

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau



(43) International Publication Date  
8 March 2012 (08.03.2012)

(10) International Publication Number  
**WO 2012/030890 A2**

(51) International Patent Classification:

*C09D 11/10* (2006.01)

(21) International Application Number:

PCT/US2011/049851

(22) International Filing Date:

31 August 2011 (31.08.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/378,529 31 August 2010 (31.08.2010) US

(71) Applicant (for all designated States except US): **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BERGE, Charles, T.** [US/US]; 30 Mayhew Avenue, Earleville, MD 21919 (US). **LI, Xiaoqing** [CN/US]; 23 East Periwinkle Lane, Newark, DE 19711 (US).

(74) Agent: **XU, Simon, L**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, DE 19805 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))



**WO 2012/030890 A2**

(54) Title: INK-JET INK COMPRISING CROSS-LINKED PIGMENT DISPERSION AND A POLYMERIC BINDER

(57) Abstract: The present disclosure provides an ink-jet ink containing an aqueous ink vehicle, an aqueous dispersion and a polymeric binder. The aqueous dispersion contains a colorant and a polyurethane dispersant, wherein the polyurethane dispersant is made with a polymer having cross-linkable moieties that are cross-linked with a cross-linking agent.

TITLE

INK-JET INK COMPRISING CROSS-LINKED PIGMENT DISPERSION AND A  
POLYMERIC BINDER

BACKGROUND OF THE INVENTION

5 This application claims priority under 35 U.S.C. §119 from U.S. Provisional Application Serial No. 61/378529, filed August 31, 2010.

This disclosure relates to novel aqueous inkjet inks containing an aqueous vehicle, an aqueous dispersion and a polymeric binder. The aqueous dispersion contains a colorant and a polyurethane dispersant with cross-linkable moieties that are cross-linked with a  
10 cross-linking agent.

Aqueous dispersions of pigment particles are widely used in ink-jet printing. Because a pigment is typically not soluble in an aqueous vehicle, it is often required to use a dispersing agent, such as a polymeric dispersant or a surfactant, to produce a stable dispersion of the pigment in the aqueous vehicle. However, because the pigment is  
15 dispersed in a liquid vehicle, there is a tendency for pigment particles to agglomerate or flocculate while the ink is being stored or while the ink is being used, for example, being printed.

There has been effort in the art directed at improving the stability of pigment dispersions. The effort to improve dispersion stability to date has included improvements  
20 in the processes used to make the dispersions, the development of new dispersants and the exploration of the interaction between dispersants and pigment particles, and between dispersants and aqueous vehicle. While much of the effort has general application at improving dispersion stability, some of that effort has not found utility in particular applications. For example, the pigment dispersions used in ink-jet printing applications  
25 have very unique and demanding requirements. It is critical that ink components comprising pigment dispersion remain stable, not only in storage but also over repeated jetting cycles. It is also desirable that the pigment dispersions offer good durability, good rub-fastness, wet-fastness and highlighter pen fastness.

A need exists for highly stable, higher-quality, better smudge and highlighter smear  
30 inks for ink-jet applications. The present invention satisfies this need by providing an ink containing a binder and a cross-linked pigment dispersion based on a polyurethane dispersant having cross-linkable moieties both pendent to the polymer backbone and

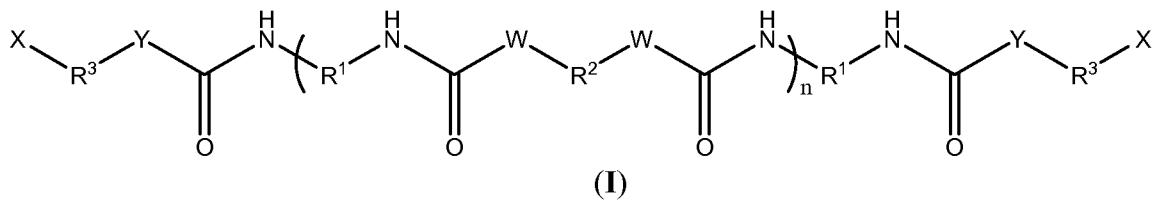
terminal to the polymer chain, and the cross-linking of these moieties with a cross-linking agent.

### SUMMARY OF THE INVENTION

An embodiment of the invention provides an ink-jet ink comprising an aqueous ink vehicle, an aqueous pigment dispersion and a polymeric binder, wherein the aqueous pigment dispersion comprises a colorant and a polyurethane dispersant, and the polymeric binder is non-reactive to the colorant, and wherein the polyurethane dispersant is comprised of a polymer with:

(a) an aqueous dispersing moiety, and

(b) a cross-linkable moiety that is cross-linked with a cross-linking agent, wherein the cross-linkable moiety is pendent to the polymer backbone and terminal to the polymer chain; wherein the polyurethane dispersant comprises at least one compound of the general structure of Formula I:



15

wherein each X is independently OH, SH, COOH or NHR<sup>4</sup>;

each Y is independently O, S or NR<sup>4</sup>;

each W is N, O or S;

each R<sup>1</sup> is independently C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> substituted alkyl, C<sub>6</sub>-C<sub>40</sub> aryl or C<sub>9</sub>-C<sub>40</sub> substituted aryl;

R<sup>2</sup> is comprised of difunctional isocyanate reactants Z<sup>1</sup>, Z<sup>2</sup> and Z<sup>3</sup>, wherein there is at least one Z<sup>1</sup>, at least one Z<sup>2</sup> and at least one Z<sup>3</sup>;

each R<sup>3</sup> is independently C<sub>1</sub>-C<sub>20</sub> alkyl or C<sub>3</sub>-C<sub>20</sub> substituted alkyl;

each R<sup>4</sup> is independently -R<sup>3</sup>-X, H, C<sub>1</sub>-C<sub>20</sub> alkyl or C<sub>3</sub>-C<sub>20</sub> substituted alkyl;

25 n is an integer from 2 to 30;

Z<sup>1</sup> is a difunctional isocyanate reactant substituted with an aqueous dispersing moiety;

Z<sup>2</sup> is a difunctional isocyanate reactant substituted with one or more cross-linkable moieties; and

Z<sup>3</sup> is a polyol with MW less than 3000.

Another embodiment provides that the polymeric binder is one or more members selected from the group consisting of polyurethane, acrylics, styrene acrylics, styrene butadienes, styrene butadiene acrylonitriles, neoprenes, ethylene acrylic acid copolymer, 5 ethylene vinyl acetate, and mixtures thereof.

Another embodiment provides that the cross-linking agent is one or more members selected from the group consisting of epoxide, isocyanate, carbodiimide, *N*-methyol, oxazoline, silane, and mixtures thereof.

Another embodiment provides that Z<sup>1</sup> is a polyol substituted with the aqueous 10 dispersing moiety.

Another embodiment provides that Z<sup>2</sup> is a polyol substituted with one or more cross-linkable moieties.

Another embodiment provides that the aqueous dispersing moiety consists of one or more carboxyl groups.

15 Another embodiment provides that the cross-linkable moiety consists of one or more carboxyl groups.

Another embodiment provides that Y is NR<sup>4</sup>.

Another embodiment provides that the polymeric binder is polyurethane.

Another embodiment provides that X is OH.

20 Another embodiment provides that X is NHR<sup>4</sup>.

Another embodiment provides that R<sup>4</sup> is -R<sup>3</sup>-X and the polymeric binder is polyurethane.

Another embodiment provides that each W is O.

Another embodiment provides that each W is N.

25 Yet another embodiment provides that the mole ratio of the cross-linkable moiety to the cross-linking agent is from 15:1 to 1:1.5.

These and other features and advantages of the present invention will be more readily understood by those of ordinary skill in the art from a reading of the following

Detailed Description. Certain features of the invention which are, for clarity, described above and below as a separate embodiment, may also be provided in combination in a single embodiment. Conversely, various features of the invention that are described in the context of a single embodiment, may also be provided separately or in any subcombination.

5

## DETAILED DESCRIPTION

Unless otherwise stated or defined, all technical and scientific terms used herein have commonly understood meanings by one of ordinary skill in the art to which this invention pertains.

Unless stated otherwise, all percentages, parts, ratios, etc., are by weight.

10

When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

15

When the term “about” is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

20

As used herein, “comprising” is to be interpreted as specifying the presence of the stated features, integers, steps, or components as referred to, but does not preclude the presence or addition of one or more features, integers, steps, or components, or groups thereof. Additionally, the term “comprising” is intended to include examples encompassed by the terms “consisting essentially of” and “consisting of.” Similarly, the term “consisting essentially of” is intended to include examples encompassed by the term “consisting of.”

25

As used herein, the dispersions produced with the polyurethane described above can be utilized to disperse particles, especially pigments for ink-jet inks. These inks can be printed on all normally used ink-jet substrates including textile substrates.

30

As used herein, the term “dispersion” means a two phase system where one phase consists of finely divided particles (often in the colloidal size range) distributed throughout a bulk substance, of the particles being the dispersed or internal phase and the bulk substance being the continuous or external phase.

As used herein, the term “dispersant” means a surface active agent added to a suspending medium to promote uniform and maximum separation of extremely fine solid particles often of colloidal size. For pigments, dispersants are most often polymeric

dispersants. The polyurethane dispersants described herein are in fact dispersions themselves.

As used herein, the term “OD” means optical density.

5 As used herein, the term “aqueous vehicle” refers to water or a mixture of water and at least one water-soluble, or partially water-soluble (i.e. methyl ethyl ketone), organic solvent (co-solvent).

As used herein, the term “ionizable groups,” means potentially ionic groups.

As used herein, the term “substantially” means being of considerable degree, almost all.

10 As used herein, the term “MW” means weight average molecular weight.

As used herein, the term “D50” means the volume particle diameter of the 50th percentile (median) of the distribution of particle sizes.

As used herein, the term ‘D95’ means the volume particle diameter of the 95th percentile of the distribution of particle sizes.

15 As used herein, the term “pendent” means that a substituent is directly attached to the backbone of a polymer or via a linkage of 1 to 10 atoms.

As used herein, the term ‘NCO’ means isocyanate.

As used herein, the term “cPs” means centipoise, a viscosity unit.

20 As used herein, the term “mN.m<sup>-1</sup>” means milliNewtons per meter, a surface tension unit.

As used herein, the term “mPa.s” means millipascal second, a viscosity unit.

As used herein, the term “prepolymer” means the polymer that is an intermediate in a polymerization process, and can be considered a polymer.

25 As used herein, the term “AN” means acid number, mg KOH/gram of solid polymer.

As used herein, the term “PUD” means the polyurethanes dispersions described herein.

As used herein, the term “BMEA” means bis(methoxyethyl)amine.

As used herein, the term “DBTDL” means dibutyltin dilaurate.

30 As used herein, the term “DEA” means diethanolamine.

As used herein, the term “DMPA” means dimethylol propionic acid.

As used herein, the term “HDI” means 1,6-hexamethylene diisocyanate.

As used herein, the term “IPDI” means isophorone diisocyanate.

As used herein, the term “TMDI” means trimethylhexamethylene diisocyanate.

35 As used herein, the term “TMXDI” means m-tetramethylene xylylene diisocyanate.

As used herein, the term "NMP" means n-Methyl pyrrolidone.

As used herein, the term "TDI" means 2,4-toluene diisocyanate.

As used herein, the term "MDI" means 4,4'-diphenylmethane diisocyanate.

As used herein, the term "H<sub>12</sub>MDI" means 4,4'-dicyclohexylmethane diisocyanate.

5 As used herein, the term "TODI" means 3,3'-dimethyl-4,4'-biphenyl diisocyanate.

As used herein, the term "C<sub>12</sub>DI" means dodecane diisocyanate.

As used herein, the term "NDI" means 1,5-naphthalene diisocyanate.

As used herein, the term "IPDI" means isophorone diisocyanate.

10 As used herein, the term "TEB" means triethylene glycol monobutyl ether, a reagent supplied by Dow Chemical.

As used herein, the term "Sulfolane" means tetramethylene sulfone.

As used herein, the term "TRB-2" means Dainichiseika® TRB-2, a cyan pigment.

As used herein, Terathane® 650 is a polyether diol from Invista, Wichita, KS

As used herein, Eternacoll® UH-50 is a polycarbonate diol from UBE Industries,

15 Tokyo, Japan.

As used herein, Denacol® 321 is trimethylolpropane polyglycidyl ether, a cross-linking reagent from Nagase Chemicals Ltd., Osaka, Japan.

Unless otherwise noted, the above chemicals were obtained from Aldrich (Milwaukee, WI) or other similar suppliers of laboratory chemicals.

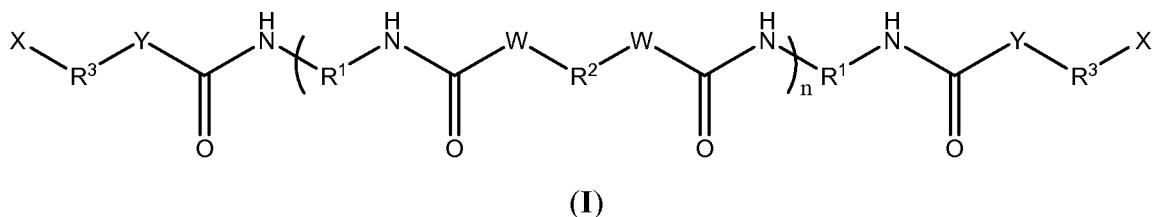
20 In addition, references in the singular may also include the plural (for example, "a" and "an" may refer to one, or one or more) unless the context specifically states otherwise.

### Polyurethane Dispersants

25 Polyurethane polymers are, for the purposes of the present disclosure, polymers wherein the polymer backbone contains urethane linkage derived from the reaction of an isocyanate group (from, e.g., a di- or higher-functional monomeric, oligomeric or polymeric polyisocyanate) with a hydroxyl group (from, e.g., a di- or higher-functional monomeric, oligomeric or polymeric polyol). Such polymers may, in addition to the urethane linkage, also contain other isocyanate-derived linkages such as urea, as well as other types of linkages present in the polyisocyanate components or polyol components

30 (such as, for example, ester and ether linkage).

The polyurethane dispersant of the present invention comprises at least one compound of the general structure of Formula I:



wherein each X is independently OH, SH, COOH or NHR<sup>4</sup>;

each Y is independently O, S or NR<sup>4</sup>;

5 each W is N, O or S;

each R<sup>1</sup> is independently C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> substituted alkyl, C<sub>6</sub>-C<sub>40</sub> aryl or C<sub>9</sub>-C<sub>40</sub> substituted aryl;

R<sup>2</sup> is comprised of difunctional isocyanate reactants Z<sup>1</sup>, Z<sup>2</sup> and Z<sup>3</sup>, wherein there is at least one Z<sup>1</sup>, at least one Z<sup>2</sup> and at least one Z<sup>3</sup>;

10 each R<sup>3</sup> is independently C<sub>1</sub>-C<sub>20</sub> alkyl or C<sub>3</sub>-C<sub>20</sub> substituted alkyl;

each R<sup>4</sup> is independently -R<sup>3</sup>-X, H, C<sub>1</sub>-C<sub>20</sub> alkyl or C<sub>3</sub>-C<sub>20</sub> substituted alkyl;

n is an integer from 2 to 30;

Z<sup>1</sup> is a difunctional isocyanate reactant substituted with an aqueous dispersing moiety;

15 Z<sup>2</sup> is a difunctional isocyanate reactant substituted with one or more cross-linkable moieties; and

Z<sup>3</sup> is a polyol with MW less than 3000.

The key features of the polyurethane dispersant are the cross-linkable moieties that are pendent to the polymer backbone and terminal to the polymer chain. The term

20 “pendent” means that a substituent is directly attached to the backbone of a polymer or via a linkage of between 1 to 10 atoms. Typically, the cross-linkable moieties that are pendent to the polymer backbone reside in the R<sup>2</sup> group of Formula I. Specifically the Z<sup>2</sup> component in R<sup>2</sup> is a polyol substituted with one or more cross-linkable moieties.

Typically these cross-linkable moieties are carboxyl, hydroxyl, amino or mercapto groups.

25 The cross-linkable moieties that are terminal to the polymer chain are represented by the X group in Formula I. These cross-linkable moieties, upon reacting with a cross-linking agent, provide a cross-linked pigment dispersion having superior properties.

The R<sup>2</sup> group in Formula I is comprised of difunctional isocyanate reactants Z<sup>1</sup>, Z<sup>2</sup> and Z<sup>3</sup>, wherein there is at least one Z<sup>1</sup>, at least one Z<sup>2</sup> and at least one Z<sup>3</sup>. This R<sup>2</sup> group

provides the polyurethanes with significant areas of hydrophobic segment which can be effective in dispersing pigments. While not being bound by theory, these areas of hydrophobic segment may be effective as the part of the dispersant that is associated with the pigment surfaces. The polyurethane dispersant must have at least one  $Z^1$ , at least one 5  $Z^2$  and at least one  $Z^3$  to satisfy the requirements that the polyurethane contains an aqueous dispersing moiety, and cross-linkable moieties both pendent to the polymer backbone and terminal to the polymer chain. The blending of  $Z^1$ ,  $Z^2$  and  $Z^3$  in the polyurethane can be in any sequence. In certain circumstances,  $Z^2$  can be the same as  $Z^1$ , and in some other circumstances,  $Z^2$  can be the same as  $Z^3$ , as long as there are cross-linkable moieties, as 10 defined above, on  $Z^2$ . Depending on the sequence of addition during the synthesis of the polyurethane, the  $R^2$  component (combination of  $Z^1$ ,  $Z^2$  and  $Z^3$ ) can be random or in blocks.

#### Difunctional Isocyanate Reactant ( $Z^2$ ) and Polyol ( $Z^3$ )

Often  $Z^2$  and  $Z^3$  are derived from polyolefins that are available from Shell as 15 KRATON LIQUID L and Mitsubishi Chemical as POLYTAIL H. More specifically,  $Z^2$  and  $Z^3$  can be derived from polyester diols, polycarbonate diols, polyestercarbonate diols and polyacrylate diols.

Suitable polyester polyols include reaction products of polyhydric; dihydric 20 alcohols to which trihydric alcohols may optionally be added, and polybasic (typically dibasic) carboxylic acids. Trihydric alcohols are limited to at most about 2 weight % such that some branching can occur but no significant cross-linking would occur, and may be used in cases in which modest branching of the NCO prepolymer or polyurethane is desired. Instead of these polycarboxylic acids, the corresponding carboxylic acid anhydrides, or polycarboxylic acid esters of lower alcohols, or mixtures thereof may be 25 used for preparing the polyesters.

The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic or heterocyclic or mixtures thereof and they may be substituted, for example, by halogen atoms, or unsaturated. The following are mentioned as examples: succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, 1,12-dodecyldioic acid, phthalic acid, isophthalic acid, 30 trimellitic acid, phthalic acid anhydride, tetrahydrophthalic acid anhydride, hexahydrophthalic acid anhydride, tetrachlorophthalic acid anhydride, endomethylene tetrahydrophthalic acid anhydride, glutaric acid anhydride, maleic acid, maleic acid

anhydride, fumaric acid, dimeric and trimeric fatty acids such as oleic acid, which may be mixed with monomeric fatty acids, dimethyl terephthalates and bis-glycol terephthalate.

Typically, polyester diols can be blended with hydroxyl terminated poly(butylene adipate), poly(butylene succinate), poly(ethylene adipate), poly(1,2-propylene adipate),  
5 poly(trimethylene adipate), poly(trimethylene succinate), polylactic acid ester diol and polycaprolactone diol. Other hydroxyl terminated polyester diols are copolyethers comprising repeat units derived from a diol and a sulfonated dicarboxylic acid and prepared as described in U.S. Patent Number 6316586.

Polycarbonates containing hydroxyl groups include those known, such as the  
10 products obtained from the reaction of diols such as propanediol-(1,3), butanediol-(1,4) or hexanediol-(1,6), diethylene glycol, triethylene glycol or tetraethylene glycol, and higher polyether diols with phosgene, diarylcarbonates such as diphenylcarbonate, dialkylcarbonates such as diethylcarbonate, or with cyclic carbonates such as ethylene or propylene carbonate. Also suitable are polyester carbonates obtained from the above-  
15 mentioned polyesters or polylactones with phosgene, diaryl carbonates, dialkyl carbonates or cyclic carbonates.

Polycarbonate diols for blending are optionally selected from the group consisting of polyethylene carbonate diol, polytrimethylene carbonate diol, polybutylene carbonate diol and polyhexylene carbonate.

20 Poly(meth)acrylates containing hydroxyl groups include those common in the art of addition polymerization such as cationic, anionic and radical polymerization and the like. Examples are alpha-omega diols. An example of these type of diols are those which are prepared by a “living” or “control” or chain transfer polymerization processes which enables the placement of one hydroxyl group at or near the termini of the polymer. For  
25 further examples of making these diols, see: U.S. Patent Nos. 6248839 and 5990245.

The MW for the polyols described above is typically less than 5000. Typically the MW for  $Z^3$  (a polyol) is less than 3000.

#### Difunctional Isocyanate Reactant ( $Z^1$ )

30 The difunctional isocyanate reactant  $Z^1$  in Formula I contains an aqueous dispersing moiety that is ionic or ionizable. In the context of this disclosure, the term “isocyanate reactant”, or “isocynate reactive”, is taken to include groups well known to those of ordinary skill in the relevant art to react with isocyanates, and typically include hydroxyl,

primary amino and secondary amino groups. The term “difunctional” means containing two of the isocyanate reactive groups.

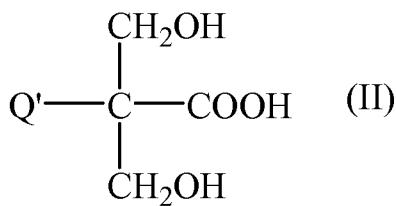
Examples of ionic dispersing groups include carboxylate groups (-COOM), phosphate groups (-OPO<sub>3</sub>M<sub>2</sub>), phosphonate groups (-PO<sub>3</sub>M<sub>2</sub>), sulfonate groups (-SO<sub>3</sub>M), 5 and quaternary ammonium groups (-NR<sub>3</sub>Q), wherein M is a cation such as a monovalent metal ion (e.g., Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, etc.), H<sup>+</sup> or NR<sub>4</sub><sup>+</sup>; Q is a monovalent anion such as chloride or hydroxide; and each R can independently be an alkyl, aralkyl, aryl or hydrogen. These ionic dispersing groups are typically located pendent to the polyurethane backbone.

The ionizable groups in general correspond to the ionic groups, except that they are 10 in the acid (such as carboxyl -COOH) or base (such as primary, secondary or tertiary amine -NH<sub>2</sub>, -NRH, or -NR<sub>2</sub>) form. The ionizable groups are such that they are readily converted to their ionic form during the dispersion/polymer preparation process as discussed below.

With respect to compounds which contain isocyanate reactive groups and ionic or 15 potentially ionic groups, the isocyanate reactive groups are typically amino and hydroxyl groups. The potentially ionic groups or their corresponding ionic groups may be cationic or anionic, although the anionic groups are preferred. Specific examples of anionic groups include carboxylate and sulfonate groups. Examples of cationic groups include quaternary ammonium groups and sulfonium groups.

20 In the case of anionic group substitution, the groups can be carboxylic acid groups, carboxylate groups, sulphonic acid groups, sulphonate groups, phosphoric acid groups and phosphonate groups. The acid salts are formed by neutralizing the corresponding acid groups either prior to, during or after formation of the NCO prepolymer.

Suitable compounds for incorporating carboxyl groups are described in U.S. Patent 25 Nos. 3479310, 4108814 and 4408008. Examples of carboxylic group-containing compounds are the hydroxy-carboxylic acids corresponding to the formula (HO)<sub>p</sub>Q(COOH)<sub>q</sub>, wherein Q is C<sub>1</sub>-C<sub>10</sub> alkyl, p is 1 or 2, and q is 1 to 3. Examples of these hydroxy-carboxylic acids include citric acid, tartaric acid and hydroxypivalic acid. Optional dihydroxy alkanoic acids include the  $\alpha,\alpha$ -dimethylol alkanoic acids represented by 30 the structure of Formula II below :



wherein Q' is hydrogen or C<sub>1</sub>-C<sub>8</sub> alkyl. Additional  $\alpha,\alpha$ -dimethylol alkanoic acids are represented by the structural formula R<sup>5</sup>C-(CH<sub>2</sub>OH)<sub>2</sub>-COOH, wherein R<sup>5</sup> is hydrogen or C<sub>1</sub>-C<sub>8</sub> alkyl. Examples of these ionizable diols include, but are not limited to,

5 dimethylolacetic acid, 2,2'-dimethylolbutanoic acid, 2,2'-dimethylolpropionic acid (DMPA), and 2,2'-dimethylolbutyric acid. Suitable carboxylates also include H<sub>2</sub>N-(CH<sub>2</sub>)<sub>4</sub>-CH(CO<sub>2</sub>H)-NH<sub>2</sub>, and H<sub>2</sub>N-CH<sub>2</sub>-CH<sub>2</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>-CO<sub>2</sub>Na.

Typical sulfonate groups for incorporation into the polyurethanes include diol sulfonates described in U.S. Patent No. 4108814. Suitable diol sulfonate compounds also 10 include hydroxyl terminated copolyethers comprising repeat units derived from the reaction of a diol and a sulfonated dicarboxylic acid. Specifically, the sulfonated dicarboxylic acid is 5-sulfo-isophthalic acid and the diol is 1,3-propanediol. Other suitable sulfonates include the ones represented by formula H<sub>2</sub>N-CH<sub>2</sub>-CH<sub>2</sub>-NH-(CH<sub>2</sub>)<sub>r</sub>-SO<sub>3</sub>Na, wherein r is 2 or 3.

15 When the ionic stabilizing groups are acids, the acid groups are incorporated in an amount sufficient to provide an acid group content for the polyurethane, known by those skilled in the art as acid number (mg KOH per gram solid polymer), of at least 6, typically at least 10, and even more typically 20 milligrams KOH per 1.0 gram of polyurethane. The upper limit for the acid number (AN) is about 120, and typically about 100.

20 Within the context of this disclosure, the term "neutralizing agents" is meant to embrace all types of agents which are useful for converting potentially ionic or ionizable groups to ionic groups. When amines are used as the neutralizing agent, the chain terminating reaction producing the urea termination is typically completed prior to the addition of the neutralizing agent that can also act as an isocyanate reactive group.

25 In order to convert an anionic group to its salt form before, during or after its incorporation into a prepolymer, either volatile or nonvolatile basic materials may be used to form the counterion of the anionic group. Volatile bases are those wherein at least about 90 % of the base used to form the counterion of the anionic group volatilizes under the conditions used to remove water from the aqueous polyurethane dispersions. Nonvolatile

bases are those wherein at least about 90 % of the base does not volatilize under the conditions used to remove water from the aqueous polyurethane dispersions.

Suitable volatile basic organic compounds for neutralizing the potential anionic groups are the primary, secondary or tertiary amines. Examples of these amines are

5 trimethyl amine, triethyl amine, triisopropyl amine, tributyl amine, N,N-dimethyl-cyclohexyl amine, N,N-dimethylstearyl amine, N,N-dimethylaniline, N-methylmorpholine, N-ethylmorpholine, N-methylpiperazine, N-methylpyrrolidine, N-methylpiperidine, N,N-dimethyl-ethanol amine, N,N-diethyl-ethanol amine, triethanolamine, N-methyldiethanol amine, dimethylaminopropanol, 2-methoxyethyldimethyl amine,

10 N-hydroxyethylpiperazine, 2-(2-dimethylaminoethoxy)-ethanol and 5-diethylamino-2-pentanone.

Suitable nonvolatile bases include alkoxides, hydroxides, carbonates or bicarbonates of monovalent metals, especially the alkali metals, lithium, sodium and potassium.

15 When the anionic groups on the polyurethane are neutralized, they provide hydrophilicity to the polymer and better enable it to stably disperse pigment in water. However, it may be desirable to control the degree of neutralization. When the anionic groups on the polyurethane are partially neutralized, the polyurethane becomes more hydrophobic and therefore adsorbs onto the pigment surface. Reducing the amount of the

20 un-adsorbed polymer from the pigment dispersion provides an advantageous condition for the cross-linkable moieties on the polyurethane, adsorbing onto the pigment surface, to react with a cross-linking agent without the competition from cross-linkable moieties on the un-adsorbed polyurethane. Typically the degree of neutralization is from 40 % to 100 %, and more typically from 50 % to 70 %, depending on the acid number of the

25 polyurethane.

#### Capping of the Polyurethane

The capping agent for terminating the polyurethane chain is usually a primary or secondary amine, an alcohol, or a mercapto. In Formula I, the capping agent is shown as a X-R<sup>3</sup>-Y- substituent on the polyurethane.

30 The amount of capping agent employed should be approximately equivalent to the free isocyanate groups in the prepolymer. The ratio of active hydrogens from amine in the capping agent to isocyanate groups in the prepolymer is in the range of from about 1.0:1.0 to about 3.0:1.0, more typically from about 1.0:1.0 to about 1.5:1.0, and still more typically from about 1.0:1.0 to about 1.05:1, on an equivalent basis. Although any isocyanate groups

that are not terminated with an amine can react with other isocyanate reactive functional group or water, the ratios of capping agent to isocyanate group is chosen to ensure a urea termination. Amine termination of the polyurethane is avoided by the choice and amount of capping agent leading to a urea terminated polyurethane. This results in better molecular  
5 weight control and better properties when used as a particle dispersant, and ease in handling when added to formulations.

Any primary or secondary amines substituted with reactive isocyanate groups may be used as chain terminators. Especially useful are aliphatic primary or secondary monoamines, or diamines. Less reactive isocyanate groups such as hydroxyl, carboxyl, and  
10 mercapto could also be used. Examples of amines useful as chain terminators include, but are not restricted to, diethanolamine, monoethanolamine, 3-amino-1-propanol, isopropanolamine, N-ethylethanolamine, diisopropanolamine, 6-aminocaproic acid, 8-aminocaprylic acid, and 3-amino adipic acid. A typical isocyanate reactive chain terminator is diethanolamine. The hydroxyl functionalities on diethanolamine serve as  
15 cross-linking moieties terminal to the polyurethane chain.

#### Polyisocyanate Component

Suitable polyisocyanates are those that contain either aromatic, cycloaliphatic or aliphatic groups bound to the isocyanate groups. Mixtures of these compounds may also be used. If aromatic isocyanates are used, cycloaliphatic or aliphatic isocyanates can be  
20 present as well.

Any diisocyanate useful in preparing polyurethanes via its reaction with polyether glycols, diols or amines can be used in this invention.

Examples of suitable diisocyanates include, but are not limited to, 2,4-toluene diisocyanate (TDI), 2,6-toluene diisocyanate, trimethyl hexamethylene diisocyanate  
25 (TMDI), 4,4'-diphenylmethane diisocyanate (MDI), 4,4'-dicyclohexylmethane diisocyanate (H<sub>12</sub>MDI), 3,3'-dimethyl-4,4'-biphenyl diisocyanate (TODI), dodecane diisocyanate (C<sub>12</sub>DI), m-tetramethylene xylylene diisocyanate (TMXDI), 1,4-benzene diisocyanate, trans-cyclohexane-1,4-diisocyanate, 1,5-naphthalene diisocyanate (NDI), 1,6-hexamethylene diisocyanate (HDI), 4,6-xylylene diisocyanate, isophorone diisocyanate  
30 (IPDI), and combinations thereof.

Small amounts, typically less than about 3 % by weight based on the weight of the diisocyanate, of monoisocyanates or polyisocyanates can be used in a mixture with the diisocyanate. Examples of useful monoisocyanates include alkyl isocyanates such as

octadecyl isocyanate and aryl isocyanates such as phenyl isocyanate. Examples of useful polyisocyanates are triisocyanatotoluene HDI trimer and polymeric MDI.

Cross-linking of Dispersant

The polyurethane dispersants have cross-linkable functional moieties both pendent to the polymer backbone and terminal to the polymer chain. The dispersants are thus capable of reacting with a cross-linking compound. Identified in the table below are suitable cross-linkable functional groups that are in the polymeric dispersant and the companion cross-linking groups that may be present in the cross-linking compound.

Cross-linkable Moieties	Cross-linking Groups
COOH	Epoxide, Carbodiimide, Oxazoline, N-Methanol
Hydroxyl	Epoxide, Silane, Isocyanate, N-Methanol
Amino	Epoxide, Carbodiimide, Oxazoline, N-Methanol

The cross-linkable moieties can be situated at the terminals of the polymer chain (group X in Formula I) or be incorporated into the R<sup>2</sup> group (in Formula I) of the 5 polyurethane dispersant by selection of appropriate Z<sup>2</sup>. Mixtures of these cross-linkable moieties may also be present in the polyurethane dispersant. Useful cross-linking compounds are those which are soluble or insoluble in the aqueous vehicle, including m-tetramethylxylene diisocyanate (TMXDI), isophorone diisocyanate (IPDI), trimethylolpropane polyglycidyl ether, polyglycerol polyglycidyl ether, oxazoline-10 functional polymers, waterborne polycarbodiimide resin, and silane.

The mole ratio of the cross-linkable moiety on the polymer chain to the cross-linking groups on the cross-linking agent is from 15:1 to 1:1.5, typically from 9:1 to 1:1.1, and most typically from 8:1 to 1:1. In calculating the mole ratio, all cross-linkable moieties on the polymer chain and all cross-linking groups on the cross-linking agent are included

15 Colorants

A wide variety of organic and inorganic pigments, alone or in combination, may be dispersed with the polyurethane dispersant to prepare an ink, especially an ink-jet ink. The term "pigment" as used herein means an insoluble colorant that requires to be dispersed with a dispersant and processed under dispersive conditions in the presence of a dispersant.

20 The colorant also includes dispersed dyes. The dispersion process results in a stable dispersed pigment. The pigment used with the inventive polyurethane dispersants does not include self-dispersed pigments. The pigment particles are sufficiently small to permit free flow of the ink through the ink-jet printing device, especially at the ejecting nozzles that usually have a diameter ranging from about 10 micron to about 50 micron. The particle 25 size also has an influence on the pigment dispersion stability, which is critical throughout the life of the ink. Brownian motion of minute particles will help prevent the particles from flocculation. It is also desirable to use small particles for maximum color strength and gloss. The range of useful particle size is typically about 0.005 micron to about 15 micron. Typically, the pigment particle size should range from about 0.005 to about 5 micron and,

most typically, from about 0.005 to about 1 micron. The average particle size as measured by dynamic light scattering is less than about 500 nm, typically less than about 300 nm.

The selected pigment(s) may be used in dry or wet form. For example, pigments are usually manufactured in aqueous media, and the resulting pigments are obtained as a 5 water-wet presscake. In presscake form, the pigment does not agglomerate to the extent like it is in dry form. Thus, pigments in water-wet presscake form do not require as much mixing energy to de-agglomerate in the premix process as pigments in dry form.

Representative commercial dry pigments are listed in U.S. Patent No. 5085698.

Some examples of pigments with coloristic properties useful in inkjet inks include: 10 cyan pigments from Pigment Blue 15:3 and Pigment Blue 15:4; magenta pigments from Pigment Red 122 and Pigment Red 202; yellow pigments from Pigment Yellow 14,

Pigment Yellow 95, Pigment Yellow 110, Pigment Yellow 114, Pigment Yellow 128 and Pigment Yellow 155; red pigments from Pigment Orange 5, Pigment Orange 34, Pigment Orange 43, Pigment Orange 62, Pigment Red 17, Pigment Red 49:2, Pigment Red 112, 15 Pigment Red 149, Pigment Red 177, Pigment Red 178, Pigment Red 188, Pigment Red 255 and Pigment Red 264; green pigments from Pigment Green 1, Pigment Green 2, Pigment Green 7 and Pigment Green 36; blue pigments from Pigment Blue 60, Pigment Violet 3, Pigment Violet 19, Pigment Violet 23, Pigment Violet 32, Pigment Violet 36 and Pigment 20 Violet 38; white pigments such as TiO<sub>2</sub> and ZnO; and black pigment carbon black. The pigment names and abbreviations used herein are the "C.I." designation for pigments established by Society of Dyers and Colourists, Bradford, Yorkshire, UK and published in The Color Index, Third Edition, 1971.

In the case of organic pigments, the ink may contain up to approximately 30 %, typically from 0.1 % to about 25 %, and more specifically from 0.25 % to 10 % of pigment, 25 by weight based on the total ink weight. If an inorganic pigment is selected, the ink will tend to contain higher percentages by weight of pigment than with comparable inks employing organic pigment, since inorganic pigments generally have higher densities than organic pigments.

The polyurethane polymer dispersant is typically present in the range of from 0.1 % 30 to 20 %, and more specifically from 0.2 % to about 10 %, by weight based on the weight of the total ink composition.

### Binder

A binder is a polymeric compound or a mixture of polymeric compounds that is added to the ink formulation. The binder can impart properties to the final printed material

that, for example, gives greater durability to the printed material. Typical polymers used as binders in inkjet inks include polyurethane dispersions and polyurethane solutions, acrylics, styrene acrylics, styrene butadienes, styrene butadiene acrylonitriles, neoprenes, ethylene acrylic acids, ethylene vinyl acetate emulsions, latexes and the like. The binder may be a 5 solution or stabilized as an emulsion by having ionic substituents such as carboxylic acids, sulfur containing acids, amine groups, and other similar ionic groups. Co-stabilizers that are non-ionic in nature, such as those containing polyethyleneoxide, may also be present. Alternatively, the binder may be stabilized by external surfactants.

10 The binder can be used singly or in combination with other binders. Typically, the binder is a polyurethane.

The binder is typically present in an ink in an amount of at least 0.2 % by weight based on the total weight of the ink.

#### Preparation of Polyurethane Dispersant

15 The polyurethane dispersants of the present invention can be prepared by a one-step mixing or a stepwise method. The physical form of the polyurethane prior to its use as a dispersant is an aqueous dispersion. In the one-step mixing process, isocyanate terminated polyurethane is prepared by mixing  $Z^1$ ,  $Z^2$  and  $Z^3$  in a solvent, followed by adding a diisocyanate to the mixture. This reaction is conducted at from about 40 °C to about 100 °C, and typically from about 50 °C to about 90 °C. The ratio of isocyanate to isocyanate 20 reactive groups ( $Z^1$ ,  $Z^2$  and  $Z^3$ ) is from about 1.3:1 to about 1.05:1, and more typically from about 1.25:1 to about 1.1:1. When the targeted percentage of isocyanate content is reached, a primary or secondary amine capping agent is added. The polyurethane solution is then converted to an aqueous dispersion via the addition of de-ionized water under a high shearing operation. Volatile solvent(s), if present, are distilled under reduced pressure.

25 The NCO-functional prepolymers should be substantially linear, and this may be achieved by maintaining the average functionality of the prepolymer starting components at or below 2:1.

30 In the stepwise method, a polyurethane is prepared by dissolving the  $Z^1$  reactant in a solvent, followed by adding a diisocyanate to the mixture. Once the initial percentage of isocyanate content target is reached, the  $Z^2$  and  $Z^3$  components are added. This reaction is conducted at from about 40 °C to about 100 °C, and typically from about 50 °C to about 90 °C. The typical ratio of isocyanate to isocyanate reactive groups is from about 1.3:1 to

about 1.05:1, and more typically from about 1.25:1 to about 1.1:1. Alternately, the  $Z^2$  and  $Z^3$  reactants may be reacted in the first step, and the  $Z^1$  reactant may be added after the initial percentage of isocyanate content target is reached. When the final targeted percentage of isocyanate content is reached, a capping agent is added. The polyurethane 5 solution is then converted to an aqueous polyurethane dispersion via the addition of water under a high shearing operation. Volatile solvent(s), if present, are distilled under reduced pressure.

Catalysts are not necessary for the preparation of the polyurethanes, but may provide advantages in a large scale manufacturing process. The catalysts most widely used 10 are tertiary amines and organo-tin compounds such as stannous octoate, dibutyltin dioctoate and dibutyltin dilaurate.

Preparation of the polyurethane for subsequent conversion to a dispersion is facilitated by using a solvent. Suitable solvents are those that are miscible with water and inert to isocyanates and other reactants utilized in forming the polyurethanes. If it is 15 desired to prepare a solvent-free dispersion, the solvent used should have sufficient volatility to allow its removal by distillation. Typical solvents useful in the practice of the present invention are acetone, methyl ethyl ketone, toluene, and N-methyl pyrrolidone. Alternatively, the polyurethane can be prepared in a melt with less than 5 % of solvent.

Mixtures of compounds or polymers having mixed NCO reactive groups can also 20 be used in the preparation of the polyurethane of the present invention.

Processing conditions for preparing the NCO containing prepolymers are well known to one skilled in the art. The finished NCO-containing prepolymer should have an isocyanate content of from about 1 to about 20 %, typically from about 1 to about 10 % by weight, based on the weight of prepolymer solids.

25 As described above, a sufficient amount of the ionic groups must be neutralized so that the resulting polyurethane can have a proper balance of hydrophilicity and hydrophobicity. Typically the degree of neutralization is from 40 % to 100 %, and more typically from 50 % to 70 %, depending on the acid number of the polyurethane.

Suitable neutralizing agents for converting the acid groups to salt groups include 30 tertiary amines, alkali metal cations and ammonia. Neutralizing agents can be trialkyl-substituted tertiary amines, such as triethyl amine, tripropyl amine, dimethylcyclohexyl amine, dimethylethanol amine, and triethanol amine and dimethylethyl amine. Substituted

amines such as diethyl ethanol amine or diethanol methyl amine are also useful neutralizing agents.

Neutralization may take place at any point in the process. Typical procedures include at least some neutralization of the prepolymer, which is then chain

5 extended/terminated in water in the presence of additional neutralizing agent.

The capping agent for terminating the polyurethane chain is usually a primary or secondary amine, an alcohol, or a mercapto. The amount of capping agent employed should be approximately equivalent to the free isocyanate groups in the prepolymer. The ratio of active hydrogens from amine in the capping agent to isocyanate groups in the prepolymer  
10 is in the range of from about 1.0:1.0 to about 3.0:1.0, more typically from about 1.0:1.0 to about 1.5:1.0, and still more typically from about 1.0:1.0 to about 1.05:1, on an equivalent basis.

Conversion of the polyurethane obtained from the methods described above to an aqueous dispersion is completed by addition of de-ionized water. If desired, solvent can

15 then be removed partially or substantially by distillation under reduced pressure. The final product is a stable, aqueous polyurethane dispersion having a solids content of up to about 60 % by weight, typically from about 10 % to about 60 % by weight, and more typically from about 20 % to about 45 % by weight. However, it is always possible to dilute the dispersions to any minimum solids content desired. The solids content of the resulting  
20 dispersion may be determined by drying the sample in an oven at 150 °C for 2 hours and comparing the weights before and after drying. The particle size is generally below about 1.0 micron, and typically between about 0.01 to about 0.5 micron. The average particle size should be less than about 0.5 micron, and typically between about 0.01 to about 0.3 micron. The small particle size enhances the stability of the dispersed particles

25 Preparation of Pigmented Dispersions

The pigmented dispersions used in this invention can be prepared using any conventional milling process known in the art. Most milling processes use a two-step process involving a first mixing step followed by a second grinding step. The first step comprises mixing of all the ingredients, that is, pigment, dispersants, liquid carriers,

30 neutralizing agent and any optional additives to provide a blended “premix”. Typically all liquid ingredients are added first, followed by the dispersants, and lastly the pigment. Mixing is generally done in a stirred mixing vessel, and a high-speed disperser (HSD) is particularly suitable for the mixing step. A Cowels type blade attached to the HSD and operated at from 500 rpm to 4000 rpm, and more typically from 2000 rpm to 3500 rpm,

provides optimal shear to achieve the desired mixing. Adequate mixing is usually achieved after mixing under the conditions described above for a period of from 15 to 120 minutes.

The second step comprises grinding of the premix to produce a pigmented dispersion. Typically, grinding involves a media milling process, although other milling techniques can also be used. In the present invention, a lab-scale Eiger Minimill (Model M250, VSE EXP) manufactured by Eiger Machinery Inc., Chicago, Illinois is employed. Grinding was accomplished by charging about 820 grams of 0.5 YTZ® zirconia media to the mill. The mill disk is operated at a speed between 2000 rpm and 4000 rpm, and typically between 3000 rpm and 3500 rpm. The dispersion is processed using a re-circulation grinding process with a typical flow rate through the mill at between 200 to 500 grams/minute, and more typically at 300 grams/minute. The milling may be done using a staged procedure in which a fraction of the solvent is held out of the grind and added after milling is completed. This is done to achieve optimal rheology that maximizes grinding efficiency. The amount of solvent held out during milling varies by dispersion, and is typically between 200 to 400 grams for a batch size with a total of 800 grams. Typically, the dispersions of the present invention are subjected to a total of 4 hours of milling.

For black dispersions, an alternate milling process using a Microfluidizer can be used. Microfluidization is a non-media milling process in which milling is done by pigment impingement through nozzles under high pressures. Typically, pigment dispersions are processed at 15,000 psi with a flow rate of 400 grams/minute for a total of 12 passes through the mill. In making the black dispersions in the Examples, a lab-scale (Model M-110Y, available from Microfluidics of Newton, Massachusetts) high pressure pneumatic Microfluidizer with a diamond Z Chamber was employed.

Fillers, plasticizers, pigments, carbon black, silica sols, other polymer dispersions and the known leveling agents, wetting agents, antifoaming agents, stabilizers, and other additives known for the desired end use, may also be incorporated into the dispersions.

#### Preparation of Cross-linked Pigment Dispersion

In the cross-linking step, a cross-linking compound is mixed with the pigmented dispersions prepared above at room temperature or elevated temperature for a period from 6 h to 8 h. To facilitate the cross-linking reaction, it may be desirable to add a catalyst. Useful catalysts can be those that are either soluble or insoluble in the liquid and can be selected depending upon the crosslinking reactions. Some suitable catalysts include dibutyltin dilaurate (DBTDL), tributyl amine (“TBA”) and dimethyldodecyl amine. After the cross-linking reaction is completed, the pH of the cross-linked dispersion can be

adjusted to at least about 8.0, more typically to between 8.0 and 12.0, and most typically between 8.0 and 11.0, if needed. Optionally, the dispersion may be further processed using conventional filtration procedures known in the art. The dispersions may be processed using ultrafiltration techniques that remove co-solvents and other contaminants, ions or 5 impurities from the dispersion. Each dispersion can be then tested for pH, conductivity, viscosity and particle size. Dispersion stability is deemed important to demonstrating the utility of the dispersant employed.

10 Fillers, plasticizers, pigments, carbon black, silica sols, other polymer dispersions and the known leveling agents, wetting agents, antifoaming agents, stabilizers, and other additives known for the desired end use, may also be incorporated into the dispersions.

#### Ink Vehicle

The pigmented ink of this disclosure comprises an ink vehicle typically an aqueous ink vehicle, also known as an aqueous carrier medium, the aqueous dispersion and optionally other ingredients.

15 The ink vehicle is the liquid carrier (or medium) for the aqueous dispersion(s) and optional additives. The term “aqueous ink vehicle” refers to an ink vehicle comprised of water or a mixture of water and one or more organic, water-soluble vehicle components commonly referred to as co-solvents or humectants. Selection of a suitable mixture depends on requirements of the specific application, such as desired surface tension and 20 viscosity, the selected pigment, drying time of the pigmented ink jet ink, and the type of paper onto which the ink will be printed. Sometimes in the art, when a co-solvent can assist in the penetration and drying of an ink on a printed substrate, it is referred to as a penetrant.

25 Examples of water-soluble organic solvents and humectants include: alcohols, ketones, keto-alcohols, ethers and others, such as thiodiglycol, Sulfolane, 2-pyrrolidone, 1,3- dimethyl-2-imidazolidinone and caprolactam; glycols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, trimethylene glycol, butylene glycol and hexylene glycol; addition polymers of oxyethylene or oxypropylene such as polyethylene glycol, 30 polypropylene glycol and the like; triols such as glycerol and 1,2,6-hexanetriol; lower alkyl ethers of polyhydric alcohols, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl, diethylene glycol monoethyl ether; lower dialkyl ethers of polyhydric alcohols, such as diethylene glycol dimethyl or diethyl ether; urea and substituted ureas.

A mixture of water and a polyhydric alcohol, such as diethylene glycol, is typical as the aqueous ink vehicle. In the case of a mixture of water and diethylene glycol, the ink vehicle usually contains from 30 % water and 70 % diethylene glycol to 95 % water and 5 % diethylene glycol, more typically from 60 % water and 40 % diethylene glycol to 95 % 5 water and 5 % diethylene glycol. Percentages are based on the total weight of the ink vehicle. A mixture of water and butyl carbitol is also an effective ink vehicle.

The amount of ink vehicle in the ink is typically in the range of from 70 % to 99.8 %, and more typically from 80 % to 99.8 %, by weight based on total weight of the ink.

The ink vehicle can be made to be fast penetrating (rapid drying) by including 10 surfactants or penetrating agents such as glycol ethers and 1,2-alkanediols. Glycol ethers include ethylene glycol monobutyl ether, diethylene glycol mono-n-propyl ether, ethylene glycol mono-iso-propyl ether, diethylene glycol mono-iso-propyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-t-butyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol mono-n-butyl ether, diethylene glycol mono-t-butyl ether, 1- 15 methyl-1-methoxybutanol, propylene glycol mono-t-butyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-iso-propyl ether, propylene glycol mono-n-butyl ether, dipropylene glycol mono-n-butyl ether, dipropylene glycol mono-n-propyl ether, and dipropylene glycol mono-isopropyl ether. Typical 1,2-alkanediols are C<sub>4</sub>-C<sub>6</sub> alkanediols with 1,2-hexanediol being most typical. Suitable surfactants include 20 ethoxylated acetylene diols (e.g. Surfynol® series commercially available from Air Products), ethoxylated alkyl primary alcohols (e.g. Neodol® series commercially available from Shell) and secondary alcohols (e.g. Tergitol® series commercially available from Union Carbide), sulfosuccinates (e.g. Aerosol® series commercially available from Cytec), organosilicones (e.g. Silwet® series commercially available from Witco) and fluoro 25 surfactants (e.g. Zonyl® series commercially available from DuPont).

The amount of glycol ether(s) and 1,2-alkanediol(s) added is typically in the range of from 1 % to 15 %, and more typically from 2 % to 10% by weight, based on the total weight of the ink. Surfactants may be used, typically in the amount of from 0.01 % to 5 % and more typically from 0.2 % to 2 %, by weight based on the total weight of the ink.

30 Biocides may be used to inhibit growth of microorganisms.

Pigmented ink jet inks typically have a surface tension in the range of about 20 mN.m<sup>-1</sup> to about 70 mN.m<sup>-1</sup>, at 25 °C. Viscosity can be as high as 30 mPa.s at 25 °C, but is typically somewhat lower. The ink has physical properties compatible with a wide range of ejecting conditions, materials construction and the shape and size of the nozzle. The inks 35 should have excellent storage stability for long periods so as not to clog to a significant

extent in an ink jet apparatus. Further, the ink should not corrode parts of the ink jet printing device it comes in contact with, and it should be essentially odorless and non-toxic.

5 Although not restricted to any particular viscosity range or printhead, the inks of the disclosure are particularly suited to lower viscosity applications. Thus the viscosity (at 25 °C) of the inks of this disclosure may be less than about 7 mPa.s, or less than about 5 mPa.s, and even more advantageously, less than about 3.5 mPa.s

The following examples illustrate the invention without, however, being limited thereto.

10

## EXAMPLES

### Extent of Polyurethane Reaction

The extent of polyurethane reaction was determined by a titration with dibutylamine to detect the isocyanate content (NCO%), a common method used in urethane chemistry.

15 In this method, a sample of the isocyanate containing prepolymer is reacted with a known amount of dibutylamine solution, and the residual amine is back titrated with aqueous HCl.

### Particle Size Measurements

20 The particle size for the polyurethane dispersions, pigments and the inks were determined by dynamic light scattering using a Microtrac® UPA 150 analyzer from Honeywell/Microtrac (Montgomeryville PA).

This technique is based on the relationship between the velocity distribution of the particles and the particle size. Laser generated light is scattered from each particle and is Doppler shifted by the particle Brownian motion. The frequency difference between the shifted light and the unshifted light is amplified, digitalized and analyzed to derive the 25 particle size distribution. Results are reported as D50 and D95.

### Solid Content Measurement

30 Solid content for the solvent free polyurethane dispersions was measured with a moisture analyzer, Model MA50 from Sartorius. For polyurethane dispersions containing a high boiling solvent, such as NMP, tetraethylene glycol dimethyl ether, or sulfolane, the solid content was determined by the weight difference before and after baking in an oven set at 150 °C oven for 180 minutes.

### Polyurethane Dispersant 1 (DEA terminated TMXDI/UH-50/DMPA)

To a dry, alkali- and acid-free, 2 liter flask equipped with an additional funnel, a condenser and a stirrer, under a nitrogen atmosphere was added Eternacoll® UH-50 (117.0 g), dimethylol propionic acid (87.0 g) and Sulfolane (220.0 g). The contents were heated to 115 °C and mixed under a nitrogen gas purge for 30 minutes. The temperature was then 5 lowered to 60 °C and DBTDL (0.08 g) was added followed by TMXDI (238.0 g) via the addition funnel. The residual TMXDI in the additional funnel was rinsed into the flask with Sulfolane (15.0 g). The stirred reaction mass was allowed to exotherm. When exotherm began to slow, the temperature was maintained at 100 °C while monitoring the isocyanate content until it reached 1.06 %. The temperature was lowered to 60 °C. To the 10 flask was added DEA (18.04 g) via the additional funnel followed by rinsing the residual BMEA in additional funnel into the flask with Sulfolane (5.0 g). The mixture was maintained at 60 °C for 90 minutes. A solution of 45 % KOH in water (56.56 g) and additional de-ionized water (776.87 g) were added over a period of 5 minutes to give a 70 % neutralized polyurethane resin in water. This was allowed to stir and cool to room 15 temperature to provide a polyurethane dispersion with 27.49 % of solids and a measured acid number of 79.03 mg KOH/gram polymer.

#### Polyurethane Binder 1 (BMEA terminated IPDI/T650/DMPA)

To a dry, alkali- and acid-free, 2 liter flask equipped with an additional funnel, a condenser and a stirrer, under a nitrogen atmosphere were added Terathane® 650 (291.5 g), 20 dimethylol propionic acid (61.85 g), tetraglyme (482.59 g) and DBTDL (0.04 g). The contents were heated to 40 °C and mixed under a nitrogen gas purge for 30 minutes. IPDI (222.86 g) was added via the addition funnel over 60 minutes. The residual IPDI in the additional funnel was rinsed into the flask with tetraglyme (9.6 g). The stirred reaction mass was allowed to exotherm to 50 °C, but not to exceed 53 °C, while monitoring the 25 isocyanate content until it reached 0.84 %. To the flask was added BMEA (20.94 g) via the additional funnel. The mixture was maintained at 50 °C for 90 minutes. A solution of 45% KOH in water (57.5 g) and additional de-ionized water (1372.4 g) were added over a period of 5 minutes to give a dispersed polyurethane resin in water. This was allowed to stir and cool to room temperature to provide a polyurethane dispersion with 24.17 % of solids and a 30 measured acid number of 45.0 mg KOH/gram polymer.

#### Preparation of Pigmented Dispersion K1

The following procedure was used to prepare a black pigmented dispersion using Nipex 180 and Dispersant 1. Using a microfluidizer, a premix was prepared at typically 20-30 % pigment loading and the targeted dispersant level was selected at a 35 pigment/dispersant (P/D) ratio of 2.0. A P/D of 2.0 corresponds to a 40 % dispersant level

on pigment. A co-dispersant, Surfynol 104 in Dowanol DPM at a P/D = 100 was added to the total dispersion formulation to facilitate wetting of pigment and dissolution of dispersant in the premix stage for ease of grinding during milling stage. Dispersant 1 was pre-neutralized with KOH to facilitate solubility and dissolution into water. An additional 5 6.91 g of a 45% KOH solution in water was added. During the premix stage and milling stage, de-ionized water (1200 g) was added to adjust viscosity and control temperature. After completion of the milling stage, the remaining letdown of de-ionized water (450.0 g) was added and thoroughly mixed. The final pigment dispersion contains 23.15 % of solids.

10 The pigment dispersion was purified using an ultrafiltration process to remove co-solvent(s) and excess dispersant, and filter out other impurities that may be present. After completion, the pigment level in the dispersion was reduced to about 10 to 15 %. A single black dispersion, listed in Table 1 was prepared using the Polyurethane Dispersant 1.

Table 1

Pigmented Dispersion	Pigment	Pigment / Dispersant	Polyurethane Dispersant No.	Particle Size D50 (nm)	Particle Size D95 (nm)
K1	Nipex 180	2	1	107	185

15 Preparation of Cross-linked Pigment Dispersion XL-K1

In the cross-linking step, Denacol® 321 was mixed with one of the pigmented Dispersion K1, and heated at temperatures between 60 °C and 80 °C with efficient stirring for 6-8 hours. After the cross-linking reaction was completed, the pH was adjusted to at least about 8.0 if needed. The composition of the cross-linked Pigment Dispersion XL-K1 20 is summarized in Table 2.

Table 2

Cross-linked Dispersion	Pigmented Dispersion	Cross-linkable Moiety	Cross-linking Compound
XL-K1	K1	COOH, OH	Denacol® 321

Preparation of Ink and Testing of Stability

25 The inks were prepared by conventional processes known to one skilled in the art using the cross-linked Dispersion XL-K1 and Polyurethane Binder 1. A comparative ink without the presence of Polyurethane Binder 1 was also prepared. The inventive ink was processed by routine operations using a typical ink vehicle suitable for ink-jet ink

formulation targeting 3 % by weight of the cross-linked Dispersion XL-K1 and 1 % by weight of the Polyurethane Binder 1 in the final ink. The comparative ink was made the same way, but without any Polyurethane Binder 1.

As shown in Table 3 below, the ink made with cross-linked black Dispersion 1 together with a binder when printed in general showed lower optical density, better smudge and highlighter smear properties compared to a comparative ink without the presence of the binder. When printed on Xerox 4200, no changes in optical density, smudge and highlighter smear properties were observed between the ink with the binder and the ink without the binder.

10

Table 3

Paper	Ink	Optical Density	Smudge*	Highlighter Smear <sup>#</sup>			
				10 min	1 hr	10 min	1h
HP Bright White	XL-K1, no binder	1.32	3	4	4	2	2
	XL-K1, 1 % Binder 1	1.25	4	4	4	2	3
HP Multipurpose	XL-K1, no binder	1.34	2	3	3	1	1
	XL-K1, 1 % Binder 1	1.22	3	4	4	1	2
Xerox 4200	XL-K1, no binder	0.84	4	5	5	4	4
	XL-K1, 1 % Binder 1	0.84	4	5	5	4	4
HP Brochure	XL-K1, no binder	1.67	3	4	4	3	3
	XL-K1, 1 % Binder 1	1.44	4	5	5	4	4

\* Visual Rating for Smudge

- 0 – Ink largely removed
- 2 – Severe smudge
- 3 – Moderate smudge
- 4 – Very slight smudge
- 5 – No smudge visible

15

# Visual Rating for Highlighter Smear

20

- 0 – Ink largely removed from stripe with highlighter
- 1 – Severe smear, considerable color transfer, may be some damage to stripe
- 2 – Noticeable smear, run full width of area between stripes
- 3 – Moderate smear, may be full width of highlighter, but light in color
- 4 – Slight smear, narrow, doesn't run clear to next stripe
- 5 – No smear visible

25

What is claimed is:

1. An ink-jet ink comprising an aqueous ink vehicle, an aqueous pigment dispersion and a polymeric binder, wherein said aqueous pigment dispersion comprises a colorant and a

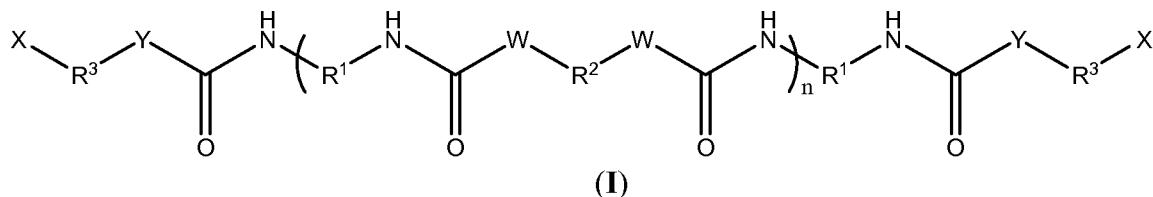
5 polyurethane dispersant, and said polymeric binder is non-reactive to said colorant, and wherein said polyurethane dispersant is comprised of a polymer with:

(a) an aqueous dispersing moiety, and

(b) a cross-linkable moiety that is cross-linked with a cross-linking agent, wherein said cross-linkable moiety is pendent to the polymer backbone and terminal to the polymer

10 chain;

wherein the polyurethane dispersant comprises at least one compound of the general structure of Formula I:



15 wherein each X is independently OH, SH, COOH or NHR<sup>4</sup>;

each Y is independently O, S or NR<sup>4</sup>;

each W is N, O or S;

each R<sup>1</sup> is independently C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> substituted alkyl, C<sub>6</sub>-C<sub>40</sub> aryl or C<sub>9</sub>-C<sub>40</sub> substituted aryl;

20 R<sup>2</sup> is comprised of difunctional isocyanate reactants Z<sup>1</sup>, Z<sup>2</sup> and Z<sup>3</sup>, wherein there is at least one Z<sup>1</sup>, at least one Z<sup>2</sup> and at least one Z<sup>3</sup>;

each R<sup>3</sup> is independently C<sub>1</sub>-C<sub>20</sub> alkyl or C<sub>3</sub>-C<sub>20</sub> substituted alkyl;

each R<sup>4</sup> is independently -R<sup>3</sup>-X, H, C<sub>1</sub>-C<sub>20</sub> alkyl or C<sub>3</sub>-C<sub>20</sub> substituted alkyl;

n is an integer from 2 to 30;

25 Z<sup>1</sup> is a difunctional isocyanate reactant substituted with an aqueous dispersing moiety;

Z<sup>2</sup> is a difunctional isocyanate reactant substituted with one or more cross-linkable moieties; and

$Z^3$  is a polyol with MW less than 3000.

2. The ink of claim 1, wherein the polymeric binder is one or more members selected from the group consisting of polyurethane, acrylics, styrene acrylics, styrene butadienes, styrene butadiene acrylonitriles, neoprenes, ethylene acrylic acid copolymer, ethylene vinyl acetate, and mixtures thereof.
3. The ink of claim 2, wherein the cross-linking agent is one or more members selected from the group consisting of epoxide, isocyanate, carbodiimide, *N*-methylol, oxazoline, silane, and mixtures thereof.
4. The ink of claim 3, wherein  $Z^1$  is a polyol substituted with the aqueous dispersing moiety.
5. The ink of claim 4, wherein  $Z^2$  is a polyol substituted with one or more cross-linkable moieties.
6. The ink of claim 5, wherein the aqueous dispersing moiety consists of one or more carboxyl groups.
- 15 7. The ink of claim 6, wherein the cross-linkable moiety consists of one or more carboxyl groups.
8. The ink of claim 7, wherein Y is  $NR^4$ .
9. The ink of claim 8, wherein the polymeric binder is polyurethane.
10. The ink of claim 3, wherein X is OH.
- 20 11. The ink of claim 10, wherein  $Z^1$  is a polyol substituted with the aqueous dispersing moiety.
12. The ink of claim 11, wherein  $Z^2$  is a polyol substituted with one or more cross-linkable moieties.
13. The ink of claim 12, wherein the polymeric binder is polyurethane.
- 25 14. The ink of claim 3, wherein X is  $NHR^4$ .
15. The ink of claim 14, wherein  $Z^1$  is a polyol substituted with the aqueous dispersing moiety.

16. The ink of claim 15, wherein  $Z^2$  is a polyol substituted with one or more cross-linkable moieties.
17. The ink of claim 16, wherein the polymeric binder is polyurethane
18. The ink of claim 3, wherein Y is  $NR^4$ .
- 5 19. The ink of claim 18, wherein  $Z^1$  is a polyol substituted with the aqueous dispersing moiety.
20. The ink of claim 19, wherein  $Z^2$  is a polyol substituted with one or more cross-linkable moieties.
21. The ink of claim 20, wherein the polymeric binder is polyurethane.
- 10 22. The ink of claim 3, wherein  $R^4$  is  $-R^3-X$  and the polymeric binder is polyurethane.
23. The ink of claim 22, wherein each W is O.
24. The ink of claim 22, wherein each W is N.
25. The ink of claim 3, wherein the mole ratio of the cross-linkable moiety to the cross-linking agent is from 15:1 to 1:1.5.

15