

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

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
5 June 2003 (05.06.2003)

PCT

(10) International Publication Number  
**WO 03/046039 A1**

(51) International Patent Classification<sup>7</sup>: **C08G 18/08**,  
18/12

Cleve Avenue, Clifton, NJ 07011 (US). **SIMONI-TRUNCCELLITO, Jeannette**; 15 Preston Street, Ridgefield Park, NJ 07660 (US).

(21) International Application Number: PCT/US01/46120

(74) Agent: **PERSLEY, Sidney**; 222 Bridge Plaza South, Fort Lee, NJ 07024 (US).

(22) International Filing Date:  
28 November 2001 (28.11.2001)

(81) Designated States (*national*): BR, CA.

(25) Filing Language: English

(84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(26) Publication Language: English

(71) Applicant: **SUN CHEMICAL CORPORATION**  
[US/US]; 222 Bridge Plaza South, Fort Lee, NJ 07024 (US).

**Published:**  
— with international search report

(72) Inventors: **ARCURIO, Ralph**; 10 Linvale Lane, Bridgewater, NJ 08807 (US). **CZARNECKI, Richard**; 55 Atherton Court, Wayne, NJ 07470 (US). **LUCCI, Sam**; 45 Van

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



**WO 03/046039 A1**

(54) Title: WATER-BORNE AQUEOUS EPOXY-ESTER/ACRYLATE AND POLY(URETHANE-UREA) BASED  
CROSSLINKED RESINS

(57) Abstract: A water based dual crosslinked resin and printing inks derived therefrom containing (a) a water borne epoxy/ester/acrylate copolymer having reactive keto groups and thyleneic unstaruation and (b) a poly(urethane/urea) having terminal amino groups; whre the crosslinking occurs between the reactive keto and terminal amino groups. The resin also contains onium carboxylate salt groups derived from carboxylic acid groups, ammonia or volatile amine so that the crosslinking system is neither neutral nor basic.

## WATER-BORNE AQUEOUS EPOXY-ESTER/ACRYLATE AND POLY(URETHANE- UREA) BASED CROSSLINKED RESINS

5

### BACKGROUND OF THE INVENTION

#### Field of the Invention

This invention relates to water-borne crosslinkable resin compositions. More particularly, this invention relates to water-borne crosslinkable printing ink compositions for printing on low density polyethylene films.

10

#### Description of Related Art

Over the years, the printing industry has turned to flexography to print images onto deformable surfaces such as polymeric films, fabrics, as well as to print conventional products in the publishing industry. Flexography is a branch of rotary typographic printing in which the printing is applied to a substrate surface by use of a flexible relief plate and highly fluid, volatile solvent based inks which dry rapidly by evaporation. In recent years, increased emphasis has been placed on using water as the solvent, rather than volatile organic solvents; and a wide variety of colorants have been developed for use in these water-based ink formulations. Recent advances in water-based ink formulations are illustrated, by Levy et al., in U.S. Patent 5,853,859 and by Hutter in U.S. Patent 5,498,661.

15

Levy et al. disclose printing compositions for printing fabric comprising thermoplastic polyolefin fibers. Levy's printing compositions comprise a room temperature curable latex polymer, pigment and a cure promoter. The composition is applied to fabric as an aqueous mixture with a pre-cure pH adjusted to above 8 using a fugitive alkali. The composition is then cured at room temperature. The dried residue of the aqueous mixture retains color-fastness when exposed to liquids with a pH between about 2 and about 13 so that the dried residue will remain on the fabric when exposed to most common cleaning chemicals and under most conditions of use.

20

Hutter discloses acrylic latex binders for use in preparing zinc-containing water-base inks for printing on plastic films such as polypropylene, polyester, and the like. The binder results from an addition emulsion polymerization reaction of four individual components. Inks containing these binders exhibit increased chemical resistance to commonly-used cleaning formulations and offer excellent heat and water-crinkle

25

30

resistance.

While advances have been made in water-based ink formulations for generally printing plastic films and fabrics, there continues to be a need for an aqueous based inks suitable for printing on low-density polyethylene films to form chemical-resistant, adherent, dried ink images which do not block with other surfaces or itself, e.g., as when stored in roll form or with other substrate surfaces.

### SUMMARY OF THE INVENTION

The above mentioned needs are met by aqueous printing inks which are derived from an aqueous crosslinkable resin system having a pH greater than 7 comprising:

10 (A) a water-dispersible poly(urethane/urea) being the reaction product of a polyurethane prepolymer prepared from a diisocyanate component and a diol component; wherein the -NCO/-OH ratio is between 1 and 2; and containing 1 to 8 % by weight of unreacted -NCO and carboxylic acid groups and between 110 % and 200 % of a diamine, based on the

15 equivalents of the unreacted -NCO groups; wherein the resulting poly(urethane/urea) contains terminal amino groups and  $-\text{CO}_2^- \text{A}^+$  groups; wherein  $\text{A}^+$  is an onium ion of ammonia or a volatile amine; and

(B) a water-dispersible poly(epoxy/ester/acrylate) being an epoxy/ester prepolymer grafted with an acrylic component; wherein, (a) the epoxy/ester prepolymer is prepared from a

20 condensation polymer of an aryl, alkyl or alkaryl dihydroxy compound with a aryl, alkyl or alkaryl bis-oxirane compound, and an unsaturated fatty acid and, (b) the acrylic component contains reactive keto groups and  $-\text{CO}_2^- \text{B}^+$  groups, wherein  $\text{B}^+$  is a second onium ion of ammonia or the volatile amine; whereby the resulting poly(epoxy/ester/acrylate) contains residual ethylenic unsaturation; and

25 (C) water.

A further embodiment of this invention is a method for producing a cured film on a substrate comprising the steps of: applying the above described aqueous crosslinkable resin system onto a surface of the substrate to form a coating and drying the coating to initiate curing; wherein the film formed is tack-free, firmly adherent to the surface of the

30 substrate, and un-blocked when contacted under pressure to a second surface of the substrate or a second substrate.

In a preferred embodiment of this invention, the film is further crosslinked by oxidative crosslinking of the residual ethylenic unsaturation.

A still further embodiment of this invention is an aqueous, crosslinkable printing ink having a pH greater than 7 comprising:

- (A) a water-dispersible poly(urethane/urea) being the reaction product of a polyurethane prepolymer prepared from a diisocyanate component and a diol component; wherein the -NCO/-OH ratio is between 1 and 2; and containing 1 to 8 % by weight of unreacted -NCO and carboxylic acid group; and  
5 between 110 % and 200 % of a diamine, based on the equivalents of the unreacted -NCO groups; wherein the resulting poly(urethane/urea) contains terminal amino groups and -CO<sub>2</sub><sup>-</sup> A<sup>+</sup> groups; wherein A<sup>+</sup> is an onium ion of ammonia or a volatile amine;
- (B) a water-dispersible poly(epoxy/ester/acrylate) being an epoxy/ester prepolymer grafted with an acrylic component; wherein (a) the epoxy/ester prepolymer is prepared from a condensation polymer of an aryl, alkyl or alkaryl dihydroxy compound with aryl, alkyl or alkaryl a bis-oxirane compound, and an unsaturated fatty acid and (b) the acrylic component contains reactive keto groups and -CO<sub>2</sub><sup>-</sup> B<sup>+</sup> groups, wherein B<sup>+</sup> is a second  
10 onium ion of ammonia or the volatile amine; whereby the resulting poly(epoxy/ester/acrylate) contains residual ethylenic unsaturation;
- (C) water;
- (D) a colorant, fluorescing agent, or mixture thereof; and optionally,
- (E) an oxidative crosslinking agent; and  
15
- (F) a dispersing agent.  
20

A still further embodiment of this invention is a method for printing an image on a substrate comprising the steps: applying the aqueous, crosslinkable printing ink of this invention onto the surface of the substrate to form an image; and drying the image to  
25 initiate curing; wherein the print image formed is tack-free, firmly adherent to the surface of the substrate, and un-blocked when contacted under pressure to a second surface of the substrate or to a second substrate.

#### DETAILED DESCRIPTION OF THE INVENTION

30 The present invention relates to a novel water based dual crosslinking resin system between a water borne epoxy/ester/acrylate copolymer component containing reactive keto groups and ethylenic unsaturation, and a water-borne poly(urethane/urea) component containing terminal amino groups. Both components contain ammonium carboxylate salt groups derived from carboxylic acid groups and ammonia or a fugitive amine so that the

water based crosslinking system can be neutral or basic. More particularly, the present invention relates to a novel water based flexographic packaging ink which exploits this dual crosslinking resin system. While not wishing to be bound by theory, it is believed that when the printing ink is applied to a substrate and dried, the ammonia or fugitive amine is lost and the pH becomes acidic which in turn initiates crosslinking. Thus, the poly(urethane/urea) component provides the required amine functionality for the predominant crosslinking to take place in the dried ink with reactive keto groups on the epoxy-ester/acrylate copolymer component. Additionally the amine functionality of the poly(urethane/urea) provides adhesion to an underlying substrate. The ethylenic unsaturation of the epoxy-ester/acrylate copolymer additionally allows the copolymer to undergo secondary oxidative crosslinking when used with metal drying compounds. This ink system exhibits excellent block resistance, printability, resolubility, and adhesion on low density polyethylene film products such as those used to manufacture diapers and other such personal care products.

15

#### Aqueous Crosslinkable Resin

The aqueous crosslinkable resin system of this invention comprises a water-borne poly(urethane/urea) hereinafter described; a water-borne poly(epoxy/ester/acrylate) hereinafter described; and water in which the resin system has a pH of 7 or greater. As used herein the terms "water borne" and "water-dilutable" are intended to mean a material that is either a water dispersion or a water solution of the material or that the material is capable of being dissolved or dispersed in water as a stable suspension or solution. Typically, these aqueous crosslinkable resin systems comprise about 25 to about 30 wt.% of the water-borne poly(urethane/urea); about 15 to about 20 wt.% of the water-borne poly(epoxy/ester/acrylate); and about 10 to about 15 wt.% of water, based on the total weight of the resin system. The aqueous crosslinkable resin system may further comprise an oxidative crosslinking agent; a colorant; a fluorescent agent ; or any mixture thereof. The system may additionally contain conventional adjuvants such as dispersing agents, matting agents, waxes, silicones, and the like.

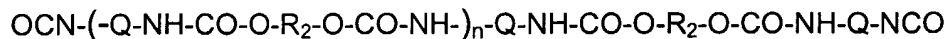
30

#### Poly(Urethane/Urea) Component

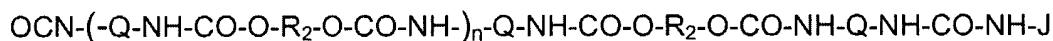
The water-dispersible poly(urethane/urea) component of this invention contains terminal amino groups, and ammonium carboxylate salt groups derived from carboxylic acid groups and ammonia or a fugitive amine, i.e.,  $-\text{CO}_2^- \text{A}^+$  groups, wherein  $\text{A}^+$  is an

onium ion of ammonia or the fugitive (i.e., volatile) amine. This poly(urethane/urea) component comprises a reaction product of a polyurethane prepolymer and a diamine, such as hydrazine.

5 The polyurethane prepolymer is a polyurethane polymer having two terminal isocyanate groups and has the Structure I:



10 wherein -Q- is an aryl or alkyl group; and R<sub>2</sub> comprises R<sub>3</sub> and R<sub>4</sub>, wherein R<sub>3</sub> is a polymeric group, and wherein R<sub>4</sub> is an alkyl group containing the carboxylic acid group or the -CO<sub>2</sub><sup>-</sup> A<sup>+</sup> group and wherein the polyurethane prepolymer contains 1 to 8.0 wt.% of unreacted -NCO groups. Typically, R<sub>2</sub> comprises from about 30 to about 80 equivalent % of R<sub>3</sub> and preferably further comprises R<sub>5</sub> which is an alkyl group; with the molar ratio of R<sub>3</sub> to R<sub>4</sub> being in the range from 70:30 to 95:5. Preferably the ratio of R<sub>3</sub> to R<sub>4</sub> is about  
15 85:15. The polyurethane prepolymer used in this invention may additionally contain up to about 10 wt. % of a second polyurethane polymer having a single terminal isocyanate group having the Structure II:



20 wherein -Q- is an aryl or alkyl group; and R<sub>2</sub> comprises R<sub>3</sub> and R<sub>4</sub>, wherein R<sub>3</sub> is a polymeric group, and wherein R<sub>4</sub> is an alkyl group containing the carboxylic acid group or the -CO<sub>2</sub><sup>-</sup> A<sup>+</sup> group, and J is a methoxypoly(oxyethylene/oxypropylene)-2-2propyl group. Preferably, the polyurethane prepolymer used in this invention contains from about 90  
25 wt.% to about 98 wt.% of the polyurethane polymer of Structure I; and from about 10 wt.% to about 2 wt.% of the second polyurethane polymer of Structure II.

The polyurethane prepolymer is prepared from a diisocyanate component and a diol component so that the -NCO/-OH ratio is between 1 and 2 and, preferably, is about 1.5.  
30 The "-NCO/-OH ratio" as used herein, has its conventional meaning which is the ratio of the number of equivalents of -NCO groups in the diisocyanate component, to the number of equivalents of -OH groups in the diol component. The resulting polyurethane prepolymer contains 1 to 8 wt. % by weight of unreacted -NCO groups, and 1 to 25 wt. % carboxylic acid groups. Preferably the polyurethane prepolymer contains about 5 wt. % of

unreacted -NCO groups, and about 10 wt.% carboxylic acid groups. Preferably the polyurethane prepolymer is prepared from a diisocyanate component comprising an aryldiisocyanate or an alkyldiisocyanate; a diol component comprising a polymeric diol, a diol-alkanoic acid; and optionally, an alkane diol, an alkoxyated amine, or a mixture thereof.

In the preparation of the prepolymer, a number of aryldiisocyanates or alkyldiisocyanates may be used such as 4,4'-diphenylmethane diisocyanate; 4,4'-dicyclohexyl diisocyanate; hexamethylene diisocyanate; isophorone diisocyanate; toluene diisocyanate, or meta-tetramethylene-xylenediisocyanate; of which meta-tetramethylene-xylenediisocyanate is preferred.

The polymeric diol used in this preparation has a molecular weight (MW) from about 650 to about 4000 and is selected from the group consisting of a polyether diol, a polyethylene diol, a polycaprolactone diol and a polypropylene diol. A number of polyether diols may be used such as PEG 650, PEG 1000, PEG 2000, PEG 3000, PEG 4000, or alpha-hydro-omega-hydroxy-poly(oxy-1,4-butyldiyl). A particularly preferred polyether diol is alpha-hydro-omega-hydroxy-poly(oxy-1,4-butyldiyl) having a MW of about 1000.

In the preparation, of the polyurethane prepolymer, a number of alkanolic acids may be used such as dimethylolpropionic acid, dimethylolbutanoic acid, and the like. A particularly preferred alkanolic acid is dimethylolpropionic acid or dimethylolbutanoic acid.

In the preparation a number of alkane diols may be used such as 1,4-butanediol, 1,5-pentanediol, or 2-methyl-1,3-propanediol. A particularly preferred alkanediol is 2-methyl-1,3-propanediol.

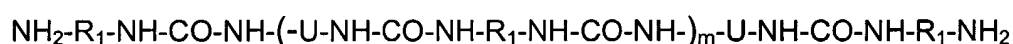
In the preparation of the prepolymer, a number of alkoxyated amines may be used. Preferably the alkoxyated amine is an ethoxyated amine, a propoxyated amine or a combination thereof, such as methoxy-poly(oxyethylene/oxypropylene)-2-propylamine. A particularly preferred alkoxyated amine is methoxy-poly(oxyethylene/oxypropylene)-2-propylamine.

Preferably, the polyurethane prepolymer is prepared from about 10 to about 70 parts by weight of the polymeric diol; about 10 to about 70 parts by weight of the aryldiisocyanate or the alkyldiisocyanate; about 1 to about 30 parts by weight of the diol-alkanoic acid; 0 to about 30 parts by weight of the alkane diol; and 0 to about 25 parts by weight of the alkoxyated amine. The reaction mixture for preparing the prepolymer may also contain 0 to about 2 parts by weight of a polymerization catalyst (e.g., a tin or zinc based catalyst), and 0 to about 25 parts by weight of an organic co-solvent such as ethyl

acetate. As used in the preparation herein, the co-solvent may also function as the processing solvent used in the preparation of the aqueous crosslinkable polymeric resin.

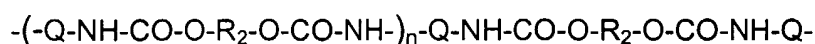
The polyurethane prepolymer is reacted with between 110 % and 200 % of the diamine, based on the equivalents of the unreacted -NCO groups in the prepolymer; then  
 5 neutralized with ammonia or a fugitive or volatile amine. As used herein a "fugitive amine" includes volatile amines which readily evaporate at room temperatures. Typically, the volatile amines will contain 1 to 5 carbon atoms and include alkyl amines or an alkanolamines such as t-butyl amine, triethyl amine, ethanolamine, methyl ethanolamine, N,N-dimethylethanol-amine. A preferred alkanolamine is N,N-dimethylethanol-amine. A  
 10 number of diamines may be used for preparing the poly(urethane/urea) of this invention, such as hydrazine, alkyl substituted hydrazines, methylenediamine, ethylenediamine, diamino cyclohexane, hexamethylene diamine, piperazine, or isophorone diamine. A particularly preferred diamine is hydrazine.

As illustrated in the following examples, the poly(urethane/urea) component is  
 15 prepared by first preparing the polyurethane prepolymer in a processing (co-solvent) as described above. The resulting prepolymer is slowly added to an aqueous solution of the diamine and the ammonia or fugitive amine at raised temperatures to produce a water-dispersible poly(urethane/urea). The water-dispersible poly(urethane/urea) prepared by this method is an aqueous dispersion comprising about 15 to about 70 wt. % of the  
 20 poly(urethane/urea); about 30 to about 85 wt. % water; and 0 to about 25 wt. % of a processing solvent such as 1-propoxy-2-propanol. The poly(urethane/urea) prepared by this method has the Structure III:



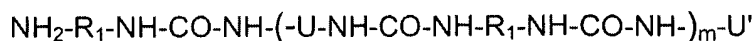
25

wherein  $R_1$  is a covalent bond or a  $C_{1-3}$  alkyl group and -U- has the Structure IV:

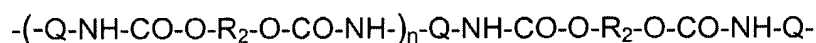


30 wherein -Q- is an aryl or alkyl group; and  $R_2$  comprises  $R_3$  and  $R_4$ , wherein  $R_3$  is an alkyl or a polymeric group, and wherein  $R_4$  is an alkyl group containing the  $\text{-CO}_2^- \text{A}^+$  group. When the poly(urethane/urea) is prepared from the polyurethane prepolymer containing both the polyurethane polymer of Structure I and the second polyurethane of Structure II, the poly(urethane/urea) additionally contains a second poly(urethane/urea) polymer of

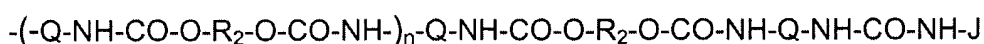
Structure V:



- 5 wherein R<sub>1</sub> is a covalent bond or an alkyl group having 1-3 carbon atoms; -U- has the Structure IV:



- 10 and -U' has the Structure VI:



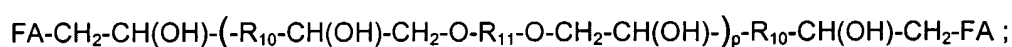
- 15 wherein -Q- is an aryl or alkyl group; and R<sub>2</sub> comprises R<sub>3</sub> and R<sub>4</sub>, wherein R<sub>3</sub> is an alkyl or a polymeric group, wherein R<sub>4</sub> is an alkyl group containing the -CO<sub>2</sub><sup>-</sup> A<sup>+</sup> group; and wherein J is a methoxypoly(oxyethylene/oxypropylene)-2-2propyl group. A preferred water-dispersible poly(urethane/urea) of this invention is propanoic acid,3-hydroxy-2-(hydroxymethyl)-2-methyl, polymer with 1,3-bis(1-isocyanato-1-methylethyl)benzene, hydrazine, alpha-hydro-omegahydroxypoly-9oxy-1,4-butanediyl) and 2-methyl-1,3-  
20 propanediol, ammonium salt, polyethylene-polypropyleneglycol 2-aminopropyl methyl ethyl (ME) ether blocked.

#### Poly(Epoxy/Ester/Acrylate) Component

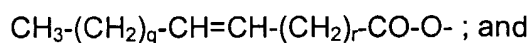
- 25 The water-borne poly(epoxy/ester/acrylate) component of this invention contains, reactive keto groups, residual ethylenic unsaturation, and ammonium carboxylate salt groups derived from carboxylic acid groups and ammonia or a volatile amine. In particular, the water-borne poly(epoxy/ester/acrylate) component comprises a polymerization product of an epoxy/ester prepolymer grafted with an acrylic component in a processing solvent. In particular, the water-dispersible poly(epoxy/ester/acrylate) has the structure:

- 30 
$$\text{EE AC}_o$$

wherein EE is an epoxy/ester prepolymer of the structure:



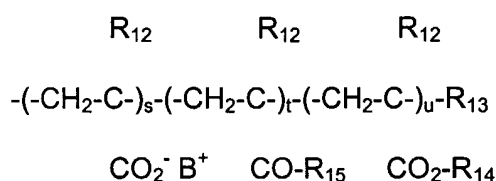
wherein R<sub>10</sub> and R<sub>11</sub> are individually selected from alkyl, aryl or alkaryl groups, and FA is a fatty acid ester group having the structure:



5

wherein AC<sub>o</sub> is the acrylic component comprising one or more acrylic polymer moieties randomly bonded to the epoxy/ester prepolymer, wherein each acrylic polymer moiety has the structure:

10



15

wherein each R<sub>12</sub> individually is selected from hydrogen or an alkyl group; R<sub>13</sub> is a chain termination group; R<sub>14</sub> is an alkyl group; and R<sub>15</sub> is an ester group which contains a keto group, or an amide group which contains a keto group; and wherein o, p, q, r, s, and t each individually are positive integers, while u is zero or a positive integer. Each acrylic polymer moiety has a random copolymer structure and the integers s, t, and u simply designate the number of moieties in the acrylic component. Preferably, R<sub>15</sub> is a diacetoneamide group; u is a positive integer; and R<sub>14</sub> is a butyl group

25

The epoxy/ester prepolymer is a condensation polymer of a bis-phenol-A with an aromatic bis-oxirane, and an unsaturated fatty acid. In particular, the epoxy/ester prepolymer is prepared from a reaction mixture comprising: about 5 to about 80 parts by weight of a condensation polymer of bis-phenol-A with an aromatic bis-oxirane; about 5 to about 70 parts by weight of the unsaturated fatty acid; 0 to about 1 part by weight of a polymerization catalyst; and about 10 to about 80 parts by weight of the processing solvent. Bis-phenol A compounds useful in preparing the condensation polymer include, bis-phenol A (i.e., 2,2-(4-hydroxyphenyl)propane). Aromatic bis-oxirane compounds useful in preparing the condensation polymer include 2,2'-((1-methylethylidene)bis(4,1-phenyleneoxymethylene))bis(oxirane). Preferably the condensation polymer is derived from bis-phenol A polymerized with 2,2'-((1-methylethylidene)bis(4,1-phenyleneoxymethylene))bis(oxirane). Unsaturated fatty acids which are useful in preparing the epoxy/ester prepolymer may be selected from the group consisting of linoleic; linolenic; and oleic acid; and mixtures thereof. A preferred unsaturated fatty acid is a fatty acid

35

mixture containing 39 wt. % linoleic acid; 40 wt. % of linolenic acid; and 21 wt. % of oleic acid; and a particularly preferred unsaturated fatty acid is this fatty acid mixture which contains additional linoleic acid.

The acrylic component which is grafted to the epoxy/ester prepolymer, contains  
5 reactive keto groups and  $-\text{CO}_2^- \text{B}^+$  groups, in which  $\text{B}^+$  is an onium ion of ammonia or the volatile amine.  $\text{B}^+$  is an onium ion of ammonia or the volatile amine and may be the same as  $\text{A}^+$  described previously in connection with the poly(urethane/urea) component. Preferably the acrylic component comprises: about 1 to about 30 parts by weight of diacetone acrylamide; about 1 to about 20 parts by weight of acrylic acid, methacrylic acid  
10 or a mixture thereof; about 0 to about 30 parts by weight of an alkyl acrylate; about 0.1 to about 5 parts by weight of a polymerization initiator; and about 1 to about 50 parts by weight of the processing solvent such as 1-propoxy-2-propanol. The alkyl acrylate may be a  $\text{C}_{1-5}$  alkyl acrylate with butyl acrylate being preferred. The grafted polymerization product is neutralized with ammonia or the volatile amine. When a volatile amine is used,  
15 it typically contains 1 to 5 carbon atoms, and is an alkyl amine or an alkanolamine such as t-butyl amine, triethyl amine, ethanolamine, methylethanolamine, N,N-dimethylethanolamine, and the like. A preferred alkanolamine is N,N-dimethylethanolamine.

As illustrated in the following examples, the epoxy resin is first esterified with an  
20 unsaturated fatty acid in the presence of a metal catalyst, such as zirconium 2-ethylhexoate. The resulting epoxy/ester is grafted with the acrylic component in the presence of an initiator compound such as azoisobutyronitrile. The water-dispersible poly(epoxy/ester/acrylate) prepared in this invention is an aqueous solution comprising about 10 to about 85 wt.% of the poly(epoxy/ester/acrylate); about 15 to about 90 wt. % water; and 0 to about 40 wt. % of a processing solvent. A preferred water-dispersible  
25 poly(epoxy/ester/acrylate) of this invention is phenol 4,4'-(1-methylethylidene)bis, polymer with (chloromethyl) oxirane, reaction products with  $\text{C}_{18}$  unsaturated fatty acids, copolymers with butyl 2-propenoate, 2-methyl-2-propenoic acid and N-(1,1-dimethyl-3-oxobutyl)acrylamide, compound with N,N-dimethylethanolamine.

### 30 Oxidative Crosslinking Agent

The aqueous crosslinkable resin system of this invention may contain an oxidative crosslinking agent to facilitate the oxidative crosslinking of the residual ethylenic unsaturation of the dried resin system. Such oxidative crosslinking agents are particularly useful for the dual curing inks using the crosslinkable resin system of this invention. While

most of such agents are useful, preferred oxidative crosslinking agents include metal salts of a fatty acids wherein the metal is manganese, cobalt, or zinc. A few examples of such metal salts are more fully described in connection with the preparation of printing inks under this invention.

5

#### Colorant/ Fluorescing Agent

The aqueous crosslinkable resin system of this invention may contain a colorant such as a dye or pigment, a fluorescing agent, or a mixture thereof. Alternatively, the colorant may possess the dual function of a fluorescing coloring agent. Colorants have their conventional function of imparting a visible color with a desired hue and density. Fluorescing agents have the function of imparting a marking typically not visible without the aid of stimulating radiation outside the visible spectral region. Although, colorants and fluorescing agents may or may not be incorporated into any crosslinkable resin system of this invention, when used they form a component of the dual crosslinkable printing ink of this invention.

10  
15

The resin systems of this invention when used in aqueous crosslinkable printing inks, typically contain one or more colorants such as a soluble dye or solid pigment. Such inks may typically contain one or more conventional solid pigments dispersed therein.

The pigment used may be any conventional organic or inorganic pigment such as Pigment Yellow 1, Pigment Yellow 3, Pigment Yellow 12, Pigment Yellow 13, Pigment Yellow 14, Pigment Yellow 17, Pigment Yellow 63, Pigment Yellow 65, Pigment Yellow 73, Pigment Yellow 74, Pigment Yellow 75, Pigment Yellow 83, Pigment Yellow 97, Pigment Yellow 98, Pigment Yellow 106, Pigment Yellow 114, Pigment Yellow 121, Pigment Yellow 126, Pigment Yellow 127, Pigment Yellow 136, Pigment Yellow 174, Pigment Yellow 176, Pigment Yellow 188, Pigment Orange 5, Pigment Orange 13, Pigment Orange 16, Pigment Orange 34, Pigment Red 2, Pigment Red 9, Pigment Red 14, Pigment Red 17, Pigment Red 22, Pigment Red 23, Pigment Red 37, Pigment Red 38, Pigment Red 41, Pigment Red 42, Pigment Red 112, Pigment Red 170, Pigment Red 210, Pigment Red 238, Pigment Blue 15, Pigment Blue 15:1, Pigment Blue 15:2, Pigment Blue 15:3, Pigment Blue 15:4, Pigment Green 7, Pigment Green 36, Pigment Violet 23, Pigment Black 7, titanium dioxide, carbon black, and the like. Pigment compositions which are also useful in the printing inks of this invention are described in U.S. Patents 4,946,508; 4,946,509; 5,024,894; and 5,062,894 each of which is incorporated herein by reference. Such pigment compositions are a blend of the pigment along with a poly(alkylene oxide) grafted

20  
25  
30

pigment.

The classes of dyes suitable for use in present invention are selected from acid dyes, natural dyes, direct dyes either cationic or anionic direct dyes, basic dyes, and reactive dyes.

5           The acid dyes, also regarded as anionic dyes, are soluble in water and mainly insoluble in organic solvents and are selected, from yellow acid dyes, orange acid dyes, red acid dyes, violet acid dyes, blue acid dyes, green acid dyes, and black acid dyes. European Patent 0 745 651, incorporated herein by reference, describes a number of acid dyes which are suitable for use in the present invention. The yellow acid dyes selected  
10 include Acid Yellow 1 (C.I. 10316); Acid Yellow 7 (C.I. 56205); Acid Yellow 17 (C.I. 18965); Acid Yellow 23 (C.I. 19140); Acid Yellow 29 (C.I. 18900); Acid Yellow 36 (C.I. 13065); Acid Yellow 42 (C.I. 22910); Acid Yellow 73 (C.I. 45350); Acid Yellow 99 (C.I. 13908); Acid Yellow 194; and Food Yellow 3 (C.I. 15985). The orange acid dyes selected include Acid Orange 1 (C.I. 13090/1); Acid Orange 10 (C.I. 16230); Acid Orange 20 (C.I.  
15 14603); Acid Orange 76 (C.I. 18870); Acid Orange 142; Food Orange 2 (C.I. 15980); and Orange B. The red acid dyes selected include Acid Red 1 (C.I. 18050); Acid Red 4 (C.I. 14710); Acid Red 18 (C.I. 16255); Acid Red 26 (C.I. 16150); Acid Red 27 (C.I. 16185); BASOVIT™ 425E (available from BASF Corporation) a xanthone based acid dye also known as Acid Red 51 (C.I. 45430); Acid Red 52 (C.I. 45100); Acid Red 73 (C.I. 27290);  
20 Acid Red 87 (C.I. 45380); Acid Red 94 (C.I. 45440); Acid Red 194; and Food Red 1 (C.I. 14700). The violet acid dyes selected include Acid Violet 7 (C.I. 18055); and Acid Violet 49 (C.I. 42640). The blue acid dyes selected include Acid Blue 1 (C.I. 42045); Acid Blue 9 (C.I. 42090); Acid Blue 22 (C.I. 42755); Acid Blue 74 (C.I. 73015); Acid Blue 93 (C.I. 42780); and Acid Blue 158A (C.I. 15050). The green acid dyes selected include Acid  
25 Green 1 (C.I. 10028); Acid Green 3 (C.I. 42085); Acid Green 5 (C.I. 42095); Acid Green 26 (C.I. 44025); and Food Green 3 (C.I. 42053). The black acid dyes selected include Acid Black 1 (C.I. 20470); Acid Black 194 (BASANTOL™ X80, available from BASF Corporation, an azo/1:2 CR-complex also known as.

The direct dyes selected for use in the present invention include Direct Blue 86 (C.I.  
30 74180), Direct Red 199, Direct Red 168, Direct Red 253 (C.I. Not Assigned) and Direct Yellow 107/132 (C.I. Not Assigned). The direct dyes are commonly used in coloration of pulp paper.

The natural dyes selected for use in the present invention include Alkanet (C.I. 75520,75530); Annatto (C.I. 75120); Carotene (C.I. 75130); Chestnut; Cochineal (C.I.

75470); Cutch (C.I. 75250, 75260); Divi-Divi; Fustic (C.I. 75240); Hypernic (C.I. 75280); Logwood (C.I. 75200); Osage Orange (C.I. 75660); Paprika; Quercitron (C.I. 75720); Sanrou (C.I. 75100); Sandal Wood (C.I. 75510, 75540, 75550, 75560); Sumac; and Turmeric (C.I. 75300).

5           The reactive dyes selected for use in the present invention include Rewactive Yellow 37 (monoazo dye); Reactive Black 31 (disazo dye); Reactive Blue 77 (phthalocyanine dye) and Reactive Red 180 and Reactive Red 108 dyes.

          Preference is given to the use of acid dyes such as, for example, Acid Black 194; Acid Red 51, Acid Blue 9; Acid Green 26; Acid Yellow 36, Acid Orange 142, Direct Blue  
10   86, Direct Red 253 and Direct Yellow 107/132 dyes.

          The printing inks of this invention may also contain one or more fluorescing agents either alone or in combination with other coloring agents as described above. A preferred fluorescing agent is Clircode™ a trademark product which is owned by and available from Isotag Inc. of Houston, TX.

15

#### Adjuvants

          The aqueous crosslinkable resin systems and inks of this invention may contain the usual adjuvants to adjust flow, surface tension and gloss of a cured coating or printed ink. Such adjuvants contained in inks or coatings typically are a surface active agent, a wax, or  
20   a combination thereof. These adjuvants may function as leveling agents, wetting agents, dispersants, defrothers or deareators, or additional adjuvants may be added to provide a specific function. Preferred adjuvants include fluorocarbon surfactants such as FC-430, a product of the 3M company; silicones, such as DC57, a product of Dow Chemical Corporation; polyethylene wax; polyamide wax; polytetrafluoroethylene wax; and the like.

25

#### Aqueous Crosslinkable Printing Ink

          The aqueous crosslinkable ink of this invention comprises the aqueous crosslinkable resin system of this invention; water; and a colorant, and optionally an oxidative crosslinking agent. The aqueous crosslinkable ink has a pH of 7 or greater. As  
30   previously described, the aqueous crosslinkable resin system comprises the water-dispersible poly(urethane/urea); and the water-dispersible poly(epoxy/ester/acrylate). The aqueous crosslinkable ink of this invention may further comprise adjuvants which function as leveling agents, wetting agents, dispersants, defrothers, deareators, etc. Typically, the ink is prepared from a varnish comprising the aqueous crosslinkable resin system of this

invention; the oxidative crosslinking agent; a non-ionic surfactant; a wax adjuvant such as oxidized polyethylene wax, paraffin wax, and the like; a defrother such as dimethyl polysiloxane, and the like; and water. The varnish is then compounded with the colorant, typically a pigment, and any further adjuvants and water to produce a stable ink having a  
5 pH of at least 7 and preferably 8 or above. Preferably, the aqueous crosslinkable ink of this invention comprises: about 40 wt.% to about 50 wt.% by weight of the aqueous crosslinkable resin system of this invention; about 5 wt.% to about 15 wt.% of water; about 30 wt.% to about 50 wt.% of the colorant, a fluorescing agent, or a mixture thereof; about 0.5 wt.% to about 5 wt.% of the oxidative crosslinking agent; about 1 wt.% to about 5 wt.%  
10 of the non-ionic surfactant; about 1 wt.% to about 7 wt.% of the wax adjuvant; and, about 0.1 wt.% to about 2 wt.% of the defrother. The inks of this invention are particularly useful in flexographic printing on low density polyethylene film such as used in the manufacture of diapers and other such personal care products.

#### 15 Method of Application

The aqueous crosslinkable resin composition may be applied to the substrate surface as a uniform coating using any conventional coating technique. Thus the composition may be spin coated, bar coated, roller coated, curtain coated or may be applied by brushing, spraying, etc. Alternatively the aqueous composition may be applied  
20 imagewise to the substrate surface, for instance as a printing ink of this invention, using any conventional printing technique. Once the aqueous coating composition is applied to the substrate surface, the resulting coating or printed image is dried thus removing residual water, ammonia or volatile amine, and any residual processing solvent from the coating or ink image to initiate curing. Typically, residual water, ammonia/volatile amines,  
25 and any solvent is removed as the coated substrate passes through the drying sections of conventional coaters or printing press systems. Although not wishing to be bound by theory, it is theorized that during this drying step the system pH is reduced to initiate crosslinking between the reactive keto groups of the epoxy/ester/acrylate component with the terminal amino functionality of the poly(urethane/urea) component to form a cured film  
30 or ink image. In a dual crosslinking mode, the cured film or ink image is further cured by oxidative crosslinking of the residual ethylenic groups of the epoxy/ester/acrylate component over an extended period of time thus further hardening and adhering the cured film or ink image to the substrate. Regardless of the mechanism involved in the application or printing method of this invention, a cured film or ink image is formed which is

tack-free and firmly adherent to the surface of the substrate, and which is un-blocked when contacted under pressure to a second surface of a second substrate or another portion of the cured film or ink image. As used herein the term "cured film" is intended to include a continuous cured film composition as well as a discontinuous cured ink image  
5 composition.

In a preferred embodiment of this invention an image is printed on a substrate comprising the steps: printing the aqueous crosslinkable ink of this invention (previously described) onto a surface of the substrate to form an image; and drying the image to initiate curing so that the image formed which is tack-free, firmly adherent to the surface of  
10 the substrate, and un-blocked when contacted under pressure to a second surface of the substrate or a second substrate. In an added embodiment of the printing method of this invention, the crosslinked ink image is further crosslinked by oxidative crosslinking of the residual ethylenic unsaturation.

#### 15 Substrate

In general, the substrate and its surface may be composed of any typical substrate material such as plastics, for example polyolefin, polystyrene, polyvinylchloride, polynaphthelene terephthalate, polyacrylate, polyacrylic, metals, composites, glass, paper, etc.; however, a polymeric substrate is preferred. Typically, the substrate is a sheet  
20 material selected from a polyolefin, metalized polyethylene terephthalate, polystyrene, polycarbonate, polyurethane, polyesters, polyamide, polyamide, a paper product or a metal. Preferred polymeric substrates include a sheet of polyethylene, polypropylene, polyethylene terephthalate, cellulose acetate, cellulose acetate butyrate, or polycarbonate. Low-density polyethylene such as used in the manufacture of diapers and other such  
25 personal care products, is particularly preferred.

The following examples further illustrate details of this invention. This invention, which is set forth in the foregoing disclosure, is not to be limited either in spirit or scope by these examples. Those skilled in the art will readily understand that known variations of the conditions of the following procedures can be used. Unless otherwise noted, all  
30 temperatures are degrees Celsius and all part and percentages are by weight.

#### Example 1

An aqueous, epoxy/ester/acrylate having reactive keto groups was prepared from the components listed in Table 1 using the procedures described herein below.

Table 1

	<u>Component</u>	<u>Wt.%</u>
	DER-661 Epoxy Resin <sup>(a)</sup>	12.17
	Pamolyn 200 <sup>(b)</sup>	3.94
5	Pamolyn 300 <sup>(c)</sup>	2.58
	Zirconium Catalyst (12%) <sup>(d)</sup>	0.04
	Arcosolve PNP Solvent <sup>(e)</sup>	18.15
	Diacetone acrylamide	4.88
	Butyl acrylate	4.88
10	Methacrylic acid	3.08
	t-Butyl peroctoate	1.36
	AIBN (Vazo 64) <sup>(f)</sup>	0.32
	n,n-Dimethylethanolamine	4.55
	D.I. Water	44.05

15

---

(a) DER-661 Epoxy Resin is phenol,4,4'-(1-methylethylidene)bis-, polymer with 2,2'-((1-methylethylidene)bis(4,1-phenylene-oxymethylene))bis(oxirane); a product of Dow Chemical.

(b) Pamolyn 200 is 9,12-octadecanedienoic acid (Z,Z) (CAS # 60-33-3); a product of Hercules.

20 (c) Pamolyn 300 is a fatty acid mixture containing 39 %by weight linoleic acid; 40 % by weight of linolenic acid; and 21 % by weight of oleic acid; a product of Hercules.

(d) Zirconium Catalyst is zirconium 2-ethylhexoate (12% in mineral spirits); a product of OMG Americas.

(e) Arcosolve PNP Solvent is 1-propoxy-2-propanol; a product of Arco corp.

(f) AIBN (Vazo 64) is azoisobutyronitrile ; a product of the DuPont Company

---

25

The DER-661, Pamolyn 200, Pamolyn 300 and Zirconium Catalyst Components were charged into a reactor, a nitrogen blanket was applied and the batch slowly heated to 150 C ± 2 C and held at that temperature for 0.5 hours. The temperature was increased to 200 C ± 2 C and held at that temperature for 1 hour. then increased to 234 C ± 2 C and held at that temperature for 5 hours. The acid number of the reaction mixture was then

30 checked and subsequently checked hourly until it was equal to or less than 5, at which point the batch was cooled to 125 C ± 2 C. When the batch had cooled heating was restored to 134 C ± 2 C and the following additions were made. t-Butyl peroctoate and 2.27 wt.% of the Arcosolve PNP Solvent were premixed and then 1% of the mixture was added to the reactor through an addition funnel. After 5 minutes, addition of the mixture

35 was continued and addition was started of a pre-prepared solution of the diacetone acrylamide, butyl acrylate, methacrylic acid and 3.4 wt.% of the Arcosolve PNP Solvent and continued at a reaction temperature of 134 C ± 2 C over a period of 2 hours 15 minutes ( ± 15 minutes). When monomer addition was complete, the polymerization

grafting reaction was continued at 134 C ± 2 C for two hours. The amount of solids formed during polymerization was determined hourly, and when the amount reached a constant value, the batch was cooled to 80 C ± 2 C. The following three charges of AIBN were added sequentially. 0.13 wt.% of AIBN was added and polymerization continued for 1 hour at which point the amount of solids was checked. 0.13 wt. % of AIBN was then added and polymerization continued for 1 hour at which point the amount of solids was checked. 0.06 wt. % of AIBN was then added and polymerization continued for 1 hour at which point the amount of solids was checked. When the solids value obtained remained constant, the batch was cooled to 60 C ± 2 C. Next, N,N- Dimethylethanolamine 3.20 wt.% and 8.37 wt.% D.I. Water were premixed and the mixture was added to the batch over a period of 15 minutes ± 5 minutes. Then 25.68 wt.% D.I. water was added to the batch over a period of 15 minutes ± 5 minutes and the final product was stirred for 30 minutes before the reactor was cooled to 40 C ± 5 C. A portion of dimethylethanolamine was then added to the batch to adjust the pH to 9.0 to 9.5; and a portion of D.I. water was added to adjust the viscosity to 2500 to 3500 cps. The resulting aqueous epoxy/ester/acrylate product was then discharged through a 150 micron cloth filter to provide a epoxy-ester-acrylate resin solution containing about 30-35 % by weight of the unsaturated fatty ester of the epoxy resin grafted with a terpolymer of methacrylic acid, butyl acrylate, and diacetoneacrylamide.

#### 20 Example 2

An aqueous, poly(urethane/urea) having terminal reactive amine groups was prepared from the components listed in Tables 2 and 3 using the procedures described herein below.

Table 2

25	<u>Component</u>	<u>Wt.%</u>
	polyTHF 1000 <sup>(g)</sup>	36.85
	Dimethylolpropionic acid (DMPA)	6.50
	MPDiol <sup>(h)</sup>	2.30
	Jeffamine M-1000 <sup>(i)</sup>	4.85
30	m-TMXDI <sup>(j)</sup>	42.00
	Ethyl acetate	7.50

(g) polyTHF 1000 is alpha-hydro-omega-hydroxy-poly(oxy-1,4-butyldiyl) having a MW of about 1000; a product of BASF.  
 (h) MPDiol is 2-methyl-1,3-propanediol; a product of Arco.  
 (i) Jeffamine M-1000 is methoxypoly(oxyethylene/oxypropylene)-2-propylamine a product of Huntsman.  
 (j) m-TMXDI is meta-tetramethylene xylene diisocyanate; a product of Cytec.

DMPA, poly THF 1000, MPDIol, Jeffamine M-1000 and ethyl acetate were added to a reactor under nitrogen. The mixture was slowly heated to 45 -55 C for at least 30 minutes, then m-TMXDI was added. The reaction batch was slowly heated to 90 C at a rate of 1 degree per minute and maintained at temperatures below 100 C. When the temperature reached 90 - 95 C, the reaction mixture was checked for its free NCO content every 30 minutes. The reaction was continued for about 2 to 3 hours until the % of free NCO was 4.9 -5.2% at which point the reaction was cooled to 65 - 70 C. The resulting pre-polymer was then sampled for its % of free NCO and % non-volatiles while being held at 65 - 70 C.

Table 3

<u>Component</u>	<u>Wt.%</u>
water	53.39
ammonia	1.55
Scav Ox Lo hydrazine <sup>(k)</sup>	7.40
Pre-Polymer	37.66

(k) Scav Ox Lo hydrazine is a 15.5% water solution of the diamine hydrazine; a product of Olin corp.

Water and ammonia were charged into a reactor at room temperature. Scav Ox Lo hydrazine was added to the reactor and mixed at a temperature of 20 -30 C. The pre-polymer was added to the reactor over a 15 minute period and the temperature increased to 40 -45 C and maintained below 45 C. After all transfers were complete, the mixture was held at 40 C for 1 hour to form a poly(urethane/urea). The batch contained 36% by weight solids, had a viscosity of about 300 cps, a pH of about 9, and had an Amine Value of 35. This poly(urethane-urea) was believed to be propanoic acid, 3-hydroxy-2-(hydroxymethyl)-2-methyl-, polymer with 1,3-bis(1-isocyanato-1-methylethyl)benzene, hydrazine, -hydro- -hydroxypoly (oxy-1,4-butanediyl) and 2-methyl-1,3-propanediol, ammonium salt, polyethylene-polypropylene glycol 2-aminopropyl methyl ether blocked.

Example 3

An aqueous crosslinkable resin varnish was prepared from the epoxy/ester/acrylate

resin of Example 1 and the poly(urethane/urea) of Example 2 having the following formulation:

	<u>Component</u>	<u>Wt.%</u>
5	Polyurethane/urea of Example 2	28.40
	Epoxy/ester/acrylate of Example 1	17.90
	Oxidized polyethylene wax	4.00
	Surfactant <sup>(l)</sup>	1.00
	Paraffin wax emulsion <sup>(m)</sup>	30.00
10	Dimethyl polysiloxane	2.00
	Metal carboxylic salts <sup>(n)</sup>	4.00
	Water	12.30

---

(l) Surfactant is Rhodmax LO surfactant (from Rhodia Corp.) a 30% aqueous solution of mixed non-ionic and cationic surfactants (CAS# 70592-80-2)

15 (m) Paraffin wax emulsion contains 30% by weight of paraffin wax emulsified in water.

(n) Metal carboxylic salts is a mixture of carboxylic salts of cobalt and manganese.

---

The components were mixed to produce a stable aqueous varnish dispersion having a  
20 viscosity of about 25 seconds using a #3 Zahn Cup.

#### Example 4

An aqueous crosslinkable printing ink was prepared from the varnish formulation of  
Example 3 having the following formula:

25

	<u>Component</u>	<u>Wt.%</u>
	Varnish formulation of Example 3	50.00
	Titanium dioxide pigment	40.00
	Oxidized polyethylene wax	2.50
30	Water	8.00

The components were mixed to produce a stable aqueous varnish dispersion having a  
viscosity of about 25 seconds using a #3 Zahn Cup. The printing ink of Example 4 was  
used in a Common Impression Flexographic printing press to print on sheets of low-  
35 density polyethylene. When dried the printed ink firmly adhered to the polyethylene  
without any evidence of blocking, i.e., Sticking of ink to non-printed film or two separate ink  
surfaces sticking together to form a single surface. The antiblocking character of the ink

and its firm adhesion to the polyethylene was further improved by oxidative exposure to air for 24 hours or more.

5 Those skilled in the art having the benefit of the teachings of the present invention as hereinabove set forth, can effect numerous modifications thereto. These modifications are to be construed as being encompassed within the scope of the present invention as set forth in the appended claims.

What is claimed is:

1. An aqueous crosslinkable resin system having a pH greater than 7 comprising:  
(A) a water-dispersible poly(urethane/urea) being the reaction product of a polyurethane  
5 prepolymer prepared from a diisocyanate component and a diol component; wherein the -  
NCO/-OH ratio is between 1 and 2, and containing 1 to  
8 wt.% of unreacted -NCO and carboxylic acid groups; and between 110 % and 200 % of  
a diamine, based on the equivalents of the unreacted -NCO groups; wherein the resulting  
poly(urethane/urea) contains terminal amino groups, and  $-\text{CO}_2^- \text{A}^+$  groups; wherein  $\text{A}^+$  is  
10 an onium ion of ammonia or a volatile amine; (B) a water-dispersible  
poly(epoxy/ester/acrylate) being an epoxy/ester prepolymer grafted with an acrylic  
component; wherein (a) the epoxy/ester prepolymer is prepared from a condensation  
polymer of an aryl, alkyl or alkaryl dihydroxy compound with a aryl, alkyl or alkaryl bis-  
oxirane compound, and an unsaturated fatty acid and; (b) the acrylic component contains  
15 reactive keto groups and  $-\text{CO}_2^- \text{B}^+$  groups, wherein  $\text{B}^+$  is a second onium ion of ammonia  
or the volatile amine; whereby the resulting poly(epoxy/ester/acrylate) contains residual  
ethylenic unsaturation; and  
(C) water;
- 20 2. The resin system of claim 1 wherein the volatile amine contains 1 to 5 carbon  
atoms, and is an alkyl amine or an alkanolamine.
3. The resin system of claim 2 wherein the alkanolamine is N,N-dimethylethanol-  
amine.
- 25 4. The resin system of claim 1 wherein  $\text{A}^+$  and  $\text{B}^+$  are the same.
5. The resin system of claim 1 wherein the polyurethane prepolymer is prepared  
30 from:
  - (1) an aryl diisocyanate or alkyl diisocyanate component;
  - (2) a polymeric diol, a diol-alkanoic acid, and optionally, an alkane diol component; and
  - (3) an ammonia or the volatile amine; and optionally,
  - (4) an alkoxyated amine.

35

6. The resin system of claim 5 wherein the aryldiisocyanate is meta-tetramethylene-xylenediisocyanate.

5 7. The resin system of claim 5 wherein the polymeric diol is selected from the group consisting of a polyether diol, a polyethylene diol, and a polypropylene diol; having a molecular weight (MW) of about 650 to about 4000.

10 8. The resin system of claim 7 wherein the polyether diol is alpha-hydro-omega-hydroxy-poly(oxy-1,4-butyldiyl) with a MW of about 1000.

9. The resin system of claim 5 wherein the diol-alkanoic acid is dimethylolpropionic acid or dimethylolbutanoic acid.

15 10. The resin system of claim 5 wherein the alkanediol is 2-methyl-1,3-propanediol.

11. The resin system of claim 5 wherein the alkoxyated amine is an ethoxylated amine or a propoxylated amine.

20 12. The resin system of claim 11 wherein the ethoxylated amine is methoxy-poly(oxyethylene/oxypropylene)-2-propylamine.

13. The resin system of claim 5 wherein the polyurethane prepolymer is prepared from a mixture of:

- 25 (1) about 10 to about 70 parts by weight polymeric diol;  
(2) about 10 to about 70 parts by weight aryldiisocyanate or alkyldiisocyanate;  
(3) about 1 to about 30 parts by weight diol-alkanoic acid;  
(4) 0 to about 30 parts by weight alkane diol; and  
(5) 0 to about 25 parts by weight alkoxyated amine.

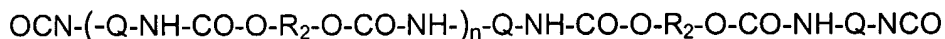
30

14. The resin system of claim 5 wherein the diamine is hydrazine.

15. The resin system of claim 1 wherein the water-dispersible poly(urethane/urea) reaction product propanoic acid,3-hydroxy-2-(hydroxymethyl)-2-methyl, polymer with 1,3-

bis(1-isocyanato-1-methylethyl)benzene, hydrazine, alpha-hydro-omegahydroxypoly-9oxy-1,4-butanediyl) and 2-methyl-1,3-propanediol, ammonium salt, polyethylene-polypropyleneglycol 2-aminopropyl methyl ethyl ether blocked.

- 5            16. The resin system of claim 1 wherein the polyurethane prepolymer comprises a polymer having the structure:



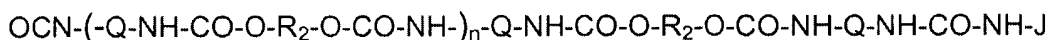
- 10          wherein -Q- is an aryl or alkyl group; and R<sub>2</sub> comprises R<sub>3</sub> and R<sub>4</sub>, wherein R<sub>3</sub> is a polymeric group, and wherein R<sub>4</sub> is an alkyl group containing the carboxylic acid group or the -CO<sub>2</sub><sup>-</sup> A<sup>+</sup> group and containing 1 to 8.0 wt. % of unreacted -NCO groups.

- 15            17. The resin system of claim 16 wherein R<sub>2</sub> further comprises R<sub>5</sub> which is an alkyl group.

18. The resin system of claim 16 wherein R<sub>2</sub> comprises from about 30 to about 80 equivalent % of R<sub>3</sub>.

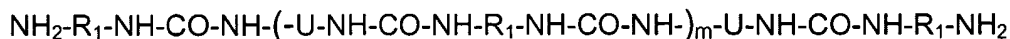
- 20            19. The resin system of claim 16 wherein the ratio of R<sub>3</sub> to R<sub>4</sub> is about 70:30 to about 95:5.

- 25            20. The resin system of claim 16 wherein the polyurethane prepolymer further comprises a second polymer having the structure:

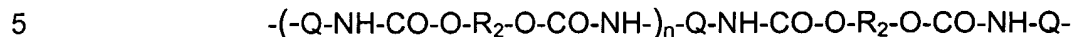


- 30          wherein -Q- is an aryl or alkyl group; and R<sub>2</sub> comprises R<sub>3</sub> and R<sub>4</sub>, wherein R<sub>3</sub> is a polymeric group; R<sub>4</sub> is an alkyl group containing the carboxylic acid group or the -CO<sub>2</sub><sup>-</sup> A<sup>+</sup> group; and J is a methoxypoly(oxyethylene/oxypropylene)-2-2-propyl group.

21. The resin of claim 1 wherein the water-dispersible poly(urethane/urea) reaction product has the structure:

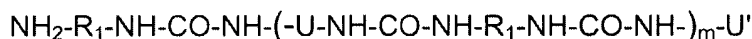


wherein  $\text{R}_1$  is a covalent bond or a  $\text{C}_{1-3}$  alkyl group and  $\text{-U-}$  has the structure:

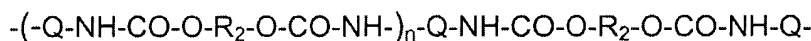


wherein  $\text{-Q-}$  is an aryl or alkyl group;  $\text{R}_2$  comprises  $\text{R}_3$  and  $\text{R}_4$ , wherein  $\text{R}_3$  is an alkyl or a polymeric group, and  $\text{R}_4$  is an alkyl group containing the  $\text{-CO}_2^- \text{A}^+$  group.

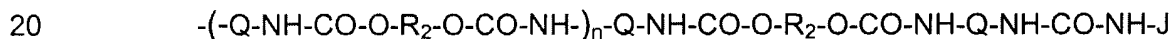
10 22. The resin of claim 21 wherein the poly(urethane/urea) resin further comprises a second reaction product having the structure:



15 wherein  $\text{R}_1$  is a covalent bond or a  $\text{C}_{1-3}$  alkyl group  $\text{-U-}$  has the structure:



and  $\text{-U}'$  has the structure:



wherein  $\text{-Q-}$  is an aryl or alkyl group; and  $\text{R}_2$  comprises  $\text{R}_3$  and  $\text{R}_4$ , wherein  $\text{R}_3$  is an alkyl or a polymeric group,  $\text{R}_4$  is an alkyl group containing the  $\text{-CO}_2^- \text{A}^+$  group; and wherein  $\text{J}$  is a methoxypoly(oxyethylene/oxypropylene)-2-2-propyl group.

25

23. The resin system of claim 1 wherein the water-dispersible poly(urethane/urea) is an aqueous dispersion comprising about 15 to about 70 wt. % of poly(urethane/urea); about 30 to about 85 wt.% water; and 0 to about 25 wt. % processing solvent.

30

24. The resin system of claim 1 wherein the epoxy/ester prepolymer is prepared from:

a. about 5 to about 80 parts by weight of a condensation polymer of bis-phenol-A

with an aryl bis-oxirane;

- b. about 5 to about 70 parts by weight unsaturated fatty acid;
- c. 0 to about 1 part by weight of polymerization catalyst; and
- d. about 10 to about 80 parts by weight of processing solvent.

5

25. The resin system of claim 24 wherein the condensation polymer is derived from bis-phenol A and 2,2'-((1-methylethyldine)bis(4,1-phenylene-oxymethylene))bis(oxirane).

10

26. The resin system of claim 24 wherein the unsaturated fatty acid is selected from the group consisting of linoleic acid, linolenic acid, and oleic acid; and mixtures thereof.

15

27. The resin system of claim 26 wherein the unsaturated fatty acid is a mixture of 39 wt. % linoleic acid; 40 wt. % linolenic acid; and 21 wt. % oleic acid.

28. The resin system of claim 27 wherein the unsaturated fatty acid is the unsaturated fatty acid mixture and additional linoleic acid.

20

29. The resin system of claim 24 wherein the processing solvent is 1-propoxy-2-propanol.

25

30. The resin system of claim 1 wherein the acrylic component comprises:  
a. about 1 to about 30 parts by weight diacetone acrylamide;  
b. about 1 to about 20 parts by weight acrylic acid, methacrylic acid or a mixture thereof;  
c. about 0 to about 30 parts by weight alkyl acrylate;  
d. about 0.1 to about 5 parts by weight polymerization initiator; and  
e. about 1 to about 50 parts by weight processing solvent;  
and reacting the acrylic component with ammonia or volatile amine.

30

31. The resin system of claim 30 wherein the alkyl acrylate is butyl acrylate.

32. The resin system of claim 1 wherein the water-dispersible poly(epoxy/ester/acrylate) is an aqueous solution comprising about 10 to about 85 wt. %

poly(epoxy/ester/acrylate); about 15 to about 90 % water; and 0 to about 40 wt. % processing solvent.

33. The resin system of claim 1 wherein the water-dispersible poly(epoxy/ester/acrylate) is phenol 4,4'-(1-methylethylidene)bis, polymer with (chloromethyl) oxirane, reaction products with C<sub>18</sub> unsaturated fatty acids, copolymers with butyl 2-propenoate, 2-methyl-2-propenoic acid and N-(1,1-dimethyl-3-oxobutyl)acrylamide, compound with N,N-dimethylethanolamine.

34. The resin system of claim 1 wherein the water-dispersible poly(epoxy/ester/acrylate) has the structure:

10

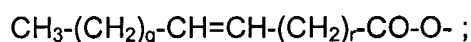


wherein EE is the epoxy/ester prepolymer having the structure:

15  $FA-CH_2-CH(OH)-(-R_{10}-CH(OH)-CH_2-O-R_{11}-O-CH_2-CH(OH)-)_p R_{10}-CH(OH)-CH_2-FA$  ;

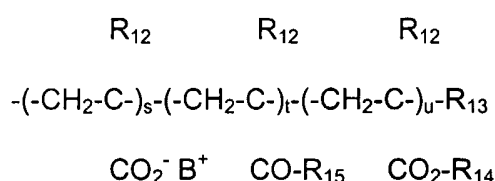
wherein R<sub>10</sub> and R<sub>11</sub> are individually selected from alkyl, aryl or alkaryl groups, FA- is a fatty acid ester group having the structure:

20



and AC<sub>o</sub> is an acrylic component comprising one or more acrylic polymer moieties randomly bonded to the epoxy/ester prepolymer the structure:

25



30

wherein each R<sub>12</sub> is individually selected from the group consisting hydrogen or alkyl; R<sub>13</sub> is a chain termination group; R<sub>14</sub> is an alkyl group; and R<sub>15</sub> is an ester group containing a keto group, or an amide group containing a keto group; and wherein o, p, q, r, s, and t all are positive integers, while u is zero or a positive integer.

35

35. The resin system of claim 34 wherein each acrylic polymer moiety has a random copolymer structure.

36. The resin system of claim 34 wherein  $R_{15}$  is a diacetoneamide group.
37. The resin system of claim 34 wherein  $u$  is a positive integer, and  $R_{14}$  is a butyl group
- 5 38. The resin system of claim 30 wherein the processing solvent is 1-propoxy-2-propanol.
39. The resin system of claim 1 further comprising an oxidative crosslinking agent.
- 10 40. The resin system of claim 39 wherein the oxidative crosslinking agent is a metal salt of a fatty acid wherein the metal is manganese, cobalt, or zinc.
41. The resin system of claim 1 further comprising a colorant, fluorescing agent, or a mixture thereof.
- 15 42. The resin system of claim 41 wherein the colorant is a dye or pigment.
43. The resin system of claim 41 further comprising a fluorescing agent that
- 20 fluoresces in the infrared spectral region.
44. A method for producing a cured film on a substrate comprising:  
applying the aqueous crosslinkable resin system of Claim 1 onto a surface of the substrate to form a coating; and
- 25 drying the coating to initiate curing; wherein the cured film formed is tack-free, firmly adherent to the surface of the substrate, and un-blocked when contacted under pressure to a second surface of the substrate or to a second substrate.
45. The method of claim 44 wherein the cured film is further cured by oxidative
- 30 crosslinking of the residual ethylenic unsaturation.
46. An aqueous crosslinkable printing ink comprising:  
(A) a water-dispersible poly(urethane/urea) being the reaction product of a polyurethane prepolymer, prepared from a diisocyanate component and a diol component; wherein the -

- NCO/-OH ratio is between 1 and 2; and the containing 1 to 8 wt.% of unreacted -NCO and carboxylic acid groups; and between 110 % and 200 % of a diamine, based on the equivalents of the unreacted -NCO groups, wherein the resulting poly(urethane/urea) contains terminal amino groups, and  $-\text{CO}_2^- \text{A}^+$  groups, wherein  $\text{A}^+$  is an onium ion of ammonia or a volatile amine;
- 5 (B) a water-dispersible poly(epoxy/ester/acrylate) being an epoxy/ester prepolymer grafted with an acrylic component; wherein, (a) the epoxy/ester prepolymer is prepared from a condensation polymer of an aryl, alkyl or alkaryl dihydroxy compound with an aryl, alkyl or alkaryl bis-oxirane compound, and an unsaturated fatty acid and; (b) the acrylic
- 10 component contains reactive keto groups and  $-\text{CO}_2^- \text{B}^+$  groups, wherein  $\text{B}^+$  is a second onium ion of ammonia or the volatile amine; and (c) the poly(epoxy/ester/acrylate) contains residual ethylenic unsaturation;
- (C) water;
- (D) a colorant, a fluorescing agent, or a mixture thereof; and optionally,
- 15 (E) an oxidative crosslinking agent; and optionally
- (F) a dispersing agent.

47. A method for printing an image on a substrate comprising:  
applying the aqueous crosslinkable printing ink of claim 46 onto the surface of the  
20 substrate to form an image; and drying the ink image to initiate curing; wherein the cured print image formed on the substrate is tack-free, firmly adherent to the surface of the substrate, and un-blocked when contacted under pressure to a second surface of the substrate or to a second substrate.

25 48. The method of claim 47 wherein the cured print image is further cured by oxidative crosslinking of the residual ethylenic unsaturation.

49. The method of claim 47 wherein the substrate is a polymeric substrate.

30 50. The method of claim 47 wherein the substrate is a polyethylene, polypropylene, polyethylene terephthalate, subbed polyethylene terephthalate, cellulose acetate, cellulose acetate butyrate, or polycarbonate.

51. The method of claim 47 wherein the substrate is a low-density polyethylene.

**INTERNATIONAL SEARCH REPORT**

International Application No  
**PCT/US 01/46120**

**A. CLASSIFICATION OF SUBJECT MATTER**  
**IPC 7 C08G18/08 C08G18/12**

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
**IPC 7 C08G 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)  
**WPI Data, EPO-Internal, PAJ**

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 057 843 A (NIPPON POLYURETHANE INDUSTRY) 6 December 2000 (2000-12-06) page 3, line 30 -page 13, line 32; claims 1-6,11 <p align="center">---</p>	1
A	WO 00 56827 A (AVECIA) 28 September 2000 (2000-09-28) page 1, line 28 -page 11, line 11; claims 1-12 <p align="center">---</p>	1
	-/--	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search  <b>7 August 2002</b>	Date of mailing of the international search report  <b>21/08/2002</b>
---	---

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  <b>Bourgonje, A</b>
--	---

## INTERNATIONAL SEARCH REPORT

In International Application No

PCT/US 01/46120

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Week 9831 Derwent Publications Ltd., London, GB; AN 1998-357528 XP002209010 "Room temperature-curable aqueous resin composition for coating agents or inks for plastic films" &amp; JP 10 139839 A (TAISEI KAKO), 26 May 1998 (1998-05-26) abstract</p> <p>-----</p>	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/46120

Patent document cited in search report	A	Publication date	US	Patent family member(s)	Publication date
EP 1057843	A	06-12-2000	US	6306947 B1	23-10-2001
			EP	1057843 A1	06-12-2000
WO 0056827	A	28-09-2000	AU	3307100 A	09-10-2000
			EP	1171534 A1	16-01-2002
			WO	0056827 A1	28-09-2000
JP 10139839	A	26-05-1998	JP	2837142 B2	14-12-1998