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(54) **Title**: INKJET INK SET FOR PRINTING ON OFFSET MEDIA

(57) **Abstract**: The present disclosure provides an ink set containing aqueous inkjet inks. The ink set is particular suitable for printing on offset media.

TITLE

INKJET INK SET FOR PRINTING ON OFFSET MEDIA

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority under 35 U.S.C. §119 from U.S. Provisional Application Serial No. 62/094141, filed December 19, 2014, which is incorporated by reference in its entirety.

BACKGROUND OF THE DISCLOSURE

This disclosure pertains to an ink set containing aqueous inkjet inks. The ink set is particular suitable for printing on offset media.

Inkjet printing is a non-impact printing process in which droplets of ink are deposited on a substrate, such as paper, to form the desired image. Inkjet printers are equipped with an ink set which, for full color printing, typically comprises a cyan, magenta and yellow ink (CMY). An ink set also typically comprises a black ink (CMYK) with the black ink being the most common ink.

Coated media traditionally has been printed with inks that are very high in viscosity and/or are solvent-based inks. Aqueous inkjet inks are usually low in viscosities resulting in greater mobility of pigments during drying. In addition, aqueous inkjet ink requires longer de-wetting time after printing on hydrophobic coated media. Thus, aqueous inkjet inks often have poor image quality such as mottle from non-uniform deposition of colorant and low color when printed on coated media.

Bleed of one color into another is a typical problem in ink jet printing especially for inkjet printers having capability of printing three or four primary colors in a simultaneous (or near simultaneous) fashion. Such bleed of one printing liquid into an adjacent printing liquid results in production of indistinct images with a poor degree of resolution. Controlling intercolor bleed is thus critical to the quality of the printed image. This is particularly difficult to achieve when printing on coated offset media where drying of the ink is slow due to low porosity of the papers. The long duration of inks remain fluid leads to greater difficulty in preventing mixing.

A need still exists for aqueous inkjet ink that can be printed on offset media with minimum intercolor bleed. The present disclosure satisfies this need by providing an ink set where each ink in the ink set contains a non-ionic surfactant and a polymeric binder.

SUMMARY OF THE DISCLOSURE

An embodiment provides an inkjet ink set for printing on offset media, said ink set comprising a magenta, a yellow, a cyan, and a black ink, wherein each of the inks in said ink set is independently comprised of a colorant, an aqueous vehicle, a polymeric binder, a nonionic surfactant, and optionally an 1,2-alkanediol, wherein said polymeric binder is dispersed in said aqueous vehicle, and wherein said inkjet ink is printed directly onto said offset media without any pretreatment/precoating of said offset media.

Another embodiment provides that the ink set is used for fixed array printing.

Another embodiment provides that the ink set has a discharge from printhead frequency of 20 kHz or greater.

Another embodiment provides that the ink has a surface tension of between 18 and 35 dyne/cm.

Another embodiment provides that one or more of said colorant is a self-dispersing pigment.

Another embodiment provides that one or more of said colorant is dispersed by a polymeric dispersant.

Another embodiment provides that the non-ionic surfactant is a fluorosurfactant.

Another embodiment provides that the non-ionic surfactant is a non-fluorosurfactant.

Yet another embodiment provides that the non-fluorosurfactant has a HLB value of less than 5.

These and other features and advantages of the present embodiments 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 disclosed embodiments which are, for clarity, described above and below as separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the disclosed embodiments that are described in the context of a single embodiment, may also be provided separately or in any subcombination.

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 disclosure pertains.

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

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.

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.

As used herein, the term "dispersion" means a two phase system wherein one phase consists of finely divided particles (often in a colloidal size range) distributed throughout a bulk substance, 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 sizes. For pigments, the dispersants are most often polymeric dispersants, and the dispersants and pigments are usually combined using a dispersing equipment.

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 "substantially" means being of considerable degree, almost all.

As used herein, the term "dyne/cm" means dyne per centimetre, a surface tension unit.

As used herein, the term "cP" means centipoise, a viscosity unit.

The materials, methods, and examples herein are illustrative only except as explicitly stated, and are not intended to be limiting.

Aqueous Vehicle

Selection of a suitable aqueous vehicle mixture depends on requirements of the specific application, such as the desired surface tension and viscosity, the selected colorant, drying time of the ink, and the type of substrate onto which the ink will be printed. Representative examples of water-soluble organic solvents which may be utilized in the present disclosure are those that are disclosed in U.S. Patent No. 5,085,698.

If a mixture of water and a water-soluble solvent is used, the aqueous vehicle typically will contain about 30 % to about 95 % of water with the remaining balance (i.e.,

about 70 % to about 5 %) being the water-soluble solvent. Compositions of the present disclosure may contain about 60 % to about 95 % water, based on the total weight of the aqueous vehicle.

The amount of aqueous vehicle in the ink is typically in the range of about 70 % to about 99.8 %; specifically about 80 % to about 99.8 %, based on total weight of the ink.

Surfactants may be used, typically in an amount of from about 0.01 % to about 5%, and specifically from about 0.2 % to about 2 %, based on the total weight of the ink.

Pigments

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. The colorant also includes dispersed dyes. The dispersion process results in a stable dispersed pigment.

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 water-wet presscake. In presscake form, the pigment does not agglomerate to the extent it would 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: 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, 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 Violet 38; white pigments such as TiO_2 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.

The pigment of the present disclosure can also be a self-dispersing (or self-dispersible) pigment. The term self-dispersing pigment (or "SDP") refers to pigment

particles whose surface has been chemically modified with hydrophilic, dispersability-imparting groups that allow the pigment to be stably dispersed in an aqueous vehicle without a separate dispersant. "Stably dispersed" means that the pigment is finely divided, uniformly distributed and resistant to particle growth and flocculation.

The SDPs may be prepared by grafting a functional group or a molecule containing a functional group onto the surface of the pigment, by physical treatment (such as vacuum plasma), or by chemical treatment (for example, oxidation with ozone, hypochlorous acid or the like). A single type or a plurality of types of hydrophilic functional groups may be bonded to one pigment particle. The hydrophilic groups are carboxylate or sulfonate groups which provide the SDP with a negative charge when dispersed in aqueous vehicle. The carboxylate or sulfonate groups are usually associated with monovalent and/or divalent cationic counter-ions. Methods of making SDPs are well known and can be found, for example, in US5554739 and US6852156.

The SDPs may be black, such as those based on carbon black, or may be colored pigments. Examples of pigments with coloristic properties useful in inkjet inks include: Pigment Blue 15:3 and Pigment Blue 15:4 (for cyan); Pigment Red 122 and Pigment Red 202 (for magenta); Pigment Yellow 14, Pigment Yellow 74, Pigment Yellow 95, Pigment Yellow 110, Pigment Yellow 114, Pigment Yellow 128 and Pigment Yellow 155 (for yellow); Pigment Orange 5, Pigment Orange 34, Pigment Orange 43, Pigment Orange 62, Pigment Red 17, Pigment Red 49:2, Pigment Red 112, Pigment Red 149, Pigment Red 177, Pigment Red 178, Pigment Red 188, Pigment Red 255 and Pigment Red 264 (for red); Pigment Green 1, Pigment Green 2, Pigment Green 7 and Pigment Green 36264 (for green); Pigment Blue 60, Pigment Violet 3, Pigment Violet 19, Pigment Violet 23, Pigment Violet 32, Pigment Violet 36 and Pigment Violet 38 (for blue); and carbon black. However, some of these pigments may not be suitable for preparation as SDP. Colorants are referred to herein by their "C.I.".

The SDPs of the present disclosure may have a degree of functionalization wherein the density of anionic groups is less than about 3.5 μmoles per square meter of pigment surface (3.5 $\mu mol/m^2$), and more specifically, less than about 3.0 $\mu mol/m^2$. Degrees of functionalization of less than about 1.8 $\mu mol/m^2$, and more specifically, less than about 1.5 $\mu mol/m^2$, are also suitable and may be preferred for certain specific types of SDPs.

The range of useful particle size after dispersion is typically from about 0.005 micrometers to about 15 micrometers. Typically, the pigment particle size should range

from about 0.005 micrometers to about 5 micrometers; and, specifically, from about 0.005 micrometers to about 1 micrometers. The average particle size as measured by dynamic light scattering is less than about 500 nm, typically less than about 300 nm.

The amount of pigment present in the ink is typically in the range of from about 0.1 % to about 25 % by weight, and more typically in the range of from about 0.5 % to about 10 % by weight, based on the total weight of ink. 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.

Polymeric Dispersant

The polymeric dispersant for the non-self-dispersing pigment(s) may be a random or a structured polymer. Typically, the polymer dispersant is a copolymer of hydrophobic and hydrophilic monomers. The "random polymer" means polymers where molecules of each monomer are randomly arranged in the polymer backbone. For a reference on suitable random polymeric dispersants, see: U.S. Patent No. 4,597,794. The "structured polymer" means polymers having a block, branched, graft or star structure. Examples of structured polymers include AB or BAB block copolymers such as the ones disclosed in U.S. Patent No. 5,085,698; ABC block copolymers such as the ones disclosed in EP Patent Specification No. 0556649; and graft polymers such as the ones disclosed in US Patent No. 5,231,131. Other polymeric dispersants that can be used are described, for example, in U.S. Patent No. 6,117,921, U.S. Patent No. 6,262,152, U.S. Patent No. 6,306,994 and U.S. Patent No. 6,433,117.

The "random polymer" also includes polyurethanes. Particularly useful are the polyurethane dispersant disclosed in U.S. Patent Application Publication No. 2012/0214939 where the polyurethane dispersant is crosslinked after dispersing a pigment to form a pigment dispersion.

Polymeric Binder

The ink of the present disclosure can contain polymeric binder. Typically the polymeric binder is a polyurethane such as the ones described in publication WO 2009/143418. The binder of the present disclosure also include the cross-linked polyurethane binders disclosed in U.S. Patent Application Publication No. 20050182154, which is incorporated by reference herein as if fully set forth, under the section entitled "Polyurethane Dispersoid Binders (PUDs)". Typically a binder is different from the polyurethane dispersant described above and non-reactive to the colorant. The binder is

typically added to an ink during the final formulation stage, not during the preparation of a pigment dispersion.

Other Additives

Other ingredients, additives, may be formulated into the inkjet ink, to the extent that such other ingredients do not interfere with the stability and jettability of the inkjet ink. This may be readily determined by routine experimentation by one skilled in the art.

Surfactants are commonly added to inks to adjust surface tension and wetting properties. Suitable surfactants include the ones disclosed in the Vehicle section above. Surfactants are typically used in amounts up to about 3 % and more typically in amounts up to 1 % by weight, based on the total weight of the ink.

Inclusion of sequestering (or chelating) agents such as ethylenediaminetetraacetic acid, iminodiacetic acid, ethylenediamine-di(o-hydroxyphenylacetic acid), nitrilotriacetic acid, dihydroxyethylglycine, trans-1,2- cyclohexanediaminetetraacetic acid, diethylenetriamine-N,N,N',N",N"-pentaacetic acid, and glycoletherdiamine-N,N,N',N'-tetraacetic acid, and salts thereof, may be advantageous, for example, to eliminate deleterious effects of heavy metal impurities.

Polymers may be added to the ink to improve durability or other properties. The polymers can be soluble in the vehicle or in a dispersed form, and can be ionic or nonionic. Soluble polymers include linear homopolymers and copolymers or block polymers. They also can be structured polymers including graft or branched polymers, stars and dendrimers. The dispersed polymers may include, for example, latexes and hydrosols. The polymers may be made by any known process including, but not limited to, free radical, group transfer, ionic, condensation and other types of polymerization. They may be made by a solution, emulsion, or suspension polymerization process. Typical classes of polymer additives include anionic acrylic, styrene-acrylic and polyurethane polymer.

When a polymer is present, its level is typically between about 0.01 % and about 10 % by weight, based on the total weight of an ink. The upper limit is dictated by ink viscosity or other physical limitations.

Ink Sets

The term "ink set" refers to all the individual inks or other fluids an inkjet printer is equipped to jet. Ink sets typically comprise at least three differently colored inks. For example, a cyan (C), magenta (M) and yellow (Y) ink forms a CMY ink set. More typically, an ink set includes at least four differently colored inks, for example, by adding a

black (K) ink to the CMY ink set to form a CMYK ink set. The magenta, yellow and cyan inks of the ink set are typically aqueous inks, and may contain dyes, pigments or combinations thereof as the colorant. Such other inks are, in a general sense, well known to those of ordinary skill in the art.

In addition to the typical CMYK inks, an ink set may further comprise one or more "gamut-expanding" inks, including differently colored inks such as an orange ink, a green ink, a red ink and/or a blue ink, and combinations of full strength and light strength inks such as light cyan and light magenta. Such other inks are, in a general sense, known to one skilled in the art.

A typical ink set comprises a magenta, yellow, cyan and black ink, wherein the black ink is an ink according to the present disclosure comprising an aqueous vehicle and a self-dispersing carbon black pigment. Specifically, the colorant in each of the magenta, yellow and cyan inks is a dye.

Ink Properties

Jet velocity, separation length of the droplets, drop size and stream stability are greatly affected by the surface tension and the viscosity of the ink. Pigmented ink jet inks typically have a surface tension in the range of about 20 dyne/cm to about 45 dyne/cm at 25 °C. Viscosity can be as high as 30 cP at 25 °C, but is typically much lower, more typically less than 10 cP at 25 °C. The ink has physical properties compatible with a wide range of ejecting conditions, i.e., driving frequency of the piezo element or ejection conditions for a thermal head for either a drop-on-demand device or a continuous device, and the shape and size of the nozzle. The inks should have excellent storage stability for long periods so as not to clog to a significant extent in an ink jet apparatus. Furthermore, 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.

Although not restricted to any particular viscosity range or printhead, the inventive ink set is particularly suited to lower viscosity applications such as those required by thermal printheads. Thus the viscosity of the inventive inks at 25 °C can be less than about 7 cP, typically less than about 5 cP, and more typically than about 3.5 cP. Thermal inkjet actuators rely on instantaneous heating/bubble formation to eject ink drops and this mechanism of drop formation generally requires inks of lower viscosity.

Substrate

The inks of the present disclosure can be printed on common print substrate such as paper and textile. The inks of the present disclosure is most advantageous for printing on low porosity media such as offset paper and coated paper.

Offset paper and coated paper are generally known to have poor receptivity to aqueous ink jet inks. These papers have low surface porosity due to calendaring and/or application of one or more layers of hydrophobic coating layers. Such surface smoothing procedures and coatings provide papers that can withstand the high tack of traditional printing paste and/or be receptive to hydrophobic toner particles. However, the resultant low porosity means less channels for the ink vehicle to access which results in a greater dependency on ink drying by evaporation. Furthermore, the hydrophobic nature of the coating layers cause reduced wetting out and spreading out of an aqueous inks upon printing which can then lead to puddling of ink drops on the media surface. The combined effect of less dot spread and slower drying leads to many more image defects when printing aqueous inks directly on offset media. The most obvious defects include non-uniform deposition of colorants on these media. These non-uniform deposition of colorants defects are known variously as mottle or coalescence or framing or edge of the square effect. Another equally unacceptable outcome due to hydrophobicity and low porosity of offset media is increased drying time of an ink which translates to increased time for adjacent colors to co-mingle leading to inter-color bleed where one color diffuses into its neighboring color. These image defects can be mitigated by application of a chemical pre-coating or pre-treatment, often colorless, that interacts with the wet ink drops to immobilize the colorants. Being immobilized chemically, the image defects of non-uniform coloration or movement of colorants in inter-color bleed can be resolved effectively. However, use of pre-coats and pre-treatments have many disadvantages including increased cost of materials, drying energy and lowered gloss and even lowered durability of the image. Thus there is a great need to being able to achieve good color uniformity and good inter-color bleed through attention to formulation of the inks that can eliminate the need for pre-coating. The ink formulations of the present disclosure allow direct printing of aqueous inks, without necessitating the application of pre-coating or pre-treatment, on offset media.

EXAMPLES

The invention is further illustrated by, but not limited to, the following examples, in which parts and percentages are by weight unless otherwise noted.

Cyan Pigment Dispersion C

Dispersion C was prepared according to procedure disclosed in U.S. Patent Application Publication No. 2012/0214939, the disclosure of which is incorporated by reference herewith for all purposes as if fully set forth. A cyan TRB2 pigment was employed, and the dispersant was crosslinked after dispersing the pigment.

Yellow Pigment Dispersion Y

Dispersion Y was prepared in a similar fashion as Dispersion A with the exception of using yellow pigment PY74.

Magenta Pigment Dispersion M

Dispersion M was prepared in a similar fashion as Dispersion A with the exception of using magenta pigment PR122.

Polymer Binder 1

This binder was prepared according to the same procedure disclosed in U.S. Patent Application Publication No. 2005/0215663 (incorporated by reference herein for all purposes as if fully set forth) under "Polyurethane Dispersoid (PUD EX 1)".

Preparation of Inks

Inks C1-C4, Y1-Y4 and M1-M4 were prepared by combining ingredients as described in Tables 1 through 4 below.

Table 1

	Ink C1	**Ink Y1**	**Ink M1**
Pigment from Dispersion C	3%		
Pigment from Dispersion Y		4%	
Pigment from Dispersion M			4%
Polymer Binder 1, solids	4.5%	4.5%	4.5%
Glycerol	3%	3%	3%
Glycol ether	3%	3%	3%
Ethylene glycol	18%	20%	18%
2-pyrrolidone	10%	10%	10%
Biocide	*0.15%*	0.15%	0.15%
1,2- hexanediol	1.00%	1.00%	1.00%
Surfynol 104	1.10%	1.10%	1.10%
D.I. Water	*Balance to 100%*		
Properties			
Surface Tension, dynes/cm	31.3	30.5	30.4
Viscosity at 32deg C, centipoise	5.75	5.62	5.89

Table 2

	Ink C2	**Ink Y2**	**Ink M2**

Pigment from Dispersion C	3%		
Pigment from Dispersion Y		4%	
Pigment from Dispersion M			4%
Polymer Binder 1, solids	4.5%	4.5%	4.5%
Glycerol	3%	3%	3%
Glycol ether	3%	3%	3%
Ethylene glycol	16%	18%	16%
2-pyrrolidone	10%	10%	10%
Biocide	*0.15%*	0.15%	0.15%
1,2- hexanediol	1.00%	1.00%	1.00%
Surfynol 104	1.50%	1.50%	1.50%
D.I. Water	*Balance to 100%*		
Properties			
Surface Tension, dynes/cm	30.2	30.3	29.5
Viscosity at 32deg C, centipoise	5.55	5.38	5.68

Table 3

	Ink C3	Ink Y3	Ink M3
Pigment from Dispersion C	3%		
Pigment from Dispersion Y		4%	
Pigment from Dispersion M			4%
Polymer Binder 1, solids	4.5%	4.5%	4.5%
Glycerol	3%	3%	3%
Glycol ether	3%	3%	3%
Ethylene glycol	15%	17%	15%
2-pyrrolidone	10%	10%	10%
Biocide	*0.15%*	0.15%	0.15%
1,2- hexanediol	3.00%	3.00%	3.00%
Surfynol 104	1.10%	1.10%	1.10%
D.I. Water	Balance to 100%		
Properties			
Surface Tension, dynes/cm	29.5	30.3	29.4
Viscosity at 32 deg C, centipoise	6.02	6.09	6.20

Table 4

	Ink C4	Ink Y4	Ink M4
Pigment from Dispersion C	3%		
Pigment from Dispersion Y		4%	
Pigment from Dispersion M			4%
Polymer Binder 1, solids	4.5%	4.5%	4.5%
Glycerol	3%	3%	3%
Glycol ether	3%	3%	3%
Ethylene glycol	13%	15%	13%
2-pyrrolidone	10%	10%	10%
Biocide	*0.15%*	0.15%	0.15%
1,2- hexanediol	3.00%	3.00%	3.00%
Surfynol 104	1.50%	1.50%	1.50%
D.I. Water	Balance to 100%		
Properties			
Surface Tension, dynes/cm	29.5	28.6	28.8
Viscosity at 32 deg C, centipoise	5.92	5.94	6.12

Evaluation of Inks

The inks were printed using a Ricoh Aficio GX e5550N printer. Printing was done on various coated media commonly used in offset, toner and other non-ink jet printing processes. These papers were exemplified by Mohawk Gloss 50/10 (Mohawk Fine Papers,

US), TerraPress Silk (Stora Enso, Finland), UPM Finesse Gloss (UPM, Finland), OK Topcoat + (Oji, Japan), New Age (Oji, Japan), and LumiArt Gloss (Stora Enso, Finland). Printing was also done on plain paper, exemplified by Xerox 4200 Business paper. After printing, the images were left to dry for at least an hour at ambient conditions before subjecting to evaluation of color-to-color bleed.

The following notations are used to succinctly record the color-to-color bleed results.

X ->> Y denotes significant flow of color X into areas where color Y is. That is to say, both notation denotes X bleeds into Y in a very significant degree.

X -> Y denotes a smaller degree of bleed of color X into color Y.

X ~ Y denotes a balanced level of flow between colors X and Y. There is not a significantly bleed between the two colors X and Y.

Results

As shown in Table 5 below, when Inks C1, Y1 and M1 were printed together as a set on plain paper, the bleed between the colors was insignificant as denoted by C1 ~ Y1 ~ M1. However, when these same three inks were printed on coated media, the following bleed interactions were observed: M1 ->> Y1 ->> C1. This is due to the fact that while plain papers absorb ink liquid relatively rapidly and thus preventing migration of inks into neighboring colors, coated media have much lower porosity and thus inks stay wet and on top of the surface of the media for a much longer time. During this longer time period, any unbalanced physical properties as the inks slowly dry will cause a flow of one ink into another, leading to inter-color bleed.

Table 5

Comparative Examples	Ink Set	Bleed	
		Xerox 4200 paper	Offset Papers
CE 1	C1, Y1, M1	C1 ~ Y1 ~ M1	M1 ->> Y1 - >> C1
CE 2	C2, Y2, M2	C2 ~ Y2 ~ M2	Y2 ~ C2 ->> M2
CE 3	C3, Y3, M3	C3 ~ Y3 ~ M3	M3 ->> Y3 ->> C3
CE 4	C4, Y4, M4	C4 ~ Y4 ~ M4	C4 ~ Y4 ~ M4

In order to provide a method of balancing the physical properties of the inks as they dry so as to maintain a good equilibrium, adjustment in the ratios of surfactant and 1,2-

hexanediol was surprisingly found to be effective in providing good intercolor bleed as shown in Table 6 below.

Table 6

Example	Ink Set	Bleed	
		Xerox 4200 paper	Offset Papers
Ex 5	C2, Y2, M3	M3 ~ Y2 ~ C2	M3 ~ Y2 ~ C2
Ex 6	C3, Y3, M2	C3 ~ Y3 ~ M2	C3 ~ Y3 ~ M2

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CLAIMS

What is claimed is:

1. An inkjet ink set for printing on offset media, said ink set comprising a magenta, a yellow, a cyan, and a black ink, wherein each of the inks in said ink set is independently comprised of a colorant, an aqueous vehicle, a polymeric binder, a nonionic surfactant, and optionally an 1,2-alkanediol, wherein said polymeric binder is dispersed in said aqueous vehicle, and wherein said inkjet ink is printed directly onto said offset media without any pretreatment/precoating of said offset media.

2. The ink set of claim 1, wherein said ink set is used for fixed array printing.

3. The ink set of claim 1, wherein said ink set has a discharge from printhead frequency of 20 kHz or greater.

4. The ink set of claim 1, wherein each of the ink has a surface tension of between 18 and 35.

5. The ink set of claim 1, wherein one or more of said colorant is a self-dispersing pigment.

6. The ink set of claim 1, wherein one or more of said colorant is dispersed by a polymeric dispersant.

7. The ink set of claim 1, wherein said non-ionic surfactant is a fluorosurfactant.

8. The ink set of claim 1, wherein said non-ionic surfactant is a non-fluorosurfactant.

9. The ink set of claim 8, wherein said non-fluorosurfactant has a HLB value of less than 5.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/064646

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D11/30 C09D11/40
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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/259989 A1 (BERGE CHARLES T [US] ET AL) 8 November 2007 (2007-11-08) paragraphs [0078], [0083], [0090], [0097], [0126], [0184] - [0192], [0200]; claims 1,2,8,9; tables 1,4,13-15	1-9
X	WO 2012/148476 A2 (DU PONT [US]; ANTON WAIFONG LIEW [US]; LEE HEE HYUN [US]; OTLEY MICHAE) 1 November 2012 (2012-11-01)	1-4,6,8, 9
A	page 37, line 1 - page 38, line 10; table 1 page 26, line 30 - page 27, line 7; claims 1,26-28; tables 1,2	5

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 February 2016	01/03/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Feldmann, Gabriele

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/111140 A1 (DU PONT [US]; SPINELLI HARRY JOSEPH [US]) 23 December 2004 (2004-12-23) page 53, lines 1-12; example 2; table 17b pages 46-47 page 20, line 16 page 65 claims 1,12,14-16; tables 8,9,17b	1-9
X	US 2005/182154 A1 (BERGE CHARLES T [US] ET AL) 18 August 2005 (2005-08-18) paragraphs [0132], [0217], [0218]; claims 1,7,8,10-20; tables 3,6,8	1-9
X	US 2008/207820 A1 (BRUST THOMAS B [US] ET AL) 28 August 2008 (2008-08-28) paragraphs [0029], [0032], [0034], [0036], [0039], [0066], [0070], [0201] - [0207]; claims 1,16-20	1-9

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International application No
PCT/US2015/064646

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