need for the image to have as good lightfastness as possible. The use of pigments in this area is perceived to offer enhanced light-fastness but often at the expense of poor physical image durability (rub fastness) and gloss. This invention relates to an ink-jet printing process using pigment formulations which leads to improvements in the light-fastness, gloss and/or rub fastness of ink-jet prints.

According to the present invention there is provided a process for ink-jet printing an image on a substrate comprising applying thereto a composition comprising:

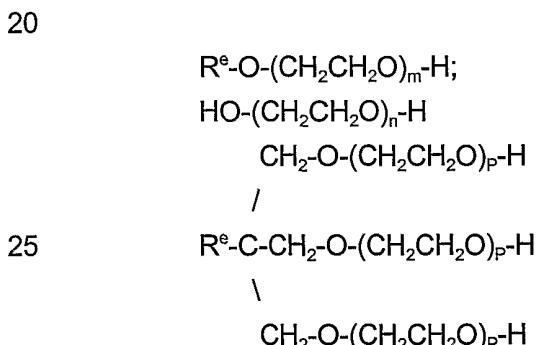
- (a) water-dissipatable polyester comprising polyethylene oxide segment(s);
- (b) pigment;
- (c) water; and
- (d) water miscible solvent.

The water-dissipatable polyester can be prepared using conventional polymerisation procedures known to be effective for polyester synthesis. Thus, it is well known that polyesters contain carbonyloxy (i.e. $-C(=O)-O-$) linking groups and may be prepared by a condensation polymerisation process in which an acid component (including ester-forming derivatives thereof) is reacted with a hydroxyl component. The acid component may be selected from one or more polybasic carboxylic acids, e.g. di- and tri-carboxylic acids or ester-forming derivatives thereof, for example acid halides, anhydrides or esters. The hydroxyl component may be one or more polyhydric alcohols or phenols (polyols), for

desired, a proportion of carbonylamino linking groups -C(=O)-NH- (i.e. amide linking groups) by including an appropriate amino functional reactant as part of the "hydroxyl component"; such as amide linkages. The reaction to form a polyester may be conducted in one or more stages. It is also possible to introduce in-chain unsaturation into the polyester by, for 5 example, employing as part of the acid component an olefinically unsaturated dicarboxylic acid or anhydride.

The polyethylene oxide segments, may be within the polyester backbone (i.e. in-chain incorporation) and/or as chain-pendant or terminal groups. Such groups may act to contribute to the dispersion stability or even water-solubility of the polyester. Their presence 10 in the water dissipatable polyester can allow a much greater range of formulations based on the present invention to be made. In particular water dissipatable polyesters containing these groups may aid the colloidal stability of the composition of the present invention, especially in the presence of polyelectrolytes. The presence of these groups in the water dissipatable polyester can also enable compositions of low viscosity to be made more 15 easily.

Polyethylene oxide chains may be introduced into the polyester during its synthesis by using as part of the hydroxyl component, ethylene oxide-containing mono, di or higher functional hydroxy compounds, especially polyethylene glycols and alkyl ethers of polyethylene glycols, examples of which include:



30 wherein R^e is C_{1-20} -alkyl, preferably C_{1-4} -alkyl, more preferably methyl; m is 1 to 500 (preferably 3 to 50), n is 3 to 500 (preferably 3 to 50); and p is 1 to 100 (preferably 3 to 50).

Alternately the polyethylene oxide chains may be introduced into the polyester during its synthesis by using an amine ended polyethylene glycol such as JeffamineTM M1000 from Huntsman. Most preferably the polyethylene oxide segment(s) is derived from methoxy polyethylene glycol preferably wherein m is in the range from 5 to 50.

35 A small segment of a polyethylene oxide chain could be replaced by a propylene oxide or butylene oxide chain in such non-ionic groups, but should still contain ethylene oxide as a major part of the chain.

40 The polyethylene oxide chain content should preferably not exceed 25% by weight and more preferably should not exceed 15% by weight, based on the total weight of the polyester, in order to avoid unacceptable water-sensitivity. Therefore the water-dissipatable

polyester preferably comprises 0.1 to 25% by weight, more preferably 0.1 to 15% by weight of the polyethylene oxide segment based on the total weight of polyester.

Preferably the water dissipatable polyester further comprises ionised carboxy and/or sulphonate groups.

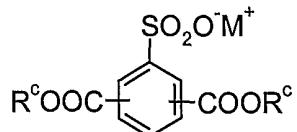
5 Polyesters bearing ionised sulphonate groups may be prepared by using at least one monomer having two or more functional groups which will readily undergo an ester condensation reaction (e.g. carboxyl groups, hydroxyl groups or esterifiable derivatives thereof) and one or more sulphonic acid groups (for subsequent neutralisation after polyester formation) or ionised sulphonate groups (i.e. neutralisation of the sulphonic acid groups already having been effected in the monomer) in the synthesis of the polyester. In some cases it is not necessary to neutralise sulphonic acid groups since they may be sufficiently strong acid groups as to be considerably ionised in water even without the addition of base. Often, the sulphonic acid or ionised sulphonate containing monomer is a 10 dicarboxylic acid monomer having at least one ionised sulphonate substituent thereby avoiding any need to effect neutralisation subsequent to polyester formation. Alternatively, alkyl carboxylic acid ester groups may be used in place of the carboxylic acid groups as 15 ester-forming groups. Such a monomer will therefore be part of the acid component used in the polyester synthesis.

20 Preferred polybasic carboxylic acids which can be used to form the polyester have two or three carboxylic acid groups. For example, one can use C₄ to C₂₀ aliphatic, alicyclic and aromatic compounds having two or more carboxy groups and their ester forming derivatives (e.g. esters, anhydrides and acid chlorides), and dimer acids such as C36 dimer acids. Specific examples include adipic acid, fumaric acid, maleic acid, succinic acid, itaconic acid, sebacic acid, nonanedioic acid, decanedioic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,2-cyclohexane dicarboxylic acid, terephthalic acid, 25 isophthalic acid, phthalic acid and tetrahydrophthalic acid and their acid chlorides. Anhydrides include succinic, maleic, phthalic and hexahydrophthalic anhydrides.

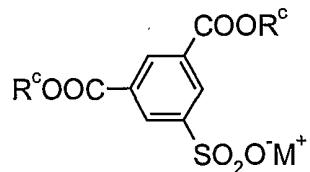
30 Preferred polyols which can be used to form the polyester include those having from 2 to 6, more preferably 2 to 4 and especially 2 hydroxyl groups per molecule. Suitable polyols having two hydroxy groups per molecule include diols such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol (neopentyl glycol), the 1,2-, 1,3- and 1,4-cyclohexanediols and the corresponding cyclohexane dimethanols, diethylene glycol, dipropylene glycol, and diols such as alkoxylated bisphenol A products, e.g. ethoxylated or propoxylated bisphenol A. Suitable polyols having three hydroxy groups per molecule include triols such as trimethylolpropane (1,1,1-tris (hydroxymethyl)ethane). Suitable polyols having four or more hydroxy groups per molecule include pentaerythritol (2,2-bis(hydroxymethyl)-1,3-propanediol) and sorbitol (1,2,3,4,5,6-hexahydroxyhexane).

40 Compounds having two or more groups which readily undergo an ester condensation reaction and have one or more sulphonate groups are dicarboxylic acid

monomers having at least one ionised sulphonate group. Examples of such compounds are aromatic dicarboxylic acids having an ionised sulphonate group, for example those of the formula:



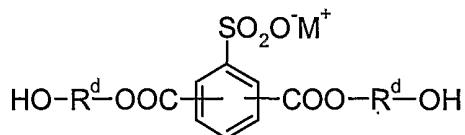
5 wherein M is a cation (preferably sodium, lithium or potassium)-, and each R^c independently is H, a cation or C₁₋₄-alkyl (preferably methyl or ethyl). Preferred compounds of the above formula are of formula:



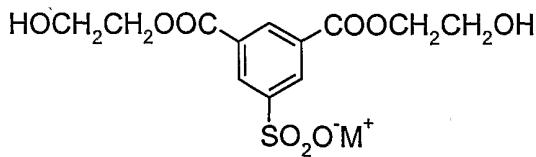
10 wherein M and R^c are as defined above. Particularly preferred is the mono sodium salt (one R^c is H, the other is Na), this material being known as sodio-5-sulphoisophthalic acid (SSIPA).

Other useful compounds which have two or more groups which readily undergo an ester condensation reaction and have one or more sulphonate groups are dihydroxy monomers having at least one sulphonate group, especially those of the formula:

15



wherein M is as hereinbefore defined above and each R^d independently is alkylene, preferably C₂₋₄-alkylene. Preferred compounds of the above formula are:



20

wherein M is as hereinbefore defined.

Polyesters bearing ionised carboxy groups can be prepared by various means. For example, if the hydroxyl component of the reactants is stoichiometrically in excess of the acid component, a hydroxyl-terminated polyester can be formed, which may be subsequently converted to a carboxy terminated polyester by wholly or partially reacting the hydroxyl groups with an appropriate reagent (e.g. an acid anhydride or a dicarboxylic acid). Alternatively, terminal carboxy functionality may be directly introduced by employing an appropriate stoichiometric excess of the acid component reactants. In another alternative, chain-pendant carboxy groups may be introduced by using reagents such as dimethylol

propionic acid (DMPA) since if appropriate reaction condition are employed (e.g. polymerisation temperature below 150°C) the hindered carboxy group thereof does not take part to any significant extent in the ester-forming reactions during the polyester synthesis and the DMPA effectively behaves as a simple diol. Chain-pendant and/or terminal carboxy groups could also be introduced by employing a tri- or higher functionality carboxylic acid or anhydride in the polyester synthesis, for example, trimellitic acid or anhydride. Combinations of the above procedures could also be used. It is thus seen that terminal or side-chain carboxy groups or both can be introduced as desired. These can be fully or partially neutralised with an appropriate base to yield ionised carboxy groups. The counter ions used may be as for the ionised sulphonate groups described above (apart from H⁺ since the carboxylic acid groups themselves are normally insufficiently ionised to provide a significant amount of ionised carboxy groups - although F substituents would increase acid strength), with alkali metal ions such as Na⁺, Li⁺ and K⁺ again being particularly preferred, and ammonium and organic amine derived cations less preferred because some have an undesirable odour.

The amount of ionised sulphonate and/or carboxy groups present in the polyester should be sufficient to provide or contribute to water-dissipatability of the polyester, although it should not be so high as to render the resulting polyester unacceptably water- sensitive. This amount will depend, *inter alia*, on factors such as the hydrophilicity/hydrophobicity of units provided by other monomers in the polyester synthesis or any surfactants (if used), and also the relative proportions of ionised sulphonate/carboxy groups. With regard to the last mentioned point, ionised sulphonate groups are more effective at providing or contributing to water-dissipatability than ionised carboxy groups and so can be used at considerably lower levels in comparison to ionised carboxy groups.

If the polyester is wholly or predominantly sulphonate stabilised (by which is meant the water dissipatability-providing groups are provided wholly or predominately by ionised sulphonate groups). The ionised sulphonate group content is preferably within the range from 7.5 to 100 milliequivalents (more preferably 10 to 75 milliequivalents and particularly 11 to 56 milliequivalents) per 100 g of polyester. When using SSIPA as the monomer for providing the ionised sulphonate groups, the amount of this monomer used in the polyester synthesis, based on the weight of all the monomers used in the polyester synthesis, will usually be within the range from 2 to 20% by weight (more usually 3 to 15% by weight). The carboxylic acid value (AV) of the polyester which is predominantly sulphonate stabilised, i.e. an AV based on the carboxylic acid groups only (i.e. excluding sulphonate groups) will generally be within the range of from 0 to 100 mgKOH/g, more preferably 0 to 50 mgKOH/g, especially 0 to 25 mgKOH/g, more especially 0 to 10 mgKOH/g.

If the polyester is predominantly stabilised by ionised carboxy groups, the carboxylic acid value AV of the polyester is preferably within the range of from 20 to 140 mgKOH/g (more preferably 30 to 100 mgKOH/g).

Usually, the polyester is either predominantly sulphonate-stabilised or predominantly carboxylate stabilised (preferably the former).

The water-dissipatable polyester preferably has a number average molecular weight (ie) Mn of up to 30,000. The Mn is preferably in the range from 500 to 30,000, more preferably 1,000 to 25,000, especially 2,000 to 20,000. These Mn lead to particularly good storage stability for the resultant inks. The measurement of Mn is well known to those skilled in the art, and may for example be effected using gel permeation chromatography in conjunction with a standard polymer such as polystyrene or polymethylmethacrylate of known molecular weight.

The water-dissipatable polyester preferably has a hydroxyl number of from 0 to 225mg KOH/g, more preferably 0 to 125mg KOH/g, especially from 0 to 50mgKOH/g. In alternative embodiments the hydroxyl number is from 10 to 350mg KOH/g or 10 to 200mg KOH/g.

The Tg of the water-dissipatable polyester (i.e. the temperature at which the polymer changes from a glassy, brittle state to a plastic, rubbery state) is preferably in the range -38°C to 105°C, more preferably -20 to 70°C, especially -10°C to 60°C.

The esterification polymerisation processes for making the polyesters for use in invention composition are known and need not be described here in more detail. Suffice to say that they are normally carried out in the melt using catalysts, for example a tin- based catalyst, and with the provision for removing any water or alcohol formed from the condensation reaction.

The water-dissipatable polyester may be dissipated in water by adding the solidified melt directly into water. The solidified melt is preferably in a form such as flake (which can often be obtained directly from the melt) or comminuted solid (obtained for example by grinding). Alternatively, water can be added directly to the hot polyester melt until the desired solids content/viscosity is reached. Still further, the polyester may be dissipated in water by adding an aqueous pre-dissipation (or organic solvent solution) of the polyester to the water phase.

The water-dissipatable polyesters normally do not need an external surfactant when being dissipated into water, although such surfactants may be used to assist the dissipation if desired and in some cases can be useful in this respect because additional surfactants reduce the required amount of dissipating groups (i.e. sulphonate, and polyethylene oxide chains).

The water-dissipatable polyester may also be formed by performing free radical polymerisation of olefinically unsaturated monomers in the presence of a polyester. This gives what could be called a polyester-acrylic hybrid. Olefinically unsaturated monomers which can be used include olefinically unsaturated carboxy functional monomers, e.g. acrylic acid, methacrylic acid, fumaric acid, itaconic acid and β -carboxyethyl acrylate; olefinically unsaturated monomers which are free from carboxy and hydroxy groups, e.g. 1,3-butadiene, isoprene, styrene, vinylidene halides, vinylidene esters and esters of acrylic acid and

methacrylic acid, e.g. methyl (meth) acrylate, ethyl (meth)acrylate n-butyl (meth)acrylate and 2-ethyl hexyl (meth)acrylate; and olefinically unsaturated monomers having a hydroxy group e.g. N-methylol (meth)acrylamide and hydroxy C₂₋₈-alkyl esters of (meth)acrylic acid. If the polyester has been prepared using a component which has unsaturation therein, e.g. 5 fumaric acid, maleic acid or muconic acid or allyl-containing dihydroxy or dicarboxy compounds, the product from the polyesterification reaction will have unsaturation incorporated into its structure which can take part in the free radical polymerisation to give a graft copolymer. The free radical polymerisation processes use a free-radical generating initiator system such as (for example) the redox radical initiator system tertiary 10 butylhydroxide/isoascorbic acid and will take place in the aqueous phase, rather than in the melt. However, excessive amounts of acrylic polymer (whether formed in the presence of polyester which has unsaturation or is free from unsaturation) often leads to a deterioration in ink properties and it is preferred that no acrylic polymer is present or, if its is present, the amount is less than 40%, preferably less than 30%, more preferably less than 10% by 15 weight relative to the weight of polyester.

Preferably the polyester is free from urethane groups.

The pigment (component (b)) is preferably a water-insoluble colorant, preferably inorganic or more preferably organic. Preferred inorganic pigments include titanium dioxide, zinc oxide, zirconium oxide, chromium oxide, iron oxide and combinations thereof.

Preferred organic pigments include phthalocyanine, anthraquinone, perinone, 20 indigoid, perylene, azo, carbon black, carbon black pigments carrying ionic groups, azomethine, condensed ring pigments and pigments as mentioned in the Colour Index International, Third Edition (1982) Pigments and Solvent dyes, pages 10 to 143, which are incorporated herein by reference thereto. Preferred pigments are yellow, red, orange, green, 25 violet, indigo, white, blue, or black organic and/or inorganic pigments. In particular it has been found that when using a coloured pigment (ie not black) the light-fastness of prints prepared using the inks is greatly improved. This improvement is particularly noticeable with coloured inorganic and/or organic pigments other than black pigments, for example yellow, red, orange, green, violet, indigo and blue pigments which tend to have lower light-fastness 30 than black pigments.

When used in ink-jet printing the particle size of the pigment is important in achieving an acceptable ink. Thus, it is preferred that the pigment has a mean particle size of from about 5 to 500 nm, more preferably of from 5 to 200 nm. However particle sizes outside of this range may be used, depending on the diameters of the ink-jet printer nozzle.

35 The pigment is preferably either a self dispersable pigment or a pigment coated with a dispersant.

Preferably the pigment carries ionic groups on its surface, for example anionic and/or 40 cationic groups. The anionic groups preferably comprise carboxylic, sulphonic or phosphonic acid groups. The cationic groups preferably comprise a quaternary ammonium groups. Pigment dispersions of this type are marketed by Rohm and Haas under the Acryjet

trademark, for example AcryJet™ black-357, orange-57, magenta-127, yellow-1547, green-367, cyan-157 and yellow-747.

An alternative approach to obtaining stable dispersions is to use an external stabilising agent.

5 The pigment used in the composition of the present invention optionally comprises a mixture of two or more pigments. Pigments are present in any effective amount in the composition, preferably from 0.1 to 20 percent, more preferably 0.1 to 10 percent, especially 0.1 to 5 percent by weight of the composition.

10 Suitable water-miscible organic solvents include methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, isobutanol, dimethylformamide, dimethylacetamide, acetone, diacetone alcohol, tetrahydrofuran, dioxane, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol, diethylene glycol, thiodiglycol, polyethylene glycol, polypropylene glycol, glycerol, 1,2,6-hexanetriol, 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy) ethanol, 2-(2-butoxyethoxy)ethanol, 3-butoxypropan-1-ol, 2-[2-(2-methoxyethoxy)-ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-ethanol, optionally substituted pyrrolidones, sulpholane and mixtures containing two or more of the aforementioned water-miscible organic solvents. Preferred water-miscible organic solvents are tetrahydrofuran, dioxane, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol, glycerol, optionally 15 substituted pyrrolidones, and sulpholane.

15

20 Preferably the water miscible solvent comprises a mixture of 2 or more, especially from 2 to 8, water miscible solvents.

25 The compositions according to the present invention may be prepared by combining components (a), (b), (c) and (d) in any order or simultaneously. Suitable combining techniques are well known in the art, for example agitation, grinding, milling, ultrasonication and/or stirring of all the components. Preferably components (a), (b), (c) and (d) are combined together under conditions which retain stability and avoid flocculation. The preferred pH of the composition is from 5 to 11, more preferably of from 5.5 to 8.

30 Preferably the composition comprises:

- (i) from 0.1 to 20 parts, more preferably 0.1 to 10 parts, especially 0.1 to 5 parts of component (a);
- (ii) from 0.1 to 20 parts, more preferably 0.1 to 10 parts, especially 0.1 to 5 parts of component (b);
- (iii) from 0.1 to 99.7 parts, more preferably 40 to 90 parts, especially 60 to 80 parts of component (c); and
- (iv) from 0.1 to 99.7 parts, more preferably 10 to 60 parts, especially 20 to 40 parts of component (d);

35 wherein all the parts are by weight and the parts by weight of (i) + (ii) + (iii) +(iv) add up to 100.

In addition to components (a), (b) (c) and (d) the composition optionally contains other components, such as a biocide, for example Proxel GXL (Proxel is a trade mark of Avecia Limited) or Kathon (Kathon is a trade mark of Rohm and Haas), a fungicide, a rheological agent, e.g. a wax (e.g. beeswax), a clay (e.g. bentonite), an IR absorber, or a fluorescent brightener, for example C.I.Fluorescent Brightener 179 and/or UV absorber, for example hydroxy phenylbenzotriazole. Furthermore the compositions optionally contain a surface active agent, wetting agent and/or an emulsifier, for example those described in McCutcheon's Emulsifiers and Detergents 1996 International Edition or in Surfactants Europa 3rd Edition 1996 each of which is incorporated herein by reference. Dyes may also be added to the composition if desired to alter the shade.

Preferably the composition is free from water immiscible solvents, it is especially preferred that the composition is free from benzyl alcohol.

The viscosity of the composition is preferably less than 100cp, more preferably less than 50cp, especially less than 20cp, more especially less than 15cp and most preferably less than 10cp at 20°C.

Preferably the composition has been filtered through a filter having a mean pore size below 10 mm, preferably below 5 mm, more preferably below 2 mm, especially below 0.5 mm. In this way particulate matter is removed which could otherwise block fine nozzles in an ink-jet printer.

The composition preferably has a total concentration of divalent and trivalent metal ions, other than those bound to the pigment, below 5000, more preferably below 1000, especially below 100, more especially below 20 parts per million by weight relative to the total weight of the composition. Pure compositions of this type may be prepared by using high purity ingredients and/or by purifying the composition after it has been prepared.

Suitable purification techniques are well known, for example ultrafiltration, reverse osmosis, ion exchange and combinations thereof.

In view of the preferences above, a preferred composition has the following characteristics;

- i) a viscosity less than 100 cp at 20°C;
- ii) the composition has been filtered through a filter having a mean pore size below 10 µm; and
- iii) a total concentration of divalent and trivalent metal ions, other than those bound to the pigment, below 5000 parts per million by weight relative to the total weight of the composition.

Preferably the composition is an ink or liquid dye concentrate, more preferably an ink suitable for use in an ink-jet printer.

These compositions have the advantage that they are suitable not only for the use in piezoelectric ink-jet printers but also in thermal and continuous ink-jet printers. Such compositions form discrete droplets on the substrate with little tendency for diffusing. Consequently sharp images with excellent print quality and little if any bleed between colours

printed side by side can be obtained. Furthermore the compositions show good storage stability, wet- and light- fastness, good gloss and rub resistance.

The ink-jet printer preferably applies the composition to the substrate in the form of droplets which are ejected through a small nozzle onto the substrate. Preferred ink-jet printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet printers, programmed pulses of heat are applied to the compositions in a reservoir by means of a resistor adjacent to the nozzle, thereby causing the compositions to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the nozzle. In piezoelectric ink-jet printers the oscillation of a small crystal causes ejection of the compositions from the nozzle. In WO 00/48938 and WO 00/55089 a new form of piezoelectric technology is described where ink is ejected from an ink ejection nozzle chamber utilizing an electromechanical actuator connected to a paddle or plunger which moves towards the ejection nozzle of the chamber for the ejection of drops of ink from the ejection nozzle chamber.

The substrate is preferably a paper, plastic, or textile material, more preferably a paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid, alkaline or neutral character. Most preferably the substrate is a coated paper.

A second aspect of the invention provides a composition comprising:

- (a) a water-dissipatable polyester comprising polyethylene oxide segment(s);
- (b) a self dispersable pigment or a pigment coated with a dispersant;
- (c) water; and
- (d) water miscible solvent.

The water-dissipatable polyester comprising polyethylene oxide segment(s) (component (a)) is preferably prepared as described in the first aspect of the invention.

Preferred water-dissipatable polyesters are those preferred in the first aspect of the invention.

The self-dispersable pigment or pigment coated with a dispersant pigment (component (b)) may be an inorganic or organic pigment able to disperse on mixing in liquid without the addition of any additional dispersing agents. Additional dispersing agents can be optionally added to improve the dispersability of the pigment.

Preferred pigment types are those preferred in the first aspect of the invention.

Preferably the self dispersable pigment or pigment coated with a dispersant carries ionic groups on its surface, for example anionic and/or cationic groups. The anionic groups preferably comprise carboxylic, sulphonic or phosphonic acid groups. The cationic groups preferably comprise a quaternary ammonium groups. Pigments coated with dispersant are marketed by Rohm and Haas under the Acryjet trademark, for example AcryJet™ black-357, orange-57, magenta-127, yellow-1547, green-367, cyan-157 and yellow-747. Self dispersable pigments are marketed by Cabot under the CAB-O-JET™ trademark, for

example CAB-O-JET™ IJX 266D, CAB-O-JET™ IJX 273B, CAB-O-JET™ IJX 318, CAB-O-JET™ IJX 157.

When used in ink-jet printing the particle size of the pigment is important in achieving an acceptable ink. Thus, it is preferred that the pigment has a mean particle size of from about 5 to 500 nm, more preferably of from 5 to 200 nm. However particle sizes outside of this range may be used, depending on the diameters of the ink-jet printer nozzle.

Preferred water miscible solvents are as in the first aspect of the invention.

Preferably the water miscible solvent comprises a mixture of 2 or more, especially from 2 to 8, water miscible solvents.

The compositions according to the second aspect of the invention may be prepared by combining components (a), (b), (c) and (d) in any order or simultaneously. Suitable combining techniques are well known in the art, for example agitation, grinding, milling, ultrasonication and/or stirring of all the components. Preferably components (a), (b), (c) and (d) are combined together under conditions which retain stability and avoid flocculation. The preferred pH of the composition is from 5 to 11, more preferably of from 5.5 to 8.

Preferably the composition of the second aspect of the invention comprises:

- (i) from 0.1 to 20 parts, more preferably 0.1 to 10 parts, especially 0.1 to 5 parts of component (a);
- (ii) from 0.1 to 20 parts, more preferably 0.1 to 10 parts, especially 0.1 to 5 parts of component (b);
- (iii) from 0.1 to 99.7 parts, more preferably 40 to 90 parts, especially 60 to 80 parts of component (c); and
- (iv) from 0.1 to 99.7 parts, more preferably 10 to 60 parts, especially 20 to 40 parts of component (d);

wherein all the parts are by weight and the parts by weight of (i) + (ii) + (iii) +(iv) add up to 100.

In addition to components (a), (b) (c) and (d) the composition of the second aspect of the invention optionally contains other components, such as a biocide, for example Proxel GXL (Proxel is a trade mark of Avecia Limited) or Kathon (Kathon is a trade mark of Rohm and Haas), a fungicide, a rheological agent, e.g. a wax (e.g. beeswax), a clay (e.g. bentonite), an IR absorber, or a fluorescent brightener, for example C.I.Fluorescent Brightener 179 and/or UV absorber, for example hydroxy phenylbenzotriazole. Furthermore the compositions optionally contain a surface active agent, wetting agent and/or an emulsifier, for example those described in McCutcheon's Emulsifiers and Detergents 1996 International Edition or in Surfactants Europa 3rd Edition 1996 each of which is incorporated herein by reference. Dyes may also be added to the composition if desired to alter the shade.

Preferably the composition of the second aspect of the invention is free from water immiscible solvents, it is especially preferred that the composition is free from benzyl alcohol.

Preferably the composition used in the process of the first aspect of the present invention and the composition according to the second aspect of the present invention is free from polyurethanes.

5 The viscosity of the composition of the second aspect of the invention is preferably less than 100cp, more preferably less than 50cp, especially less than 20cp, more especially less than 15cp and most preferably less than 10cp at 20°C.

10 Preferably the composition of the second aspect of the invention has been filtered through a filter having a mean pore size below 10 mm, preferably below 5 mm, more preferably below 2 mm, especially below 0.5 mm. In this way particulate matter is removed which could otherwise block fine nozzles in an ink-jet printer.

15 The composition of the second aspect of the invention preferably has a total concentration of divalent and trivalent metal ions, other than those bound to the pigment, below 5000, more preferably below 1000, especially below 100, more especially below 20 parts per million by weight relative to the total weight of the composition. Pure compositions of this type may be prepared by using high purity ingredients and/or by purifying the composition after it has been prepared.

Suitable purification techniques are well known, for example ultrafiltration, reverse osmosis, ion exchange and combinations thereof.

20 In view of the preferences above, a preferred composition of the second aspect of the invention has the following characteristics;

i) a viscosity less than 100 cp at 20°C;

ii) the composition has been filtered through a filter having a mean pore size below 10 µm; and

25 iii) a total concentration of divalent and trivalent metal ions, other than those bound to the pigment, below 5000 parts per million by weight relative to the total weight of the composition.

Preferably the composition of the second aspect of the invention is an ink or liquid dye concentrate, more preferably an ink suitable for use in an ink-jet printer.

30 The compositions according the invention have the advantage that they are suitable not only for the use in piezoelectric ink-jet printers but also in thermal and continuous ink-jet printers. Such compositions form discrete droplets on the substrate with little tendency for diffusing. Consequently sharp images with excellent print quality and little if any bleed between colours printed side by side can be obtained. Furthermore the compositions show good storage stability, wet- and light- fastness, good gloss and rub resistance and fastness to both acidic and alkaline highlighter pens.

35 A third aspect of the present invention provides a substrate, especially paper, overhead projector slide, textile material, plastic, glass and metal printed with a composition as described in the second aspect of the invention or by means of a process as described in the first aspect of the invention.

A fourth aspect of the present invention provides an ink-jet printer cartridge comprising a chamber and a composition wherein the composition is in the chamber and the composition is as described in the first and second aspects of the present invention.

The invention will now be described by example only. All parts and percentages are 5 by weight unless specified otherwise.

Example 1

Preparation of Water-Dissipatable Polyester

Monomer	Abbreviation	Weight (g)
Stage 1		
Diethylene glycol	A	273.6
Neopentyl glycol (100%)	B	725
5-Sodiosulphoisophthalic acid	C	432
Isophthalic acid	D	850
Fastcat 4101	E	3
Sodium acetate	F	8
Water	G	11.5
1,6 Hexanediol	H	400
Methoxy polyethylene glycol 750	I	400
Stage 2		
Isophthalic acid	J	1025
Fastcat 4101	K	1

10

Stage 1

A reactor was assembled with agitator, condenser and nitrogen sparge. The reactor was sparged with nitrogen and charged with reactants A to I. The reaction temperature was raised to 170°C and stirring was commenced as soon as the reactants allowed. At about 15 170°C the reaction commenced and the column head temperature was maintained at 100°C by gradually increasing the reactor temperature (at a rate of about 10°C/30 mins) from 170°C to 230°C. The reaction temperature was maintained at 230°C until the column head temperature was seen to decrease and the acid value was <3 mg(KOH)g⁻¹. The hydroxy value was checked and found to be 280 +/- 5 mg(KOH)g⁻¹.

20

Stage 2

The reactor was allowed to cool to 120°C and components J and K were added in a molten form. The reaction temperature was raised to 200°C with stirring and the column head temperature was maintained at 100°C by gradually increasing the reactor temperature 25 from 200°C to 230°C. When the column head temperature began to fall vacuum was

applied and maintained, the reaction mixtures acid value and viscosity being sampled occasionally (braking the vacuum with nitrogen) until the desired end point was achieved. The final material is a solid resin with the following properties.

Acid value mgHOH/g (dichloromethane)	10
Hydroxyl value mgKOH/g	7.4
ICI C/P melt Viscosity (Poise)	
125°C	>500
150°C	>500
165°C	260
185°C	120
200°C	68
Onset Tg/C	25

5

Example 2

Two sets of yellow, magenta and cyan ink-jet inks were produced based on the AcryJet^R 10 range of pigment dispersions. The sets differed in that one set contained the polyester resin of Example 1.

Table 1 Ink Formulations

Components	Without Resin (wt %)	With Resin (wt %)
Pigment	3	3
Butyl Glycol	10	10
2-Pyrolidone	4	4
Glycerol	10	10
Surfynol 465	1	1
Polyester of Example 1	0	2
Water	72	70

15

Pigments: AcryJet^R 122 Magenta

AcryJet^R 747 Yellow

AcryJet^R 157 Cyan

20

All Inks were filtered through a 0.45-micron filter and printed as individual block prints on a range of media types using an Epson 660 printer. The prints were split in two. One half was kept in the dark and the other half was exposed for 100 hours in an Atlas Ci 5000 Weatherometer with a B10092 - 3000Watt Water Cooled Long Arc Xenon Lamp and

borosilicate inner and a soda lime outer filers at 16°C and a relative humidity of 40%. These conditions simulate exposure behind window glass in continuous light.

Light fastness was determined by measuring the difference in absorption of the print kept in the dark and that exposed in the Weatherometer (ΔE). The results are shown in
5 Table 2 below

Table 2 Light Stability

Media	Light Stability ΔE after 100 Hours		
	Xerox 4024 Plain Paper	Epson Glossy Film	Epson Photo Paper
Magenta no polyester	5.7	6.4	5.9
Magenta + Polyester	1.7	0.8	3.2
Yellow no polyester	5.9	7.2	4.8
Yellow + Polyester	0.7	1.3	2
Cyan no polyester	5.2	9.5	4.9
Cyan + Polyester	3.6	1.7	3.3

10 The greater the change in optical density (ΔE) after 100 hours exposure the poorer the light fastness of the prints. Thus, the presence of the polyester in all three inks improved the light fastness of all three inks on three different media.

Example 3

15 The inks of Example 2 were block printed on to Epson Glossy Film and left to dry. Rub resistance was determined by applying a thumb to print and smearing sideways. Good equates to no transfer or limited transfer of ink to the unprinted area and poor equates to a significant transfer.

20 Table 3 Rub Resistance and Gloss

Epson Glossy Film	Rub Resistance	Gloss - angle of incident light		
		20°	60°	85°
Magenta (AcryJet® 122)	Poor	30	45	60
Magenta + Polyester	Good	45	65	93
Yellow (AcryJet® 747)	Poor	22	47	64
Yellow + Polyester	Good	46	50	91
Cyan (AcryJet® 157)	Poor	28	49	62
Cyan + Polyester	Good	48	52	91

The rub resistance and gloss of those inks comprising the water dissipatable polyester was superior to inks lacking the polyester.

Example 4

5

Two sets of yellow, magenta, cyan and black ink-jet inks were produced based on the CAB-O-JET™ range of functionalised self dispersable coloured pigments. The sets differed in that one set contained the polyester of Example 1.

10 Table 4 Ink Formulations

Components	All Components As Weight % Solid							
CAB-O-JET™ IJX 266D Magenta	4				4			
CAB-O-JET™ IJX 273B Yellow		3				3		
CAB-O-JET™ IJX 318 Cyan			3				3	
CAB-O-JET™ IJX 157 Black				4				4
Butyl Glycol	10	10	10	10	10	10	10	10
2-Pyrolidone	4	4	4	4	4	4	4	4
Glycerol	10	10	10	10	10	10	10	10
Surfynol 465	1	1	1	1	1	1	1	1
Polyester	0	0	0	0	5	5	5	5
Water	71	72	72	71	66	67	67	66

15 All Inks were filtered through a 0.45-micron filter and printed as individual block prints on Epson Semi Glossy Photo Paper using an Epson 900 printer. The prints were split in two. One half was kept in the dark and the other half was exposed for 24 hours to 1 ppm ozone at 40°C and 50% relative humidity using a Hampden Test Equipment Ozone Model 903.

20 Ozone Resistance was determined by measuring the difference in absorption of the print kept in the dark and that exposed to the ozone (ΔE). The results are shown in Table 5 below.

Table 5 Ozone Resistance

Pigment Ink Colour	ΔE 24 Hours Ozone No Polyester	ΔE 24 Hours Ozone With Polyester
Magenta 266D	3.9	1.5
Yellow 273B	1.7	0.4
Cyan 318	10.7	1.8
Black 157	0.7	0.7

5 The greater the change in optical density (ΔE) after exposure to ozone the poorer the ozone resistance of the prints. Thus magenta, yellow and cyan inks comprising the polyester displayed better ozone resistance than the corresponding inks lacking a water dissipatable polyester.

Claims

1. A process for ink-jet printing an image on a substrate comprising applying thereto a composition comprising:
 - 5 (a) water-dissipatable polyester comprising polyethylene oxide segment(s);
 - (b) pigment;
 - (c) water; and
 - (d) water miscible solvent.
- 10 2. A process according to claim 1 wherein the water dissipatable polyester comprises 0.1 to 25% by weight of the polyethylene oxide segment based on the total weight of polyester.
- 15 3. A process according to claim 1 or claim 2 wherein the water dissipatable polyester further comprises ionised carboxy and/or sulphonate groups.
4. A process according to any one of the preceding claims wherein the water dissipatable polyester comprising polyethylene oxide segment(s) comprises polyethylene oxide segment(s) derived from methoxy polyethylene glycol.
- 20 5. A process according to anyone of the preceding claims wherein the water-dissipatable polyester comprising polyethylene oxide segment(s) has a Mn of up to 30,000.
- 25 6. A process according to any one of the preceding claims wherein the pigment is selected from yellow, red, orange, green, violet, indigo, white, blue, or black organic and/or inorganic pigment.
7. A process according to any one of the preceding claims wherein the pigment is a self dispersable pigment or a pigment coated with a dispersant.
- 30 8. A process according to any one of the preceding claims wherein the composition has a total concentration of divalent and trivalent metal ions, other than those bound to the pigment, below 5000 parts per million by weight relative to the total weight of the composition.
- 35 9. A process according to any one of the preceding claims wherein the composition has a viscosity less than 100 cp at 20°C.
- 40 10. A process according to any one of the preceding claims wherein the composition has the following characteristics:

(i) a viscosity less than 100 cp at 20°C;

(ii) the composition has been filtered through a filter having a mean pore size below 10 μ m; and

(iii) a total concentration of divalent and trivalent metal ions, other than those associated with the pigment, below 5000 parts per million by weight relative to the total weight of the composition.

11. A process according to any one of the preceding claims wherein the composition comprises:

(i) from 0.1 to 20 parts of component (a);

(ii) from 0.1 to 20 parts of component (b);

(iii) from 0.1 to 99.7 parts of component (c);

(iv) from 0.1 to 99.7 parts of component (d);

wherein all the parts are by weight and the parts by weight of (i) + (ii) + (iii) + (iv) add up to 100.

12. A composition comprising:

(a) a water-dissipatable polyester comprising polyethylene oxide segment(s);

(b) a self dispersable pigment or a pigment coated with a dispersant;

(c) water; and

(d) water miscible solvent.

13. A composition according to claim 12 wherein the water dissipatable polyester comprises 0.1 to 25% by weight of the polyethylene oxide segment based on the total weight of polyester.

14. A composition according to claim 12 or claim 13 wherein the water dissipatable polyester further comprises ionised carboxy and/or sulphonate groups.

15. A composition according to any one of claims 12 to 14 wherein the water dissipatable polyester comprising polyethylene oxide segment(s) comprises polyethylene oxide segment(s) derived from methoxy polyethylene glycol.

16. A composition according to anyone of claims 12 to 15 wherein the water-dissipatable polyester comprising polyethylene oxide segment(s) has a Mn of up to 30,000.

17. A composition according to any one of claims 12 to 16 wherein the pigment is selected from yellow, red, orange, green, violet, indigo, white, blue, or black organic and/or inorganic pigment.

18. A composition according to any one of claims 12 to 17 wherein the pigment carries ionic groups on its surface.

19. A composition according to any one of claims 12 to 18 wherein the composition has 5 a total concentration of divalent and trivalent metal ions, other than those bound to the pigment, below 5000 parts per million by weight relative to the total weight of the composition.

20. A composition according to any one of claims 12 to 19 wherein the composition has a 10 viscosity less than 100 cp at 20°C.

21. A composition according to any one of claims 12 to 20 wherein the composition has the following characteristics:

- (i) a viscosity less than 100 cp at 20°C;
- (ii) the composition has been filtered through a filter having a mean pore size 15 below 10µm; and
- (iii) a total concentration of divalent and trivalent metal ions, other than those associated with the pigment, below 5000 parts per million by weight relative to the total weight of the composition.

20 22. A composition according to any one of claims 12 to 21 wherein the composition comprises:

- (i) from 0.1 to 20 parts of component (a);
- (ii) from 0.1 to 20 parts of component (b);
- (iii) from 0.1 to 99.7 parts of component (c);
- (iv) from 0.1 to 99.7 parts of component (d);

25 wherein all the parts are by weight and the parts by weight of (i) + (ii) + (iii) + (iv) add up to 100.

30 23. An ink or liquid dye concentrate comprising a composition according to any one of claims 12 to 22.

35 24. A paper, an overhead projector slide, textile material, plastic, glass and metal printed with a composition according to any one of claims 12 to 23 or by means of a process according to any one of claims 1 to 11.

25. An ink-jet printer cartridge comprising a chamber and a composition wherein the composition is in the chamber and the composition is as described in any one of claims 1 to 40 24.

INTERNATIONAL SEARCH REPORT

Inte nal Application No
PCT/GB 01/03355

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/00

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 7 C09D

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)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 98 14524 A (HOLBROOK MARK ;ZENECA LTD (GB); MEYRICK BARRY HUSTON (GB)) 9 April 1998 (1998-04-09) page 1, line 20-30 page 2, line 4-17 page 4, line 3 -page 5, line 13 page 6, line 3-17 page 9, line 27 -page 10, line 12 page 11, line 31 -page 13, line 3 page 14, line 1-14</p> <p>---</p> <p style="text-align: center;">-/--</p>	1-6,11, 24,25

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 October 2001	19/10/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl Fax: (+31-70) 340-3016	Authorized officer Miller, A

INTERNATIONAL SEARCH REPORT

Inte nal Application No
PCT/GB 01/03355

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 977 209 A (MACKINNON DAVID N ET AL) 2 November 1999 (1999-11-02) column 5, line 34 -column 6, line 17 claims 4-15,21-23,32 -----	1,3,6,9, 24,25

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