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(54) Title: CONTINUOUS INKJET PRINTER AQUEOUS INK COMPOSITION

(57) Abstract: A continuous ink jet printer aqueous ink composition including pigment particles dispersed with a dispersant or self dispersing pigment particles without the need for a dispersant, and a polymer additive distinct from any dispersant used to disperse the pigment particles, wherein the polymer additive comprises a water soluble block copolymer having one or more poly(ethylene oxide) block segments wherein the polymer additive is present in an amount effective to stabilize the ink composition against shear induced agglomeration caused by pumping the ink composition through a continuous ink jet printing fluid system. A method of continuous ink jet printing includes A) providing a main fluid supply of a continuous inkjet printer with an aqueous ink composition used in the invention; B) pumping the ink composition from the main fluid supply to a print head and ejecting a continuous stream of the ink composition from the print head which continuous stream is broken into spaced droplets; and C) in response to electrical signals received from a control mechanism, controlling the spaced droplets to select between printing droplets for marking a substrate and nonprinting droplets that are collected and returned to the main fluid supply.



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CONTINUOUS INKJET PRINTER AQUEOUS INK COMPOSITION

FIELD OF THE INVENTION

The present invention related to an aqueous inkjet ink composition
5 for continuous inkjet printing applications comprising pigment dispersion and a water soluble polymer.

BACKGROUND OF THE INVENTION

Continuous ink jet (CIJ) printers typically consist of two main components, a fluid system and a print head or multiple print heads. Ink is
10 pumped through a supply line from a supply reservoir to a manifold that distributes the ink to a plurality of orifices, typically arranged in linear array(s), under sufficient pressure to cause ink streams to issue from the orifices of the print head. Stimulation is applied to the print head to cause those ink streams to form streams of uniformly sized and spaced droplets, which are deflected into printing
15 or non-printing paths. The non-printing droplets are returned to the supply reservoir via a droplet catcher and a return line. US patents 4,734,711 and 5,394,177 and EP 1,013,450 describe in detail the design of a fluid system for CIJ apparatus. The more recent development of CIJ printing apparatus and print head fabrication can be found in US 6,588,888 and US 6,943,037.

20 Ink drop uniformity requires maintaining a uniform pressure in the print head cavity. US patent 4,614,948 describes that a positive displacement pump, such as gear pump, is preferred for use as the ink supply pump. The need to limit pulsation produced by the pump is recognized in US 4,971,527. In addition, filters are employed at appropriate location in fluid system to remove oversized
25 particles prior to ink entering into print head orifices and avoid print head clogging.

Commercially available CIJ inks are mostly aqueous dye-based inks, where issues regarding robust system runnability, such as easy start up/shut down, extended printing time without crooked jet, and reduced frequency for filter
30 changing have been minimized. In such traditional dye-based inks, no particles are observable under the microscope. Although there have been many recent

advances in the art of dye-based ink jet inks, such inks still suffer from deficiencies such as low optical densities on coated glossy paper and poor light-fastness. When water is used as the carrier, such inks also generally suffer from poor water fastness and poor smear resistance.

5 Pigment-based inks have been proposed as a means of addressing limitations of dye based inks, particularly in drop-on-demand (DOD) inkjet printing systems. In pigment-based inks, the colorant exists as discrete particles. Pigment dispersions known in the art include self-dispersion pigment dispersions, dispersant stabilized pigment dispersions and encapsulated pigment dispersions.

10 For non-self-dispersion pigment, these pigment particles are usually treated with addenda known as dispersants or stabilizers that serve to keep the pigment particles from agglomerating and/or settling out. Development on dispersants/stabilizers for pigment dispersions has made great progress in recent years, materials are commonly classified into small surfactant molecules or

15 polymers, containing both hydrophilic and hydrophobic segments. Small molecule surfactants disclosed in US patents 5,651,813 and 5,985,017 are found useful due to their compatibility to a wide variety of pigments. Useful polymeric stabilizers include acrylic and styrene-acrylic random or block copolymers, such as those disclosed in U.S. Patents 4,597,794, 5,085,698, 5,172,133, 5,821,283,

20 6,245,832, and 6,326,449. Polymeric dispersants have the additional advantage of offering image durability once the inks are dried down on the ink receiver substrate.

 It has been discovered, however, severe filter plugging issues may be encountered when running pigment inks in a CIJ fluid system, requiring

25 frequent change of filters, over the time period of a few hours vs. a few months for dye-based inks. The consequence of filter plugging is the loss of fluid pressure and fluid jets, leading to system shutdown. Further investigation has discovered that the gear pump commonly used in the fluid system to maintain fluid pressure with minimal pulsation can cause agglomeration of pigment particles, leading to filter

30 clogging and system shutdown. Therefore, there exists a need for pigment ink formulations which are stable in CIJ fluid systems.

It is an object of this invention to provide an aqueous ink jet ink composition for CIJ printing apparatus containing dispersed pigment, and to allow the ink to be run in a CIJ fluid system for extended periods without significant pressure build up or filter clogging.

5

SUMMARY OF THE INVENTION

The heretofore need of a pigment ink for CIJ apparatus with extended runnability can be met by the present invention of a continuous ink jet printer aqueous ink composition comprising pigment particles dispersed with a dispersant or self dispersing pigment particles without the need for a dispersant, and a polymer additive distinct from any dispersant used to disperse the pigment particles, wherein the polymer additive comprises a water soluble block copolymer having one or more poly(ethylene oxide) block segments which in total comprise from 50 to 99 wt% of the polymer additive, and from 1 to 50 wt% of segments relatively more hydrophobic than the poly(ethylene oxide) block segments, where the molecular weight of at least one poly(ethylene oxide) segment of the additive is greater than 500, and wherein the polymer additive is present in an amount effective to stabilize the ink composition against shear induced agglomeration caused by pumping the ink composition through a continuous ink jet printing fluid system.

20

The invention further provides a method of continuous ink jet printing comprising: A) providing a main fluid supply of a continuous inkjet printer with an aqueous ink composition used in the invention; B) pumping the ink composition from the main fluid supply to a print head and ejecting a continuous stream of the ink composition from the print head which continuous stream is broken into spaced droplets; and C) in response to electrical signals received from a control mechanism, controlling the spaced droplets to select between printing droplets for marking a substrate and nonprinting droplets that are collected and returned to the main fluid supply.

25

DETAILED DESCRIPTION OF THE INVENTION

The inkjet ink composition used in the invention comprises dispersed pigment particles and a polymer additive distinct from any dispersant

used to disperse the pigment particles. The additive comprises a water soluble block copolymer having one or more poly(ethylene oxide) block segments which in total comprise from 50 to 99 wt% of the polymer additive, and from 1 to 50 wt% of segments relatively more hydrophobic than the poly(ethylene oxide) block segments, and where the molecular weight of at least one poly(ethylene oxide) segment of the additive is greater than 500. The polymer additive is present in the ink composition an amount effective to stabilize the ink composition against shear induced agglomeration caused by pumping the ink composition through a continuous ink jet printing fluid system.

10 Pigment-based ink compositions are used because such inks render printed images having higher optical densities and better resistance to light and ozone as compared to printed images made from other types of colorants. A wide variety of organic and inorganic pigments, alone or in combination with additional pigments or dyes, can be in the present invention. Pigments that may be used in
15 the invention include those disclosed in, for example, US 5,026,427; 5,085,698; 5,141,556; 5,160,370; and 5,169,436. The exact choice of pigments will depend upon the specific application and performance requirements such as color reproduction and image stability. Dispersed pigment particles are typically present at from 1 to 10 wt% in the continuous inkjet printing inks used in the invention,
20 preferably 1 to 6 wt%.

 Pigments suitable for use in the invention include, but are not limited to, azo pigments, monoazo pigments, di-azo pigments, azo pigment lakes, β -Naphthol pigments, Naphthol AS pigments, benzimidazolone pigments, di-azo condensation pigments, metal complex pigments, isoindolinone and isoindoline
25 pigments, polycyclic pigments, phthalocyanine pigments, quinacridone pigments, perylene and perinone pigments, thioindigo pigments, anthrapyrimidone pigments, flavanthrone pigments, anthanthrone pigments, dioxazine pigments, triarylcarbonium pigments, quinophthalone pigments, diketopyrrolo pyrrole pigments, titanium oxide, iron oxide, and carbon black.

30 Typical examples of pigments that may be used include Color Index (C. I.) Pigment Yellow 1, 2, 3, 5, 6, 10, 12, 13, 14, 16, 17, 62, 65, 73, 74,

75, 81, 83, 87, 90, 93, 94, 95, 97, 98, 99, 100, 101, 104, 106, 108, 109, 110, 111, 113, 114, 116, 117, 120, 121, 123, 124, 126, 127, 128, 129, 130, 133, 136, 138, 139, 147, 148, 150, 151, 152, 153, 154, 155, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 179, 180, 181, 182, 183, 184, 185, 187, 188, 190, 191, 192, 193, 194; C. I. Pigment Red 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 21, 22, 23, 31, 32, 38, 48:1, 48:2, 48:3, 48:4, 49:1, 49:2, 49:3, 50:1, 51, 52:1, 52:2, 53:1, 57:1, 60:1, 63:1, 66, 67, 68, 81, 95, 112, 114, 119, 122, 136, 144, 146, 147, 148, 149, 150, 151, 164, 166, 168, 169, 170, 171, 172, 175, 176, 177, 178, 179, 181, 184, 185, 187, 188, 190, 192, 194, 200, 202, 204, 206, 207, 210, 211, 212, 213, 214, 216, 220, 222, 237, 238, 239, 240, 242, 243, 245, 247, 248, 251, 252, 253, 254, 255, 256, 258, 261, 264; C.I. Pigment Blue 1, 2, 9, 10, 14, 15:1, 15:2, 15:3, 15:4, 15:6, 15, 16, 18, 19, 24:1, 25, 56, 60, 61, 62, 63, 64, 66, bridged aluminum phthalocyanine pigments; C.I. Pigment Black 1, 7, 20, 31, 32; C. I. Pigment Orange 1, 2, 5, 6, 13, 15, 16, 17, 17:1, 19, 22, 24, 31, 34, 36, 38, 40, 43, 44, 46, 48, 49, 51, 59, 60, 61, 62, 64, 65, 66, 67, 68, 69; C.I. Pigment Green 1, 2, 4, 7, 8, 10, 36, 45; C.I. Pigment Violet 1, 2, 3, 5:1, 13, 19, 23, 25, 27, 29, 31, 32, 37, 39, 42, 44, 50; or C.I. Pigment Brown 1, 5, 22, 23, 25, 38, 41, 42.

White pigments, which may be used in ancillary white ink compositions, may be those which are capable of rendering said ink composition white. Any of several white pigments, which are commonly used in this field, may be employed. Employed as such white pigments may be, for example, white inorganic pigments, white organic pigments, and fine white hollow polymer particles. White pigments include inorganic pigments such as sulfates of alkaline earth metals such as barium sulfate, carbonates of alkaline earth metals such as calcium carbonate, silica such as fine silicic acid powder, synthetic silicates, calcium silicate, alumina, alumina hydrates, titanium oxide, zinc oxide, talc, and clay. Specifically, titanium oxide is known as a white pigment which exhibits desired covering properties, coloring (tinting) properties, and desired diameter of dispersed particles. White organic pigments include organic compound salts disclosed in JP-A No. 11-129613, and alkylenebismelamine derivatives disclosed in JP-A Nos. 11-140365 and 2001-234093. Specific commercially available

products of the aforesaid white pigments are Shigenox OWP, Shigenox OWPL, Shigenox FWP, Shigenox FWG, Shigenox UL, and Shigenox U (all are commercial product names, by Hakkoru Chemical Co.). Additionally fine white hollow polymer particles such as fine thermoplastic particles comprised
5 substantially of an organic polymer, which are disclosed in US 4,089,800 may be employed.

Pigment-based ink compositions employing non-self-dispersed pigments that are useful in the invention may be prepared by any method known in the art of inkjet printing. Useful methods commonly involve two steps: (a) a
10 dispersing or milling step to break up the pigments to primary particles, where primary particle is defined as the smallest identifiable subdivision in a particulate system, and (b) a dilution step in which the pigment dispersion from step (a) is diluted with the remaining ink components to give a working strength ink. The milling step (a) is carried out using any type of grinding mill such as a media mill,
15 a ball mill, a two-roll mill, a three-roll mill, a bead mill, and air-jet mill, an attritor, or a liquid interaction chamber. In the milling step (a), pigments are optionally suspended in a medium that is typically the same as or similar to the medium used to dilute the pigment dispersion in step (b). Inert milling medium is optionally present in the milling step (a) in order to facilitate break up of the
20 pigments to primary particles. Inert milling media include such materials as polymeric beads, glasses, ceramics, metals and plastics as described, for example, in US 5,891,231. The milling media described in US patent 5,679,138 is preferred to obtain pigment dispersion of finer particle size. Milling media are removed from either the pigment dispersion obtained in step (a) or from the ink
25 composition obtained in step (b).

A dispersant is optionally present in the milling step (a) in order to facilitate break up of the pigments into primary particles. For the pigment dispersion obtained in step (a) or the ink composition obtained in step (b), a dispersant is optionally present in order to maintain particle stability and prevent
30 settling. Dispersants suitable for use in the invention include, but are not limited to, those commonly used in the art of inkjet printing. For aqueous pigment-based

ink compositions, particularly useful dispersants include anionic, cationic or nonionic surfactants such as sodium dodecylsulfate, or potassium or sodium oleylmethyltaurate as described in, for example, US 5,679,138, US 5,651,813 or US 5,985,017.

5 Self-dispersing pigments that are dispersible without the use of a dispersant or surfactant can be used in the invention. Pigments of this type are those that have been subjected to a surface treatment such as oxidation/reduction, acid/base treatment, or functionalization through coupling chemistry. The surface treatment can render the surface of the pigment with anionic, cationic or non-ionic
10 groups such that a separate dispersant is not necessary. The preparation and use of covalently functionalized self-dispersed pigments suitable for inkjet printing are reported by Bergemann et al. in US 6,758,891 and US 6,660,075; Belmont in US 5,554,739; Adams and Belmont in US 5,707,432; Johnson and Belmont in US 5,803,959 and 5,922,118; Johnson et al. in US 5,837,045; Yu et al. in US
15 6,494,943; in published applications WO 96/18695, WO 96/18696, WO 96/18689, WO 99/51690, WO 00/05313, and WO 01/51566; Osumi et al. in US Patents 6,280,513 and US 6,506,239; Karl et al. in US 6,503,311; Yeh, et al. in US 6,852,156 B2; Ito et al. in US 6,488,753; and Momose et al. in EP 1,479,732 A1. Examples of commercially available self-dispersing type pigments include CAB-
20 O-JET 200, CAB-O-JET-250, CAB-O-JET-260, CAB-O-JET-270, and CAB-O-JET 300 (Cabot Specialty Chemicals, Inc.) and BONJET CW-1 and CW-2 (Orient Chemical Industries, Ltd.).

 Polymeric dispersants are also known and useful in aqueous pigment-based ink compositions. Polymeric dispersants may be added to the
25 pigment dispersion prior to, or during the milling step (a), and include polymers such as homopolymers and copolymers; anionic, cationic or nonionic polymers; or random, block, branched or graft polymers. Polymeric dispersants useful in the milling operation include random and block copolymers having hydrophilic and hydrophobic portions; see for example, US 4,597,794; US 5,085,698; US
30 5,519,085; US 5,272,201; 5,172,133; US 6,043,297 and WO 2004/111140A1; and graft copolymers; see for example, US 5,231,131; US 6,087,416; US 5,719,204; or

US 5,714,538. Typically, these polymeric resins are copolymers made from hydrophobic and hydrophilic monomers. The copolymers are designed to act as dispersants for the pigment by virtue of the arrangement and proportions of hydrophobic and hydrophilic monomers. The pigment particles are colloiddally stabilized by the dispersant and are referred to as a polymer dispersed pigment dispersion. Polymer stabilized pigment dispersions have the additional advantage of offering image durability once the inks are dried down on the ink receiver substrate.

Polymeric dispersants, typically copolymers, are not limited in the arrangement of the monomers comprising the copolymer. The arrangement of monomers may be totally random, or they may be arranged in blocks such as AB or ABA wherein, A is the hydrophobic monomer and B is the hydrophilic monomer. In addition, the polymer may take the form of a random terpolymer or an ABC tri-block wherein, at least one of the A, B and C blocks is chosen to be the hydrophilic monomer and the remaining blocks are hydrophobic blocks dissimilar from one another.

Especially useful copolymer dispersants are those where the hydrophobic monomer is selected from benzyl methacrylate or acrylate, or from methacrylic or acrylic acid esters containing an aliphatic chain having twelve or more carbons, which aliphatic chains may be linear or branched. Examples of methacrylic and acrylic acid esters having twelve or more carbons include; lauryl acrylate, lauryl methacrylate, tridecyl acrylate, tridecyl methacrylate, tetradecyl acrylate, tetradecyl methacrylate, cetyl acrylate, iso-cetyl acrylate, stearyl methacrylate, *iso*-stearyl methacrylate, stearyl acrylate, stearyl methacrylate, decyltetradecyl acrylate, decyltetradecyl methacrylate, and the like. Preferably the methacrylate or acrylate monomer is stearyl or lauryl methacrylate or acrylate. The hydrophobic portion of the polymer may be prepared from one or more of the hydrophobic monomers.

Preferred copolymer dispersants are those where the hydrophilic monomer is selected from carboxylated monomers. Preferred polymeric dispersants are copolymers prepared from at least one hydrophilic monomer that is

an acrylic acid or methacrylic acid monomer, or combinations thereof. Preferably, the hydrophilic monomer is methacrylic acid. Particularly useful polymeric pigment dispersants are further described in US 2006/0012654 and US 2007/0043144.

5 Typically, the weight average molecular weight of the copolymer dispersant has an upper limit such that it is less than 50,000 Daltons. Desirably the weight average molecular weight of the copolymer is less than 25,000 Daltons; more preferably it is less than 15,000 and most preferably less than 10,000 Daltons. The copolymer dispersants preferably have a weight average molecular
10 weight lower limit of greater than 500 Daltons.

 Encapsulating type polymeric dispersants and polymeric dispersed pigments thereof can also be used in the invention. Specific examples are described in US 6,723,785, US 6,852,777, US 2004/0132942, 2005/0020731, 2005/0075416, 2005/0124726, and 2005/0124728. Encapsulating type polymeric
15 dispersants can be especially useful because of their high dispersion stability on keeping and low degree of interaction with ink components. Composite colorant particles having a colorant phase and a polymer phase are also useful in aqueous pigment-based inks used in the invention. Composite colorant particles are formed by polymerizing monomers in the presence of pigments; see for example,
20 US 2003/0199614; US 2003/0203988; or US 2004/0127639. Microencapsulated-type pigment particles are also useful and consist of pigment particles coated with a resin film; see for example US 6,074,467.

 The pigment particles useful in the invention may have any particle sizes which can be jetted through a print head. Preferably, the pigment particles
25 have a mean particle size of less than 0.5 micron, more preferably less than 0.2 micron, and most preferably less than 0.1 micron.

 In addition to dispersed pigment colorants, the inks used in the invention can further contain dyes as supplemental colorants. Dyes suitable for use in the invention include, but are not limited to, those commonly used in the art
30 of inkjet printing. For aqueous-based ink compositions, such dyes include water-soluble reactive dyes, direct dyes, anionic dyes, cationic dyes, acid dyes, food

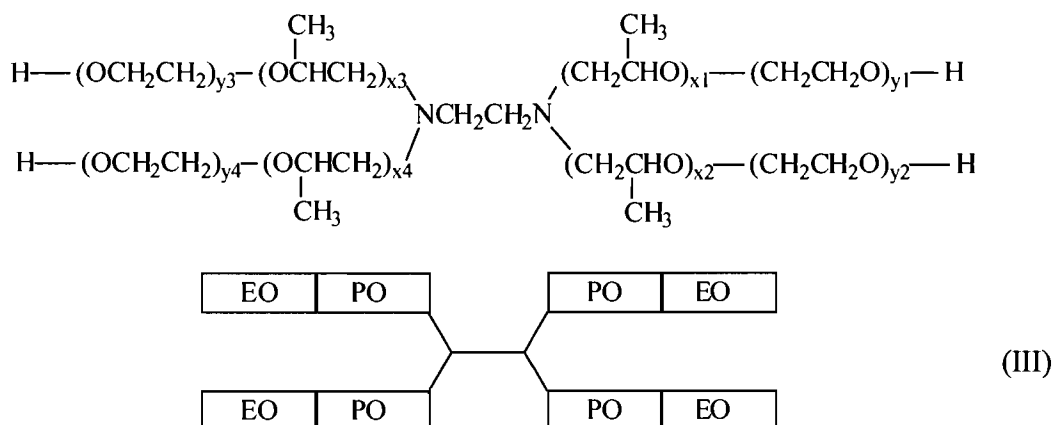
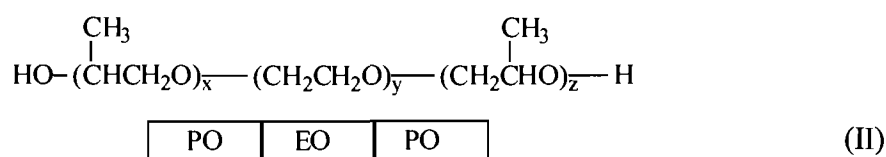
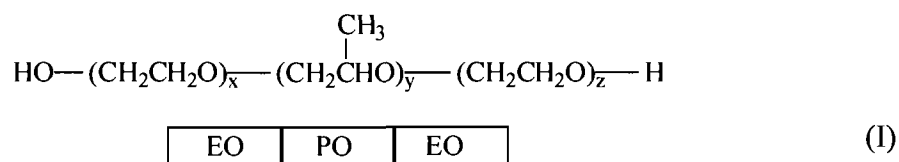
dyes, metal-complex dyes, phthalocyanine dyes, anthraquinone dyes, anthrapyridone dyes, azo dyes, rhodamine dyes, solvent dyes and the like. Specific examples of dyes usable in the present invention include but are not limited to: Acid Yellows, Reactive Yellows, Food Yellows, Acid Reds, Direct
5 Reds, Reactive Reds, Food Reds, Acid Blues, Direct Blues, Reactive Blues, Food Blues, Acid Blacks, Direct Blacks, Reactive Blacks, Food Black, CAS No. 224628-70-0 sold as JPD Magenta EK-1 Liquid from Nippon Kayaku Kabushiki Kaisha; CAS No. 153204-88-7 sold as Intrajet® Magenta KRP from Crompton and Knowles Colors; and the metal azo dyes disclosed in US Patents 5,997,622
10 and 6,001,161. Also useful in the invention as supplemental colorants are polymeric dyes or loaded-dye/latex particles. Examples of polymeric dyes are described in US 6,457,822 and references therein. Examples of loaded-dye/latex particles are described in US 6,431,700; US 2004/0186199; US 2004/0186198; US 2004/0068029; US 2003/0119984; and US 2003/0119938. The supplemental
15 colorants may be present in any effective amount when employed, generally from 0.1 to 10% by weight, and preferably from 0.3 to 5% by weight.

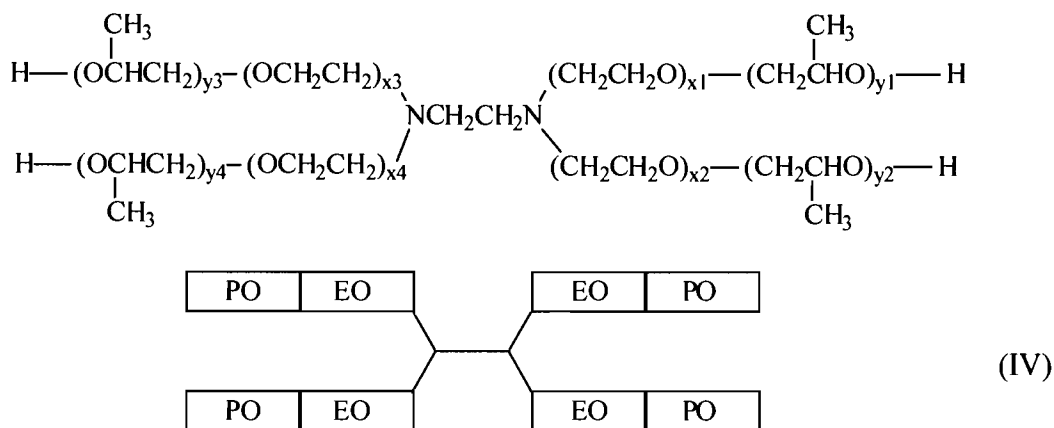
In accordance with this invention, in addition to the pigment dispersion, a water-soluble polymer additive distinct from any dispersant used to disperse the pigment is further employed to increase the stability of the pigment
20 dispersion to shear in a CIJ fluid system. The polymer additive comprises a water soluble block copolymer having one or more poly(ethylene oxide) block segments which in total comprise at least 50 wt% of the polymer additive, where the molecular weight of at least one poly(ethylene oxide) segment of the additive is greater than 500, more preferably at least 1000. The polymer additive additionally
25 comprises from 1 to 50 wt% of segments relatively more hydrophobic than the poly(ethylene oxide) block segments, preferably from 10 to 45wt% of such relatively more hydrophobic segments. The polymer additive preferably has a weight average molecular weight, Mw, of from 1,000 to 100,000, more preferably from 4,000 to 50,000. Such polymer additives may comprise, e.g., one or more
30 poly(ethylene oxide) chains copolymerized with other monomers or attached to another species. In one preferred embodiment, the polymer additive may comprise

a block copolymer of poly(ethylene oxide) and poly(propylene oxide). For example, the polymer additive may comprise an adduct of one or more poly(propylene oxide)-poly(ethylene oxide) block copolymers with another compound or the reaction product of ethylene oxide and/or propylene oxide, to

5 form a blocked copolymer, with another compound. The polymer additive preferably has an HLB value of greater than 16, more preferably of from 20 to 40.

Some examples of preferred types of polymer additives, including architecture with respect to the block copolymer chains, are shown below. Variations in the architecture are also included in the scope of this invention.





In the above structures (I) to (IV), the various subscripts x, y, z, x1, y1, x2, y2, etc. independently represent the number of the ethylene oxide and propylene oxide monomeric units in the formula. Preferably, the relative amounts of the various units (and the various subscript numbers) are selected so that the hydrophilic portion (the ethylene oxide portion) in the compound represents at least 50 weight percent with respect to the total amount of both the hydrophilic and hydrophobic portions (respectively, the ethylene oxide and propylene oxide portions) in the compound. Other examples of polymer additives for use in the present invention include poly (ethylene oxide) containing polyurethanes, poly (ethylene oxide) containing polyesters, and poly (ethylene oxide) covalently attached to an alkyl group and the likes. Preferably the molecular weight of each poly(ethylene oxide) chain is greater than 500, more preferably at least 1000.

The polymer additive is present in the ink jet ink compositions used in the invention in an amount effective to stabilize the ink composition against shear induced agglomeration caused by pumping the ink composition through a continuous ink jet printing fluid system, but not to substantially displace any dispersant used to disperse the pigment in the ink composition. The concentration of the polymer additive material in the ink is typically from 0.05% to 5% by weight, preferably from 0.1% to 3% by weight, more preferably from 0.2% to 1.5% by weight.

The inkjet ink compositions used in the invention are designed specifically for use in a continuous ink jet printer, in which a main fluid supply is provided with the aqueous ink composition, which is then pumped from the main fluid supply to a print head, where a continuous stream of the ink composition is ejected from the print head, which continuous stream then is broken into spaced droplets. In response to electrical signals received from a control mechanism, the droplets are then selected between printing droplets for marking a substrate and nonprinting droplets that are collected and returned to the main fluid supply, as described more fully in the above referenced US 4,734,711, US 5,394,177, EP 1,013,450, US 6,588,888, US 6,943,037, US 4,614,948, and US 4,971,527. In contrast to drop-on-demand printing, CIJ is a very high speed printing process, and it is desired to operate at substrate transport speeds in excess of 200 m/min. Printing speed alone imposes some limitations on ink formulation relative to slower drop-on-demand printing techniques, simply on the basis of the short time requirements for adequately drying the printed substrate moving at full speed in the press before roll wind-up. Surprisingly, features of CIJ printhead operation can allow wider ink formulation latitude than is possible in DOD printing in other respects, however. Ink formulation considerations specific to traditional CIJ printing are described in W. Wnek, *IEEE Trans.* 1986, 1475-81, which elucidates the ink performance requirements for drop formation, deflection and catching of non-printing drops, recirculation of the ink to the printhead from the storage reservoir for future printing, and also for commercial ink-media image quality and durability.

An ink jet ink composition for use in a continuous ink jet printer desirably contains water as the principal vehicle or carrier medium, pigment colorant, humectant, biocide, and surfactant; it can desirably further contain one or more types of other components, including and not limited to a film-forming binder or mordant, a solubilizing agent, a co-solvent, a base, an acid, a pH buffer, a wetting agent, a chelating agent, a corrosion inhibitor, a viscosity modifier, a penetrant, a wetting agent, an antifoamant, a defoamer, an antifungal agent, a jetting aid, a filament length modifier, a trace of multivalent cationic flocculating

salt, a solution conductivity control agent, or a compound for suppressing electrostatic deflection charge shorts when ink dries on the charge ribbon electrodes.

Any water-soluble humectant known in the ink-jet art and compatible with the other requirements of the invention can be employed. By water-soluble is meant that a mixture of the employed humectant(s) and water is homogeneous. While an individual humectant can be employed, useful inkjet inks can employ mixtures of two, three or more humectants, each of which imparts a useful property to the inkjet ink. Representative examples of humectants and co-solvents used in aqueous-based ink compositions include (1) alcohols, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, iso-butyl alcohol, furfuryl alcohol, and tetrahydrofurfuryl alcohol; (2) polyhydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropyleneglycol, the polyethylene glycols with average molecular weights ranging from 200 to 5000 Daltons, the polypropylene glycols with average molecular weights ranging from 200 to 5000 Daltons, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,2,4-butanetriol, 3-methyl-1,3-butanediol, 2-methyl-1,3-propanediol, 1,5-pentanediol, 1,6-hexanediol, 2-methyl-2,4-pentanediol, 1,7-heptanediol, 2-ethyl-1,3-hexane diol, 2,2,4-trimethyl-1,3-pentane diol, 1,8-octane diol, glycerol, 1,2,6-hexanetriol, 2-ethyl-2-hydroxymethyl-propanediol, 2-methyl-2-hydroxymethyl-propanediol, saccharides and sugar alcohols and thioglycol; (3) polyoxygenated polyols and their derivatives such as diglycerol, polyglycerols, glycerol ethoxides, glycerol propoxides, glyceryths, alkylated and acetylated glyceryths, pentaerythritol, pentaerythritol ethoxides, and pentaerythritol propoxides and their alkylated and acetylated derivatives; (4) nitrogen-containing compounds such as urea, 2-pyrrolidone, N-methyl-2-pyrrolidone, imidazolidinone, N-hydroxyethyl acetamide, N-hydroxyethyl-2-pyrrolidinone, 1-(hydroxyethyl)-1,3-imidazolidinone, 1,3-dimethyl-2-imidazolidinone, and 1,3-dihydroxy-2-imidazolidinone; (5) sulfur-containing compounds such as 2,2'-thiodiethanol, dimethyl sulfoxide and

tetramethylene sulfone; and (6) water soluble N-oxides such as 4-methylmorpholine-N-oxides. Of these, glycerol and the polyhydric alcohol derivatives thereof are preferred and glycerol is especially preferred. The polyhydric alcohol derivatives of glycerol include the glycerol ethoxides, glycerol propoxides and glyceryths. The humectant can be employed alone or in combination with one or more additional listed humectants. The useful humectants have melting points below the typical operating temperature of the intended printer system to avoid the formation of crystalline deposits on the printhead or in the maintenance system. Practically, this means that the useful humectants have melting points below 30⁰C, preferably below 20⁰C and more preferably below 10⁰C.

While higher levels are typically preferred for use in drop-on-demand printers, the total humectant level of the ink jet ink composition for CIJ printing in accordance with the present invention is desirably 10% or less by weight, more preferably 8% or less by weight, and most preferably 6% or less by weight. A preferred range of humectant is from 0.5 to 8% by weight, more preferably from 0.5 to 6% by weight. The total humectant level of the ink is the sum of the individual sources of humectant ingredients, which may include humectant added directly during ink formulation, and for example humectant associated with a commercial biocide preparation as a supplemental ingredient, or with a commercial pigment dispersion preparation that may be present to prevent so-called "paint-flakes" of dried pigment cake forming around a bottle cap, as described in U.S. 2005/0075415 A1 to Harz et al. More desirably, the total humectant level is from 1% to less than 10%, in order to facilitate drying of the ink jet printing recording material in a high speed printer while simultaneously encouraging higher equilibrium moisture content in dried ink film on hardware for redispersion and clean-up by ink, or by start-up and shut-down fluids, or by a printhead storage fluid.

The pH of the aqueous ink compositions used in the invention may be adjusted by the addition of organic or inorganic acids or bases. The pH of the ink jet ink composition directed at CIJ is desirably adjusted from 7 to 12; more

desirably, the pH is 8 to 10. When the ink composition is used in hardware with nickel or nickel-plated apparatus components, an anticorrosion inhibitor such as the sodium salt of 4- or 5-methyl-1-H-benzotriazole is desirably added and the pH adjusted to be from 10 to 11. When the ink composition is used with printheads with components fabricated from silicon that are in contact with the fluid, the ink composition pH is desirably adjusted to be from 7 to 9.5; more desirably, the pH ranges from 7.5 to 9. In order to minimize the risk of excessively protonating carboxylate anions associated with polymeric dispersants and anionic charge stabilized anti-abrasion polymers that might render the ink composition more susceptible to flocculation, pH levels lower than 7 are desirably avoided. With hardware components fabricated from silicon in contact with the ink composition, pH levels higher than 10 can induce significant rates of etch and corrosion that may impair the operation of the device over time. Typical inorganic acids include nitric, hydrochloric, phosphoric and sulfuric acids. Typical organic acids include methanesulfonic, acetic, formic and lactic acids. Typical inorganic bases include alkali metal hydroxides and carbonates. Typical organic bases include ammonia, triethanolamine and tetramethylethylenediamine. Amine bases especially desirable in the application of the invention to CIJ printing include 3-amino-1-propanol, N,N-dimethanolamine, N,N-dimethylethanolamine, N,N-diethylethanolamine, and triethanolamine. The well known Goods buffers can also be employed.

The inks used in the invention may contain surfactants added to adjust the static surface tension or dynamic surface tension of the ink to an appropriate level. The surfactants may be anionic, cationic, amphoteric or nonionic and used at, e.g., levels of 0.01 to 5% of the ink composition. Defoaming agents comprised of phosphate esters, polysiloxanes, or acetylenic diols may further optionally be used with the ink compositions directed at CIJ to minimize foam formation caused the fluid agitation associated with drop catching and ink recirculation.

Inkjet ink compositions may also contain non-colored particles such as inorganic particles or polymeric particles. The use of such particulate addenda has increased over the past several years, especially in inkjet ink

compositions intended for photographic-quality imaging. For example, US 5,925,178 describes the use of inorganic particles in pigment-based inks in order to improve optical density and rub resistance of the pigment particles on the image-recording element. In another example, US 6,508,548 describes the use of
5 a water-dispersible polymer in dye-based inks in order to improve light and ozone resistance of the printed images. For use of such particles to improve gloss differential, light and/or ozone resistance, waterfastness, rub resistance and various other properties of a printed image; see for example, US 6,598,967. Colorless ink compositions that contain non-colored particles and no colorant may
10 also be used. Colorless ink compositions are often used in the art as “fixers” or insolubilizing fluids that are printed under, over, or with colored ink compositions in order to reduce bleed between colors and waterfastness on plain paper; see for example, US 5,866,638 or US 6,450,632. Colorless inks are also used to provide an overcoat to a printed image, usually in order to improve scratch resistance and
15 waterfastness; see for example, US 2003/0005945 or EP 1,022,151A1. Colorless inks are also used to reduce gloss differential in a printed image; see for example, US 6,604,819; US 2003/0085974; US 2003/0193553; or US 2003/0189626.

Examples of inorganic particles useful in the invention include, but are not limited to, alumina, boehmite, clay, calcium carbonate, titanium dioxide,
20 calcined clay, aluminosilicates, silica, or barium sulfate.

The non-colored particles used in the ink compositions may be present in any effective amount, generally from 0.01 to 20% by weight, and preferably from 0.01 to 6% by weight. The exact choice of non-colored particles will depend upon the specific application and performance requirements of the
25 printed image.

A biocide may be added to an inkjet ink composition to suppress the growth of microorganisms such as molds, fungi, etc. in aqueous inks. A preferred biocide for an ink composition is PROXEL GXL (Zeneca Specialties Co.) at a final concentration of 0.0001-0.5 wt. % or KORDEK. Additional
30 additives, which may optionally be present in an inkjet ink composition include thickeners, conductivity enhancing agents, drying agents, waterfastness agents,

dye solubilizers, chelating agents, binders, light stabilizers, viscosifiers, buffering agents, anti-mold agents, anti-curl agents, anti-corrosion agents, stabilizers and defoamers.

5 The exact choice of ink components will depend upon the specific application and performance requirements of the printhead from which they are to be jetted. For current continuous ink ejection mode, acceptable viscosities are no greater than 10 cP, preferably in the range of 1.0 to 5.0 cP.

10 In the method of continuous ink jet printing in accordance with the invention, a main fluid supply of a continuous inkjet printer is provided with an aqueous ink composition used in the invention, and the ink composition is pumped from the main fluid supply to a print head. A continuous stream of the ink composition is ejected from the print head, which continuous stream is broken into spaced droplets. In response to electrical signals received from a control mechanism, the spaced droplets are controlled to select between printing droplets
15 for marking a substrate and nonprinting droplets that are collected and returned to the main fluid supply.

In one embodiment of the method used in the invention, the ink jet ink composition for use in a continuous ink jet printer is printed by employing a plurality of drop volumes formed from the continuous fluid stream, with non-
20 printing drops of a different volume than printing drops being diverted by a drop deflection means into a gutter for recirculation, as disclosed in US Patent Numbers 6,588,888, 6,554,410, 6,682,182, and 6,575,566 to Jeanmaire et al.; US Publication No. 2003/0202054 to Jeanmaire et al.; US Patent Numbers 6,793,328 and 6,866,370 to D. Jeanmaire; and US Patent No. 6,517,197 to Hawkins et al. In
25 another preferred embodiment, the ink jet ink composition is printed using an apparatus capable of controlling the direction of the formed printing and non-printing drops by asymmetric application of heat to the fluid stream that initializes drop break-up and serves to steer the resultant drop, as disclosed in US Patent Numbers 6,079,821 and 6,505,921 to Chwalek et al. Useful ink agitation, heated
30 ink supply and printhead and fluid filtration means for CIJ pigmented ink jet ink compositions are described in US Patent No. 6,817,705 to Crockett et al. Printer

replenishing systems for maintaining ink quality and countering the effects of ink volatile component evaporation are described in US Patent No. 5,526,026 to M. Bowers and 5,473,350 to Mader et al., and EP 0 597 628 A1 to Loyd et al.

The following examples illustrate the utility of the present
5 invention.

EXAMPLES

Example 1

10 **Black pigment dispersion K-1**

To a 10-gallon, 13-inch diameter and 17-inch deep, double-walled stainless steel mixing vessel containing four baffles was added 2,560 g water and 2,240 g of a 15% solution of potassium hydroxide-neutralized dispersant copolymer prepared from benzyl methacrylate, stearyl methacrylate, and
15 methacrylic acid at the feed ratio of 45:30:25 by weight, and having an average molecular weight M_w of 8,070 (polymer P-1). A nominal 6-inch, ring-style disperser impeller (Hockmeyer Equipment Corp. D-Blade) driven by a Hockmeyer Model HBI-7.5-11-99 High Shear Mixer was centered 3 inches above the bottom of the mixing vessel, and stirring was initiated. CABOT BLACK PEARLS 880
20 carbon black pigment (1,200 g) was slowly integrated into the fluid. Milling media comprising beads of polystyrene resin (copolymer of styrene and divinylbenzene/ethylvinylbenzene mixture) with an average particle diameter of 50 micrometers (7,200 g) was added slowly while increasing impeller speed. The mixture was milled with an impeller blade tip speed of ca. 20 meter/second for 20
25 hours at an internal temperature of 25 – 30 °C. The dispersion/media mixture was further diluted with water (5,940 g) and biocide KORDEK MLX (available from Rohm and Haas Co., 60 g) to a final pigment concentration of 10% and polymer P-1 2.8%. The impeller was removed from the mixture, and the dispersion was separated from the milling media. A final filtration through a 0.3-micrometer
30 removal efficiency Pall Corp. Profile II® depth filter yielded roughly 10.6 kg of dispersion. The dispersion has a medium particle size of 60 nanometers as characterized by Nanotrac Auto Sampler NAS35 (Nanotrac Inc., Nanotrac Brand).

Black pigment dispersion K-2

Black pigment dispersion 2 was prepared very similar to Black dispersion K-1, except CABOT BLACK PEARLS 900 was used in place of
5 CABOT BLACK PEARLS 880. The dispersion has a medium particle size of 48 nanometers as characterized by Nanotracs Auto Sampler NAS35.

Black pigment dispersion K-3

Black pigment dispersion 3 was prepared very similar to Black
10 dispersion K-1, except surfactant potassium oleylmethylsulfate (KOMT) was used in place of polymer P-1 at 25% by weight based on pigment. The dispersion has a medium particle size of 65 nanometers as characterized by Nanotracs Auto Sampler NAS35.

15 Ink Preparation

Inks were prepared according to the formulas listed in Table 1 (percents are weight percents). All components employed, except for the pigments, were water soluble at the quantities used.

Water soluble materials used in the inks in Table-1 are:

20 P-1: the polymer dispersant used for pigment dispersions K-1 and K-2. It is a terpolymer of benzyl methacrylate, stearyl methacrylate, and methacrylic acid at the feed ratio of 45:30:25 by weight, and having an average molecular weight Mw of 8,070), 90% of the acid was neutralized by potassium hydroxide.

P-2: Tetronic® 908, available from BASF, a block copolymer of 80%
25 polyethylene oxide and 20% polypropylene oxide, having Mn of 13,400 and Mw of 19,200.

High Shear Stability Test - A

600 ml of ink was re-circulated in a gear pump manufactured by
30 Diener Precision Pumps (PM0113 Rev0) with 13.5 mm diameter PEEK helical gears for 6 hours at a flow rate of approximately 1000 cc/minute. 370 cc of the

recirculated ink was then tested for its ability to pass through a 25 mm 3 μ m Versapor filter at the vacuum level of 3" \pm 0.5"Hg. The volume of ink passed through the filter was measured volumetrically and the ratio of volume passed through the filter to the original volume is calculated to be "percentage of ink passed through the filter". All inks were tested for the same filterability prior to high shear test, and they all had 100% ink passed through the filter.

Table 1

Ink ID	Pigment concentration (Dispersion)	Additive	Percentage of ink passed through the filter
1-1 (comparison)	5% (K-1)	None	6.8%
1-2 (comparison)	5% (K-1)	1% P-1	13.5%
1-3 (comparison)	5% (K-2)	None	8.1%
1-4 (comparison)	5% (K-3)	None	9.5%
1-5 (invention)	5% (K-3)	1% P-2	28.6%

As shown in Table 1, dispersions without additional additive (1-1, 1-3, and 1-4) were badly agglomerated and would not pass through the filter after the recirculation in the gear pump. Ink 1-2 is an example of adding the same polymer dispersant to the ink would not help stabilizing the dispersion very much. Ink 1-5 of this invention significantly improved the dispersion stability against high shear, and thus a significantly higher percentage of the ink would pass through the filter.

Example 2

Cyan pigment dispersion C-1

Cyan pigment dispersion C-1 was prepared very similar to Black pigment dispersion K-1, except Pigment Blue 15:3 was used in place of Cabot Black Pearls 900 and polymer dispersant P-3 (a terpolymer of benzyl methacrylate, stearyl methacrylate, and methacrylic acid at the feed ratio of 37/30/33 by weight, 100% of acid was neutralized with dimethylaminoethanol after polymerization, the final polymer having an average molecular weight Mw of 8,950) was used in place of P-1. The resulting dispersion has approximately 10%

pigment and 2.8% polymer dispersant. The mean particle size is 21 nm as characterized by Nanotracs Auto Sampler NAS35.

Cyan pigment dispersion C-2

5 Cyan pigment dispersion C-2 was prepared very similar to C-1, except polymer dispersant P-3 (description above) was used at 40% based on the weight of pigment. The resulting dispersion has approximately 10% pigment and 4% polymer dispersant. The mean particle size is 21 nm as characterized by Nanotracs Auto Sampler NAS35.

10

Ink Preparation

 Inks were prepared according to the formulas listed in Table 2 (percents are weight percents). In addition, each one also contained glycerol at 5%, SURFYNOL 465 (available from Air Products) at 0.02%, Cobratec TT-50S
15 (available from PMC Specialties) at 0.1% and Proxel GXL (available from Arch Chemical) at 0.1% by weight. All components employed, except for the pigments, were water soluble at the quantities used. HLB values were available from the respective product literatures.

 Water soluble materials used in the inks in Table-2 are:

20 P-4: SOLSPERSE 46000 from Lubrizol, a polyurethane of isophorone diisocyanate and poly(ethylene oxide) having a Mw of 4,510. The weight percentage of poly(ethylene oxide) is 50%.

 P-5: Pluronic F88 available from BASF, a block copolymer of 80% polyethylene oxide and 20% polypropylene oxide, having a Mn of 8,570 and Mw
25 of 10,000.

 P-6: Pluronic L44 available from BASF, a block copolymer of 40% polyethylene oxide and 60% polypropylene oxide, having a Mn of 2110 and Mw of 2680.

 P-7: Pluronic P84 available from BASF, a block copolymer of 40% polyethylene oxide and 60% polypropylene oxide, having a Mn of 3950 and Mw
30 of 4830.

High Shear Stability Test – B

When pigment inks are destabilized by recirculation through a gear pump, the average pigment particle size increases. The increase may be small, and
 5 may be difficult to detect using commercially available particle size measurement instrumentation, but it can be readily detected and quantified through simple measurements of the transmission of near infrared radiation through the ink.

When a collimated beam of radiation traverses a suspension of particles, some of the radiation is scattered and the intensity of the beam is
 10 reduced. The process is analogous to that of light absorption, and the coefficient that describes it is generally denoted as turbidity τ :

$$\tau = \frac{1}{l} \log\left(\frac{I_0}{I}\right) \quad \text{or} \quad \tau = \frac{OD}{l} \log(10)$$

where OD denotes optical density, which is the quantity actually measured, and l is the optical pathlength of the suspension. The magnitude of the turbidity
 15 depends on the optical properties of the suspension and of the concentration of particles in it. But, for particles that are smaller than or similar in size to the radiation wavelength, it depends strongly on their size. Turbidimetry, a simple and inherently precise technique, can thus be used to provide a measure of an average particle size that is very sensitive to small changes in that average.

20 In designing a turbidimeter suitable for monitoring ink pigment particle size, primary consideration was given to the selection of the radiation wavelength. For ease of data interpretation the wavelength needed to be long compared to the particle size, but not so long that the measured optical density (which varies with wavelength to the inverse 3rd power) was unmeasurably small.
 25 It was also important to select a wavelength that was not absorbed by the pigment. In our work we made use of collimated diode laser modules as radiation sources. Studies of yellow and magenta inks made use of 830nm lasers; studies of cyan inks made use of a 965nm lasers. Each laser was installed in a compact turbidimetric instrument that was also fitted with an optical cell to contain the ink,
 30 and a silicon photodiode light detector to measure the transmitted light intensity.

The turbidimeter was interfaced to a computer capable of recording this intensity and converting it to optical density.

The pathlength of the cell was selected according to the pigment concentration to give optical densities in the range 0.1 to 1. This is the range that
5 can be measured with optimum precision. In our work we used flow cells with pathlengths in the range 1mm to 5mm. At the selected wavelengths and pathlengths, our inks could be measured without the need for dilution.

A system was designed to be capable of in-line monitoring of gear pump induced destabilization of inks. This system comprised a small reservoir to
10 contain the ink sample, a gear pump, and a turbidimeter, all connected in a recirculation loop. The volume of ink required to fill the system was minimized in order to maximize the destabilization effect for a given pump at a given flow rate. The loop made use of tubing with a 1/16" internal diameter. The reservoir volume was 20mL. The total system volume was 30mL. The gear pumps used were
15 Micropump Model 180s. The recirculation flow rate was 150mL/minute.

Before pumping ink through the flow cell, it was filled with water so that a baseline reading of the transmitted light intensity could be obtained by the computer. The system was then filled with ink and the pump was turned on. The computer then continuously monitored the optical density, displayed it as a
20 chart of optical density vs. time, and saved these data in a file.

It was typical for the optical density to increase linearly with time. This linear behavior often extended over long time periods and over large increases in the measured optical density. The initial slope of the trace (normally obtained by fitting a straight line through the data collected over the first 2 hours
25 and expressed in milliabsorbance units per hour) was used as the relative measure of the ink's gear pump stability. The most stable inks had slopes that were not distinguishable from zero. The least stable inks had slopes as high as 100mAU/hour.

Table 2

Ink ID	Pigment concentration (Dispersion)	Additive	HLB of additive	Rate of OD increase (mAU/Hour)
2-1 (comparison)	4% (C-1)	None		38.3
2-2 (comparison)	4% (C-2)	None		26.8
2-3 (invention)	4% (C-1)	0.8% P-4		1.3
2-4 (invention)	4% (C-1)	0.8% P-5	28	2.2
2-5 (invention)	4% (C-1)	0.8% P-2	31	3.7
2-6 (comparison)	4% (C-1)	0.8% P-3		24.8
2-7 (comparison)	4% (C-1)	0.8% P-6	16	29.9
2-8 (comparison)	4% (C-1)	0.8% P-7	15	32.0

As shown in Table 2, cyan pigment dispersion C-1 having 28% by weight of dispersant polymer based on pigment had very poor stability against high shear force in gear pump. C-2 with increased level of dispersant P-3 to 40% only improved stability slightly, as indicated by lower rate of OD increase. Ink 2-6 is an example where additional polymer P-3 was added after dispersing the pigment, and only a very small improvement was recognized. Inks of this invention significantly improved the dispersion stability against high shear, and thus the rate of OD increase was almost not detectable.

Example 3

Magenta pigment dispersion M-1

Magenta pigment dispersion M-1 was prepared very similar to cyan pigment dispersion C-1, same polymer dispersant P-3 was used. CIBA CROMOPHTAL Jet Magenta 2BC was used in place of Pigment blue 15:3. The final pigment dispersion contained 10% pigment and 2.8% P-3. Dispersion has a medium particle size of 15 nanometers as characterized by Nanotracer Auto Sampler NAS35.

Ink Preparation

Inks were prepared according to the formulas listed in Table 4 (in weight percents). In addition, each one also contained glycerol at 5%,

- 5 SURFYNOL 465 (available from Air Products) at 0.02%, Cobratec TT-50S (available from PMC Specialties) at 0.1% and Proxel GXL (available from Arch Chemical) at 0.1% by weight. All components employed, except for the pigments, were water soluble at the quantities used.

Inks were tested for high shear stability as described in Example 2.

- 10 The data is also shown in Table 3.

Table 3

Ink ID	Pigment concentration (Dispersion)	Additive	Rate of OD increase (mAH/Hour)
3-1 (comparison)	4% (M-1)	None	14.9
3-2 (comparison)	4% (M-1)	0.8% P-3	5.0
3-3 (invention)	4% (M-1)	0.8% P-4	0.8

- As shown in Table 4, increasing the level of pigment dispersant P-3 is not as effective as adding the additive of this invention to stabilize the pigment dispersion.
- 15

Example 4

Yellow pigment dispersion Y-1

- 20 Yellow pigment dispersion Y-1 was prepared very similar to cyan pigment dispersion C-1, except that polymer dispersant P-8 (terpolymer of benzyl methacrylate, stearyl methacrylate, and methacrylic acid at the feed ratio of 37/30/33 by weight, 90% of acid was neutralized with potassium hydroxide after polymerization, the final polymer had an average molecular weight Mw of 8,410)
- 25 and yellow pigment PY74 (grade 272-5147 from Sun Chemical) were used. The final pigment dispersion contained 10% pigment and 3% P-8. Dispersion has a medium particle size of 12 nanometers as characterized by Nanotracer Auto Sampler NAS35.

Ink Preparation

Inks were prepared according to the formulas listed in Table 4 (in weight percents). In addition, each one also contained glycerol at 5%,

- 5 SURFYNOL 465 (available from Air Products) at 0.02%, Cobratec TT-50S (available from PMC Specialties) at 0.1%, and Proxel GXL (available from Arch Chemical) at 0.1% by weight. All components employed, except for the pigments, were water soluble at the quantities used.

Inks were tested for high shear stability as described in Example 2.

- 10 The data is also shown in Table 4.

P-9, PLURONIC 38 (available from BASF), is a block copolymer of 80% polyethylene oxide and 20% polypropylene oxide, having Mn of 4,020 and Mw of 4,500.

15 **Table 4**

Ink ID	Pigment concentration (Dispersion)	Additive	HLB of additive	Rate of OD increase (mAH/Hour)
4-1 (comparison)	4% (Y-1)	None		22.4
4-2 (invention)	4% (Y-1)	0.8% P-4		9.9
4-3 (invention)	4% (Y-1)	0.8% P-5	28	7.0
4-4 (invention)	4% (Y-1)	0.8% P-9	25	9.4
4-5 (comparison)	4% (Y-1)	0.8% Surfynol ® 465	13	19.1

As demonstrated in Table 4, the inks of this invention 4-2 to 4-4 are much more stable against high share force in gear pump, and thus the OD increase is much reduced.

20

CLAIMS:

1. A continuous ink jet printer aqueous ink composition comprising pigment particles dispersed with a dispersant or self dispersing pigment particles
5 without the need for a dispersant, and a polymer additive distinct from any dispersant used to disperse the pigment particles, wherein the polymer additive comprises a water soluble block copolymer having one or more poly(ethylene oxide) block segments which in total comprise from 50 to 99 wt% of the polymer additive, and from 1 to 50 wt% of segments relatively more hydrophobic than the
10 poly(ethylene oxide) block segments, where the molecular weight of at least one poly(ethylene oxide) segment of the additive is greater than 500, and wherein the polymer additive is present in an amount effective to stabilize the ink composition against shear induced agglomeration caused by pumping the ink composition through a continuous ink jet printing fluid system.
- 15
2. A continuous ink jet printer aqueous ink composition according to claim 1, wherein the polymer additive comprises a block copolymer of polyethylene oxide and polypropylene oxide.
- 20
3. A continuous ink jet printer aqueous ink composition according to claim 2, wherein the polymer additive has an HLB value of greater than 16.
4. A continuous ink jet printer aqueous ink composition according to claim 1, wherein the polymer additive comprises a poly(ethylene oxide) block
25 containing polyurethane polymer.
5. A continuous ink jet printer aqueous ink composition according to claim 1, wherein the polymer additive has an HLB value of greater than 16.
- 30
6. A continuous ink jet printer aqueous ink composition according to claim 1, wherein the pigment is dispersed with a dispersant.

7. A continuous ink jet printer aqueous ink composition according to claim 6, wherein the pigment comprises carbon black.

5 8. A continuous ink jet printer aqueous ink composition according to claim 6, wherein the pigment comprises a cyan, a magenta, or a yellow colored pigment.

9. A continuous ink jet printer aqueous ink composition according to claim 6, wherein the dispersant is a polymeric dispersant.
10

10. A continuous ink jet printer aqueous ink composition according to claim 6, wherein the dispersant is a non-polymeric dispersant.

11. A continuous ink jet printer aqueous ink composition according to claim 1, comprising 10 or less percent by weight of humectant.
15

12. A continuous ink jet printer aqueous ink composition according to claim 1, comprising 8 or less percent by weight of humectant.

13. A continuous ink jet printer aqueous ink composition according to claim 1, comprising 6 or less percent by weight of humectant.
20

14. A continuous ink jet printer aqueous ink composition according to claim 1, comprising from 0.05 to 5 percent by weight of the polymer additive.
25

15. A continuous ink jet printer aqueous ink composition according to claim 1, comprising from 0.1 to 3 percent by weight of the polymer additive.

16. A method of continuous ink jet printing comprising:

A) providing a main fluid supply of a continuous inkjet printer with an aqueous ink composition according to claim 1;

5 B) pumping the ink composition from the main fluid supply to a print head and ejecting a continuous stream of the ink composition from the print head which continuous stream is broken into spaced droplets; and

C) in response to electrical signals received from a control mechanism, controlling the spaced droplets to select between printing droplets for marking a substrate and nonprinting droplets that are collected and returned to the
10 main fluid supply.

17. A method of continuous ink jet printing according to claim 16, wherein the polymer additive comprises a block copolymer of polyethylene oxide and polypropylene oxide having an HLB value of greater than 16.

15

18. A method of continuous ink jet printing according to claim 16, wherein the polymer additive comprises a poly(ethylene oxide) block containing polyurethane polymer.

20 19. A method of continuous ink jet printing according to claim 16, wherein the ink composition is pumped from the main fluid supply to the print head through a positive displacement pump.

25 20. A method of continuous ink jet printing according to claim 19, wherein the positive displacement pump is a gear pump.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/055888

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D11/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D

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)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/182280 A1 (KOGA NARUMI [JP] ET AL) 23 September 2004 (2004-09-23) column 48; table b3 -----	1-20
X	US 6 406 143 B1 (CHEN TIEN-TEH [US] ET AL) 18 June 2002 (2002-06-18) column 3, lines 63-65; claims -----	1-20
X	US 6 008 270 A (SANTILLI DOMENIC [US]) 28 December 1999 (1999-12-28) column 4, lines 9-11; examples -----	1-20
X	WO 03/066743 A1 (BASF AG [DE]; REISACHER HANSULRICH [DE]; GONZALEZ GOMEZ JUAN ANTONIO []) 14 August 2003 (2003-08-14) page 7, line 25ff; examples 14-17 page 9, lines 23-41 ----- -/--	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

7 February 2011

Date of mailing of the international search report

17/02/2011

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/055888

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	EP 2 223 980 A1 (DAINIPPON INK & CHEMICALS [JP]) 1 September 2010 (2010-09-01) paragraphs [0014], [0031]; example 1	1-20
X	& WO 2009/066577 A1 (DAINIPPON INK & CHEMICALS [JP]; ENOMOTO YUUYA [JP]; YASUI KENGO [JP];) 28 May 2009 (2009-05-28) the whole document -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/055888

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004182280	A1	23-09-2004	NONE
US 6406143	B1	18-06-2002	NONE
US 6008270	A	28-12-1999	EP 0780451 A2 25-06-1997 JP 9176544 A 08-07-1997
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