

POLYMERIC ADDITIVES TO IMPROVE PRINT QUALITY
AND PERMANENCE ATTRIBUTES IN INK-JET INKS

TECHNICAL FIELD

The present invention is directed to ink-jet inks, and, more particularly, to fixer compositions used in ink-jet printing to enhance printing performance, such as smear-fastness, smudge resistance, waterfastness, and lightfastness.

BACKGROUND ART

There is a considerable demand in a better image quality of ink-jet. The low smearfastness, waterfastness, and lightfastness and the tendency to smudge seem to be the main drawbacks of ink-jet, and this invention addresses these issues.

Several techniques has been used in the prior art to address these issues. One such technique is underprinting, which helps to stratify the colorant to the surface of the paper, reduce wicking, and improve color performance. Underprinting is defined as applying a transparent fluid on substrate prior the ink deposition. There are several patents addressing the technique of underprinting for better waterfastness and bleed control; see, e.g., U.S. Patent 5,624,484, "Liquid Composition and Ink Set, and Image-Forming Process and Apparatus Using the Same", issued to K. Takahashi et al on April 29, 1997, and U.S. Patent 5,640,187, "Ink Jet Recording Method and Ink Jet Recording Apparatus Therefor", issued to A. Kashiwazaki et al on June 17, 1997, both assigned to Canon; U.S. Patent 5,723,179, "Method and Composition for Obtaining Waterfast Images From Ink Jet Inks", issued to R.W. Wong et al on March 3,

1998, and assigned to Xerox Corp.; and U.S. Patent 5,746,818, "Pigment Ink Composition Capable of Forming Image Having No Significant Bleeding or Feathering", issued to M. Yatake on May 5, 1998, and assigned to Seiko Epson. The underlying idea in underprinting is to bind the dyes with oppositely charged species. For example,
5 anionic dyes can be bound by a cationic polymer, and cationic dyes can be bound by an anionic polymer. The clear underprinting fluid will be referred below as a fixing fluid, or fixer.

It is known that underprinting can increase the chroma (or, for black, optical density) of pigmented dispersions, such as carbon black-based inks. For example,
10 black inks in Hewlett-Packard's DeskJet 890C printer are underprinted with a composite black, resulting in a considerable increase in the optical density. Also, the edge acuity of underprinted pigmented inks is improved.

However, for dye-based inks, the underprinting techniques known in art only marginally increase, or, most often, decrease chroma. Thus, as can be judged from the
15 above-mentioned U.S. Patent 5,723,179, underprinting decreased the optical density of the images (although underprinting made them waterfast). Similarly, in the commercial Canon BJC-700 printer, underprinting improves the edge acuity and bleed, but decreases the color vividness (see Examples, below). The decrease in chroma results from the increase in the volume of liquid poured on the paper. As a result, the
20 complex of the dye with the underprinting fixer penetrates into the paper and the chroma decreases. As for the edge acuity of dye-based systems, it often improves, but at the expense of area fill uniformity.

On the other hand, overprinting with a clear fluid is also known. For example, application Serial Nos. 09/295,665 and 09/296,456, both filed on April 21, 1999, in
25 the name of Makarand P. Gore and assigned to the same assignee as the present application, disclose overprinting ink-jet inks with a clear fluid that comprises a fusible material and then fusing the printed image with a fuser in the ink-jet printer, much like the fuser of a laser printer. While this approach is certainly suitable for providing improved permanent images, it does require modification of an ink-jet printer.

However, a need remains for a method for improving smearfastness, waterfastness, lightfastness, and smudgefastness in ink-jet inks.

DISCLOSURE OF INVENTION

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In accordance with the present invention, one-part and two-part fixatives are provided in conjunction with underprinting or overcoating at least one ink printed on a print medium.

The one-part fixative of the present invention comprises a polymer in a vehicle.
10 The polymer is selected from the group consisting of vinyl-based polymers, condensation polymers, and copolymers thereof and the polymer has a glass transition temperature within a range of -50°C to $+100^{\circ}\text{C}$, a melting temperature within a range of 30°C to 150°C , and a molecular weight (weight average basis) within a range of 3,000 to 100,000. The fixative is contained in a separate cartridge from the ink-jet ink print cartridge(s).
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The two-part fixative of the present invention comprises (1) a reactive monomer or oligomer in a vehicle, the reactive monomer or oligomer selected from the group consisting of iso-cyanates and epoxy-terminated oligomers, and (2) at least one second component selected from the group consisting of polyols, polyvinyl alcohols, and base
20 catalysts. The reactive monomer or oligomer is contained in a separate cartridge from the ink-jet ink print cartridge(s), while the second component(s) is contained in at least one ink-jet ink print cartridge. The reactive monomer or oligomer reacts with the second component(s) on the print medium to form a polymer, which has a glass transition temperature within a range of -20°C to $+50^{\circ}\text{C}$ and a melting temperature within a range of
25 30°C to 100°C .

Enhancement of waterfastness, smearfastness, smudgefastness, and lightfastness, as well as print quality (optical density and chroma, for example), is provided by use of the fixative solution in the present invention.

BEST MODES FOR CARRYING OUT THE INVENTION

Reference is now made in detail to a specific embodiment of the present invention, which illustrates the best mode presently contemplated by the inventors for practicing the invention. Alternative embodiments are also briefly described as applicable.

Color inks in ink-jet typically have cyan, magenta and yellow colors. Accordingly, the primary colors are cyan, magenta and yellow (C, M, Y). Binary colors are their binary combinations, that is, blue $B = C+M$, red $R = M+Y$, and green $G = Y+C$. Composite black (Comp-K= $C+M+Y$) is the black color formed by printing cyan, yellow and magenta inks together. It differs from the true black ink (true K), which is often supplied by ink-jet printers as a separate ink cartridge. Thus, in conventional color ink-jet printing, there are four pen cartridges - cyan (C), yellow (Y), magenta (M), and black (K).

The inks comprise a vehicle and at least one colorant, as is well-known.

The vehicle comprises one or more co-solvents and water. The co-solvents comprise one or more organic, water-miscible solvents commonly employed in ink-jet printing. Classes of co-solvents employed in the practice of this invention include, but are not limited to, aliphatic alcohols, aromatic alcohols, diols, glycol ethers, poly(glycol) ethers, lactams, formamides, acetamides, and long chain alcohols. Examples of compounds employed in the practice of this invention include, but are not limited to, primary aliphatic alcohols of 30 carbons or less, primary aromatic alcohols of 30 carbons or less, secondary aliphatic alcohols of 30 carbons or less, secondary aromatic alcohols of 30 carbons or less, 1,2-alcohols of 30 carbons or less, 1,3-alcohols of 30 carbons or less, 1, ω -alcohols of 30 carbons or less, ethylene glycol alkyl ethers, propylene glycol alkyl ethers, poly(ethylene glycol) alkyl ethers, higher homologs of poly(ethylene glycol) alkyl ethers, poly(propylene glycol) alkyl ethers, higher homologs of poly(propylene glycol) alkyl ethers, N-alkyl caprolactams, unsubstituted caprolactams, substituted formamides, unsubstituted formamides, substituted acetamides, and unsubstituted acetamides. Specific examples of co-solvents that are preferably employed in the practice of this invention include, but are not limited to, N-

methyl pyrrolidone, 1,5-pentanediol, 2-pyrrolidone, diethylene glycol, 1,3-(2-methyl)-propanediol, 1,3,5-(2-methyl)-pentanetriol, tetramethylene sulfone, 3-methoxy-3-methylbutanol, glycerol, and 1,2-alkyldiols.

5 The colorant(s) may comprise one or more dyes (water-soluble) or pigments (water-insoluble). If a pigment is employed, a dispersant is used to disperse the pigment in the vehicle. Alternatively, the pigment may be chemically treated to render it dispersible in the vehicle.

10 Additives, such as surfactants, biocides, pH adjusters, and the like may be added as appropriate. Such additives are well-known to those skilled in this art. The purity of all components is that customarily employed in ink-jet inks.

The use of fixative solutions in a fifth and/or sixth pen cartridge for overprinting or underprinting modes to improve print quality and archivability is disclosed herein. This enables a receptive layer in underprinting or a coating in overprinting that provides specific interactions between the colorants and the fixative polymers. Enhancement of the following printing attributes - waterfastness, smearfastness, smudgefastness, and lightfastness - is obtained.

The fifth pen is employed when either underprinting or overprinting is contemplated. In that situation, there is only one fixative, and it is contained in the fifth pen.

20 The sixth pen is employed when both underprinting and overprinting are contemplated. In that situation, there are two fixatives, which may be the same or different. One fixative is contained in the fifth pen and the other fixative is contained in the sixth pen.

25 In the case of underprinting, a precise alignment of fixative and ink is required, in order to realize the benefits of the present invention. In that case, an ink-jet printhead is employed, so as to achieve precise control over the fixative.

In the case of overprinting, such a precise alignment of fixative and ink is not so important, so long as the fixative covers the printed ink. Thus, an ink-jet printhead is not necessary, although it can be used, if desired. Alternatively, a mechanical device that ejects fluid under pressure is employed, such as an atomizer or an air-brush. Since

the fixative is clear, the fixative may be said to be deposited by a clear fluid deposition device, whether printhead, atomizer, air-brush, or other suitable system. Consequently, the use of fixative to cover the printed ink is alternatively referred to herein as overprinting or overcoating.

5 Two fixative systems are described herein, a one-part system and a two-part system.

One-part systems comprise a high molecular weight polymer dispersed either in aqueous (water-based) or solvent-based, depending on the polymer composition, molecular weight, and solubility parameters in a chosen vehicle solution. Upon removal of vehicle on printing media, coalescence of particles forms a polymeric network or a film. Examples of polymers employed in the practice of the present invention include polyurethanes, poly(acrylic-urethane)s, polyacrylates, fluorinated polyacrylates, polymethacrylates, polyvinyl acetate, and poly(vinyl alcohol-vinyl acetate). Physical properties of polymer such as glass transition temperature (T_g), melting temperature (T_m), and weight average molecular weight, are important for film-forming characteristics and mechanical properties of the formed films.

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Two-part systems that consist of: (a) reactive monomers or oligomers in the 5th and/or 6th pen cartridge and (b) a reactive components in a color cartridge. Examples include isocyanate- (TDI or MDI) or epoxy-terminated oligomers in the 5th and/or 6th pen, and polyols, polyvinyl alcohols and a catalyst in the color cartridge. Polymerization takes place by mixing of solutions (a) and (b) during overprinting and underprinting. Catalysts for isocyanate typically consist of amines and alkoxides, while amines, alkoxides, and metal ions are useful for epoxies.

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In overcoating experiments, the present inventors found that a one-part system consisting of water-dispersed polyacrylic-urethane, and polyurethane greatly enhanced waterfastness and highlighter smearfastness. The colorant was evaluated along with an overcoating consisting of a fixative solution containing 6 wt% polyacrylic-urethane in a vehicle consisting of 40 wt% 2-pyrrolidone. No colorant transfer was observed in the following print media: Gilbert Bond (GNBD), Champion Data-copy (CDCY), and Stora Papyrus Multicopy (PMCY). Without the polymer coating,

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the colorant is not waterfast; typically, 300 to 400 mOD of ink transfer occurred. Similarly, highlighter smearfastness also improved. Transfer values of less than 50 mOD was observed with alkaline highlighter up to 2 passes on GNBD, CDCY and PMCY. Acid highlighter provided even lower transfer.

5 As mentioned above, the solvent in either the one-part system or the two-part system is either water-based or is solvent-based. Water-based systems refer to those where water is the major, or only, solvent component. Water-soluble organic solvents and surfactants may be incorporated to provide uniform spreading and drying on print media. Examples of such water-soluble, or water-miscible, organic solvents and surfactants include those listed above in connection with vehicle components.

10 On the other hand, solvent-based systems refer to those where the polymer is either soluble or dispersed in a vehicle consisting of one or more organic solvents. Typically, the mixtures would have limited miscibility with water of about 5 to 10 wt%. Examples of organic solvents include the following: (1) halogenated hydrocarbons such as
15 dichloroethane, methylene chloride, perchloroethylene, trichloroethane, and trichloroethylene; (2) aliphatic hydrocarbons such as de-aromatized petroleum distillate, white spirit, and synthetics; (3) aromatic hydrocarbons such as heavy naphtha, solvent naphtha, toluene, trimethyl benzene, and xylene; (4) alcohols such as ethanol, isopropanol, n-propanol, n-butanol, sec-butanol, and diacetone alcohol; (5) esters such as ethyl acetate,
20 ethyl lactate, and N-butyl acetate; (6) ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, and ethylene glycol monobutyl ether; (7) ketones such as cyclohexanone, methyl ethyl ketone, and methyl isobutyl ether; and (8) terpenes such as dipentene, terpineol, and terpine. The concentration of the organic solvent(s) is within the range of about 0.1 to 98 wt% of the
25 fixative system.

 The fixative system may also include one or more surfactants within the concentration range of about 0.1 to 20 wt%. The surfactant(s) is preferably organic solvent soluble, such as those with low ethylene oxide repeating units, available in the SURFYNOLS, TERGITOLS, and TRITONS series of surfactants. The SURFYNOLS are
30 acetylenic ethoxylated diols available from Air Products, the TERGITOLS are poly-

ethylene or polypropylene oxide ethers available from Union Carbide, and the TRITONS are alkyl phenyl polyethylene oxides available from Rohm & Haas Co. It is well-known in the art of coating industry, a mixture of the above are used to achieve the desired coating properties such as drying speed, coating uniformity, and glossiness.

5 The present invention is directed to the use of a clear solution (fixer) to overcoat a printing page to enhance printing performance such as smearfastness, smudge, waterfastness, and lightfastness. The solution is delivered as fine aerosol using a pressurized apparatus such as an air-brush or atomizer onto printed pages as an overcoat. Therefore, it is called a fixative solution or fixer.

10 The fixer solution can consist of a one- or two-part system. The one-part system consists of a high molecular weight polymer dispersed either in an aqueous medium (waterborne) or in an organic solvent. Desirable properties are the following:

glass transition temperature (T_g) ranges from -50° to 100°C ;

melting temperature (T_m) ranges from 30° to 150°C ; and

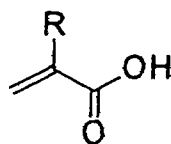
15 molecular weight (MW) of the polymer should be sufficiently high to form a film.

Although the molecular weight is structurally dependent, it typically ranges from 3,000 to 100,000 (weight average) for linear polymers (MW is not meaningful when crosslinking take place). The preferred range is when the polymer begins to
20 form a film, or about 5,000 to 20,000.

Examples of polymers useful as overcoating fixatives include those synthesized from vinyl-based monomers (e.g., acrylates) or condensation/addition monomers (e.g., isocyanates). Copolymers can be formed from vinyl-based monomers and condensation monomers.

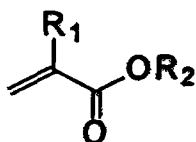
25 The polymers are selected from the group consisting of

1. Acrylic and methacrylic acids and salts thereof:



where R is H or CH₃.

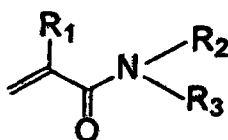
2. Esters of acrylic and methacrylic acids:



where R₁ is as defined above and R₂ is a radical of C₁ to C₅₀.

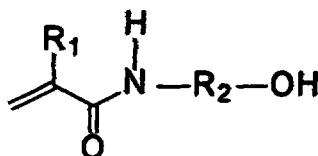
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3. Amides of acrylic or methacrylic acids:



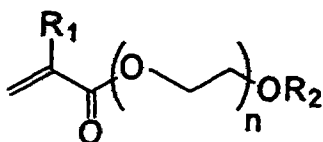
where R₁ is as defined above and R₂ and R₃ are independently radicals of C₁ to C₅₀.

4. Hydroxy amides of acrylic and methacrylic acids:



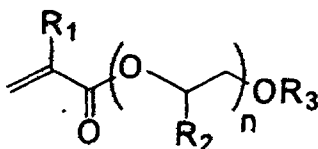
10 where R₁ and R₂ are as defined above.

5. Polyethylene glycols and esters of acrylic and methacrylic acid:



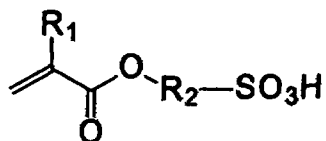
where R₁ and R₂ are as defined above and n is an integer from 1 to 100.

6. Polyalkylene glycols and esters of acrylic and methacrylic acid:



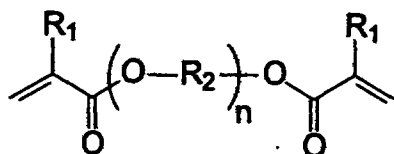
where R_1 , R_2 , R_3 , and n are as defined above.

7. Sulfoalkyl(aryl) acrylate and methacrylate, and salts thereof:



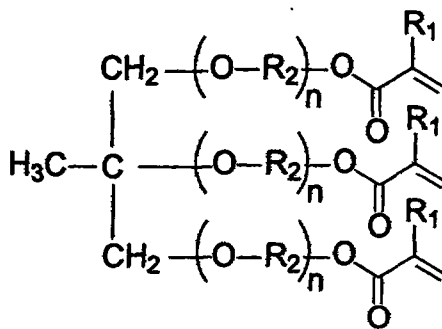
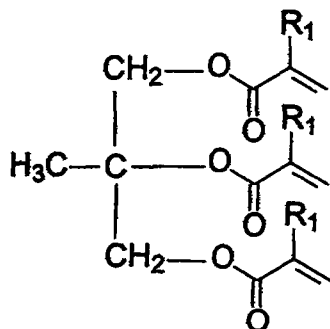
5 where R_1 and R_2 are as defined above.

8. Polyalkylene (aryl) glycol diacrylates and dimethacrylates:



where R_1 and R_2 are as defined above and n is an integer from 1 to 50.

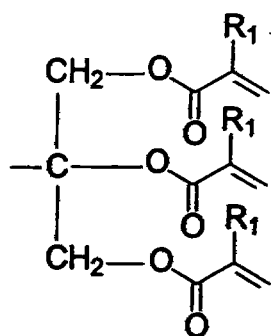
9. triacrylates, trimethacrylates, tetraacrylates, and tetramethacrylates:



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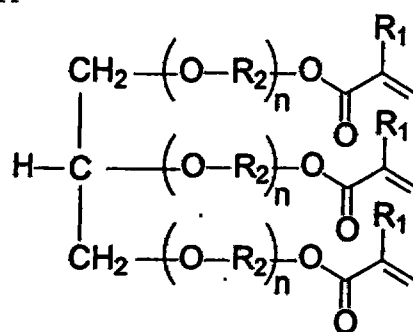
trimethylolpropane triacrylates
and trimethylacrylates

alkoxylated trimethylolpropane
triacrylate and trimethacrylate

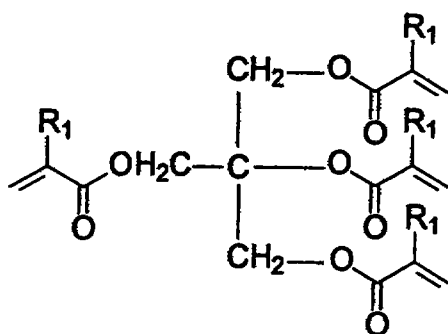


glyceryl triacrylates
and trimethacrylates

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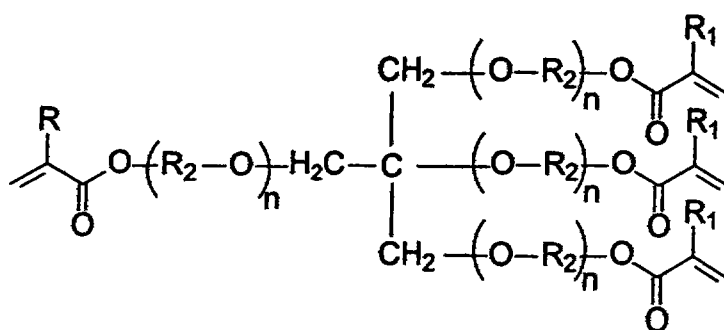


alkoxylated glyceryl
triacylate and trimethacrylate



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pentaerythritol tetraacylate and tetramethacrylate

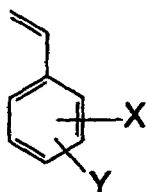


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alkoxylated pentaerythritol tetraacylate and tetramethacrylate

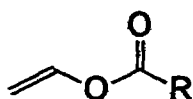
where R_1 and R_2 are as defined above and n is an integer from 1 to 50.

10. Styrene and its derivatives:



where X and Y are independently H, NH_2 , SO_3H , OCH_3 , or a radical of C_1 to C_{20} .

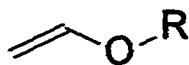
11. Vinyl esters and alcohols:



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where R is a radical of C_1 to C_{50} (esters) or OH (alcohol).

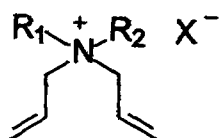
12. Vinyl ethers:



where R is a radical of C_1 to C_{50} .

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13. Diallyldialkyl ammonium halides:



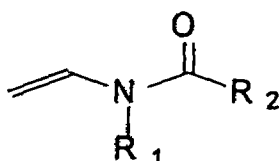
where R_1 and R_2 are independently H or a radical of C_1 to C_{20} and X^- is F^- , Cl^- , Br^- , I^- , SO_4^{2-} , or PO_4^{3-} .

14. Vinyl sulfonic acid and salts thereof:



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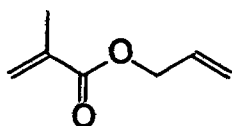
15. N-Vinylamides



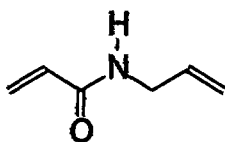
where R_1 is H or a radical of C_1 to C_{20} and R_2 is independently H or a radical of C_1 to C_{50} .

16. Any of the following compounds:

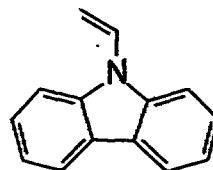
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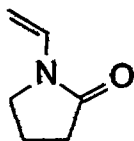
allyl methacrylate



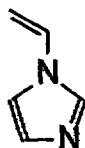
allyl acrylamide



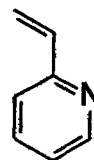
N-vinylcarbazole



N-vinyl pyrrolidone

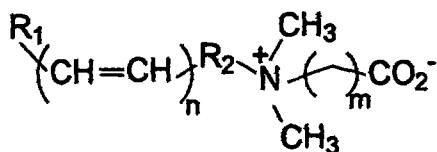


vinyl imidazole

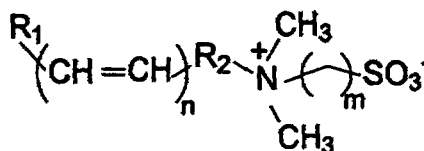


vinyl pyridine

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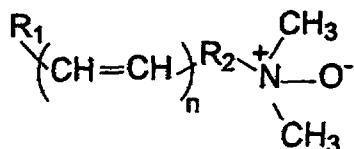


polyunsaturated betaines

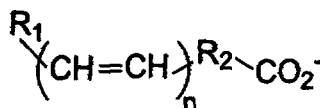


polyunsaturated sulfo-betaines

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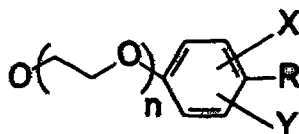
polyunsaturated amine oxides



polyunsaturated fatty acids

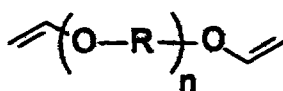
where R_1 and R_2 are independently radicals of C_1 to C_{50} and m and n are independently integers of 1 to 10.

17. Polyethylene oxide alkyenyl phenol:



where X and Y are independently H or $\text{CH}=\text{CH}_2$, R is a radical of C_1 to C_{50} , and n is an integer of 1 to 100.

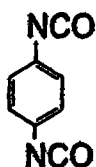
5 18. Polyalkylene (aryl) divinyl ethers:



where R is a radical of C_1 to C_{50} and n is an integer from 1 to 50.

19. Any of the following molecules:

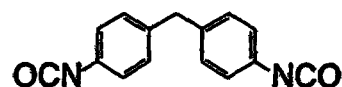
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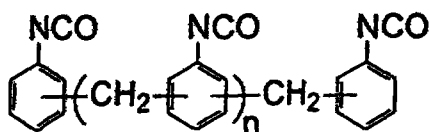
1,4-diisocyanatobenzene



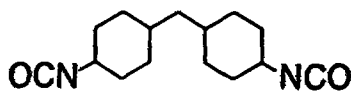
toluene diisocyanate



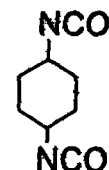
4,4'-methylenebis(phenylisocyanate)



polymethylene poly(phenylisocyanate)



dicyclohexylmethane diisocyanate



1,4-cyclohexane diisocyanate

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Preferably, the polymer employed in the one-part fixer composition is selected from the group consisting of allyl methacrylate, allyl acrylamide, N-vinyl carbazole, N-vinyl pyrrolidone, vinyl imidazole, vinyl pyridine, 1,4-diisocyanatobenzene, toluene diisocyanate, 4,4'-methylenebis-(phenyl isocyanate), polymethylene poly(phenyl isocyanate), dicyclohexylmethane di-isocyanate, and 1,4-cyclohexane diisocyanate.

The concentration of the polymer in the fixer solution ranges from 2 to 30 wt%, with 3 to 10 wt% preferred.

Examples of one-part, water-based polymer fixer compositions are listed in Table IA below.

Table IA. Examples of One-Part, Water-Based Polymer Fixer Compositions.

Example	1	2	3	4	5
Polymer	10 wt% Neo Rez R-966	5 wt% Neo Rez R-966	5 wt% Neo Rez R-966	5 wt% Neo Rez R-960	7 wt% Neo Rez R-960
2-pyrrolidone	40 wt %	20 wt %	10 wt %	10 wt %	15 wt %
1,5-pentanediol		20 wt %			
SURFYNOL 465			2 wt %	2 wt %	2 wt %
Water	Balance	Balance	Balance	Balance	Balance

Notes: NeoRez R-960 and R-966 are urethane-type polymers, available from ICI.

SURFYNOL 465 is an ethoxylated tetramethyl decynediol, available from Air Products.

Examples of one-part, solvent-based polymer fixer compositions are listed in Table IB below.

Table IB. Examples of One-Part, Solvent-Based Polymer Fixer Compositions.

Example	6	7	8
Polymer	10 wt% SAA-100	7 wt% SAA-100	10 wt% SAA-101
tetrahydrofuran	90 wt %		90 wt %
methyl ethyl ketone		93 wt %	

Notes: SAA-100 and SAA-101 are poly(styrene-allyl alcohol), available from Arco Chemical.

- 5 The polymer fixers of the present invention have been found to work well with both dyes and pigments to improve smearfastness, smudgefastness, and waterfastness. Table IIA below lists examples of ink compositions, the colorant, whether or not a fixer solution (water-based) was employed, and the results obtained.

10 Table IIA. Results of One-Part, Water-Based Fixer Compositions with Inks.

	Print Medium	Ink Example 9	Ink Example 10	Ink Example 11	Ink Example 12
Colorant		Black pigment	Black pigment	Water-soluble black dye	Water-soluble black dye
Fixer solution		Example 3*	No	Example 3*	No
Optical density (1)	GBND	1.45	1.45	1.31	1.31
Waterfastness (2)	GBND	0	20	9	70
	CDCY	2	38	6	120
	PMCY	4	24	19	165

Acid Smearfastness (3)	GBND	0	110	8	35
	CDCY	0	75	5	11
	PMCY	12	280	19	50
Alkaline Smearfastness (3)	GBND	7	320	15	70
	CDCY	2	186	11	56
	PMCY	20	460	25	97

Notes: GBND = Gilbert Bond, CDCY = Champion Datacopy, PMCY - Stora Papyrus Multicopy.

5 (1) Measured in optical density units.

(2) Amount of colorant transfer by dripping deionized water onto a printed pattern, 10 minutes after printing.

(3) Amount of colorant transfer by running aqueous based highlighter twice over printed pattern. Measured in milli-optical density units.

10 * Example 3 is from Table IA, above.

The results of one-part, solvent-based fixer compositions with inks are depicted in Table IIB, below.

Table IIB. Results of One-Part, Solvent-Based Fixer Compositions with Inks.

	Print Medium	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
Colorant #		cyan dye	cyan dye	magenta dye	magenta dye	yellow dye	yellow dye
Fixer solution		Example 6*	No	Example 6*	No	Example 6*	No
Optical density (OD) (1)	HFDP	1.1	1.1	1.1	1.0	1.2	1.1
	LL	1.5	0.9	1.3	0.8	1.4	0.8
	KK	1.5	1.0	1.2	0.8	1.4	0.9
	UD	1.7	1.2	1.5	1.0	1.8	1.4
	HPBF	2.0	1.7	1.5	1.4	1.8	1.4
Chroma (5)	HFDP	41	41	57	55	76	72
	LL	51	42	67	54	76	72
	KK	51	47	72	67	84	70
	UD	50	48	71	75	90	76
	HPBF	55	53	76	73	92	87
Waterfastness (2)	HFDP	2	190	4	93	12	73
	LL	21	208	35	168	15	162

	KK	5	167	5	107	0	147
	UD	2	297	0	243	0	227
	HPBF	1	278	1	218	0	118
Alkaline smearfastness (3)	HFDP	0	110	5	443	n.m. (6)	n.m.
	LL	1	65	0	22	n.m.	n.m.
	KK	0	37	2	20	n.m.	n.m.
	UD	0	40	0	27	n.m.	n.m.
	HPBF	0	145	1	58	n.m.	n.m.
Smudgefastness (4)	HFDP	5	142	8	82	2	88
	LL	0	182	12	122	18	138
	KK	2	97	5	57	0	80
	UD	2	260	18	230	0	217
	HPBF	1	248	1	138	0	62

Notes: # Colorant is a water-soluble dye.

* Example 6 is from Table IB above.

HFDP is Hammermill Fore DP;

LL is SpectraTech Lustro Laser (Warren);

KK is Kromekote 2000 IS cover (Champion);

UD is Utopia Dull (Appleton); and

HPBF is Hewlett-Packard Professional Brochure and Flyer paper.

(1) Measured in optical density units.

(2) Amount of colorant transfer by dripping deionized water onto a printed pattern, 10 minutes after printing.

5 (3) Amount of colorant transfer by running aqueous based highlighter twice over printed pattern. Measured in milli-optical density units.

(4) Amount of colorant transfer by dripping deionized water onto a printed pattern 10 minutes after printing, followed immediately by running a finger over the wetted area.

(5) Measured in chroma units.

10 (6) n.m. = not meaningful.

With regard to a measurement of waterfastness, smearfastness, and smudgefastness in Tables IIA and IIB, a lower value of colorant transfer indicates a better result. Thus, it can be seen that for the three print media tested, waterfastness, smearfastness (both acid and alkaline), and smudgefastness were considerably improved using the fixer of the present invention as compared to printing with no fixer.

By the same approach, improvement of the lightfastness properties of printed media is anticipated by incorporating anti-oxidants, ultraviolet absorbers/quenchers, and free radical scavengers in the fixer solution. This would be particularly suitable for dye-based inks, since lightfastness is not easily attainable at the present. It is well-recognized in the coating industry that these techniques enhance lightfastness performance of exterior paints, for example. Some examples for anti-oxidants, ultraviolet absorber / quencher, and free radical scavengers are para-aminobenzoic acid (PABA), ascorbic acid, quinone, coumarin, anthraquinone, and sterically hindered amines.

Substantial improvement in print quality in terms of optical density and chroma is found with the polymer fixer (Tables IIA and IIB). In coated media such as SpectraTech Lustro Laser, Kromekote 2000 1S cover, Utopia Dull, and Professional Brochure & Flyer paper, optical density increased significantly from 0.8 to 1.3, for example. This effect is much smaller in the plain papers such as Gilbert Bond and Hammermill Fore DP. Similarly, chroma values of the primary colors of cyan, magenta, and yellow increased substantially with the polymer fixer. Chroma, C^* , is one of the three components of L.c.h. values that quantitatively describe the three-dimensional space of a given color; hence, the higher the chroma value the brighter the color. In order to attain the largest color space possible, it is highly desirable to maximize the chroma values of the primary colors, especially in imaging applications.

In a two-part system, the fixer solution of the present invention comprises (1) a reactive monomer or oligomer in a vehicle, the reactive monomer or oligomer selected from the group consisting of iso-cyanates and epoxy-terminated oligomers, and (2) at least one second component selected from the group consisting of polyols, polyvinyl alcohols, and base catalysts. The reactive monomer or oligomer is contained in a separate cartridge from the ink-jet ink print cartridge(s), while the second component(s) is contained in at least one ink-jet ink print cartridge. The reactive monomer or oligomer re-

acts with the second component(s) on the print medium to form a polymer, which has a glass transition temperature within a range of -50° to +100°C and a melting temperature within a range of 30° to 150°C. The vehicle may comprise water alone or water in combination with one or more water-soluble organic solvents, listed above.

- 5 If the fixer is not reactive toward the colorants, it serves as a hydrophobic overcoat against exposure to the environment including water and smear/smudge.

INDUSTRIAL APPLICABILITY

- 10 The fixer compositions of the present invention are expected to find use in ink-jet printing.

- 15 Thus, there have been disclosed one-part and two-part fixer systems for underprinting, overprinting, or both in conjunction with ink-jet printing on print media. It will be readily apparent to those skilled in this art that various changes and modifications may be made, and all such changes and modifications are considered to fall within the scope of the appended claims.



What Is Claimed Is:

- 5 1. A fixative for ink-jet printing, said fixative for underprinting or overcoating, or both, at least one ink printed on a print medium, each said ink printed from a separate print cartridge, said fixative comprising either (a) a one-part system and comprising a polymer in a vehicle, said polymer selected from the group consisting of vinyl-based polymers, condensation polymers, and copolymers thereof, said polymer having a glass
- 10 transition temperature within a range of -50°C to $+100^{\circ}\text{C}$, a melting temperature within a range of 30° to 150°C , and a molecular weight (weight average basis) within a range of 3,000 to 100,000, said fixative contained in a separate cartridge from said at least one ink-jet ink print cartridge or (b) a two-part system and comprising (1) a reactive mono-
- 15 mer or oligomer in a vehicle, said reactive monomer or oligomer selected from the group consisting of iso-cyanates and epoxy-terminated oligomers and (2) at least one second component selected from the group consisting of polyols, polyvinyl alcohols, and base catalysts, said reactive monomer or oligomer contained in a separate cartridge from said at least one ink-jet ink print cartridge and said at least one second component contained in said at least one ink-jet ink print cartridge, said reactive monomer or oli-
- 20 gomer reacting with said at least one second component on said print medium to form a polymer, said polymer having a glass transition temperature within a range of -50°C to $+100^{\circ}\text{C}$ and a melting temperature within a range of 30°C to 150°C .
2. The fixative of Claim 1 wherein at least three color inks in three separate
- 25 print cartridges are provided.
3. The fixative of Claim 2 wherein said at least three color inks are cyan, yellow, and magenta.
- 30 4. The fixative of Claim 2 wherein three color inks in three separate print cartridges and one black ink in a fourth separate print cartridge are provided.



5. The fixative of Claim 1 wherein said polymer is selected from the group consisting of (a) acrylic and methacrylic acids and salts thereof, (b) esters of acrylic and methacrylic acids, (c) amides of acrylic and methacrylic acids, (d) hydroxy amides of acrylic and methacrylic acids, (e) polyethylene glycols and esters of acrylic and methacrylic acid, (f) polyalkylene glycols and esters of acrylic and methacrylic acid, (g) sulfoalkyl(aryl) acrylate and methacrylate, and salts thereof, (h) polyalkylene (aryl) glycol diacrylates and dimethacrylates (i) triacrylates, trimethacrylates, tetraacrylates, and tetramethacrylates (j) styrene and its derivatives, (k) vinyl esters and alcohols, (l) vinyl ethers, (m) diallyldialkyl ammonium halides, (n) vinyl sulfonic acid and salts thereof, (o) N-vinylamides, (p) polyunsaturated betaines, (q) polyunsaturated sulfo-betaines, (r) polyunsaturated amine oxides, (s) polyunsaturated fatty acids, (t) polyethylene oxide alkyl alkyenyl phenols, (u) polyalkylene and polyaryl glycol diacrylates and dimethacrylates, (v) polyalkylene and polyaryl divinyl ethers, (w) trimethylolpropane triacrylates and trimethacrylates, (x) alkoxylated trimethylolpropane triacrylates and trimethacrylates, (y) glycerol triacrylates and trimethacrylates, (z) alkoxylated glycerol triacrylates and trimethacrylates, (aa) pentaerythritol tetraacrylates and tetramethacrylates, and (ab) alkoxylated pentaerythritol tetraacrylates and tetramethacrylates.

6. The fixative of Claim 5 wherein said polymer is selected from the group consisting of allyl methacrylate, allyl acrylamide, N-vinyl carbazole, N-vinyl pyrrolidone, vinyl imidazole, vinyl pyridine, 1,4-diisocyanatobenzene, toluene diisocyanate, 4,4'-methylenebis(phenyl isocyanate), polymethylene poly(phenyl isocyanate), dicyclohexylmethane diisocyanate, and 1,4-cyclohexane diisocyanate.

7. The fixative of Claim 1 wherein said polymer has a concentration in said vehicle within a range of about 2 to 30 wt%.

8. The fixative of Claim 1 wherein said molecular weight is within a range of about 5,000 to 20,000.

9. The fixative of Claim 1 wherein said monomer or oligomer has a concentration in said vehicle within a range of about 2 to 30 wt%.

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