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United States Patent [19]

[11] E

Patent Number: Re. 34,329**Baker et al.**[45] **Reissued Date of Patent: Aug. 3, 1993**[54] **OVERPRINT AQUEOUS VARNISH**4,865,908 9/1989 Liu et al. 428/248
4,908,063 3/1990 Baker et al. 106/31[75] **Inventors: Timothy J. Baker, Claremore; John H. Woods, Tulsa, both of Okla.**[73] **Assignee: Petrolite Corporation, St. Louis, Mo.**[21] **Appl. No.: 849,292**[22] **Filed: Mar. 10, 1992****Related U.S. Patent Documents**

Reissue of:

[64] **Patent No.: 5,008,144**
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U.S. Applications:

[63] **Continuation-in-part of Ser. No. 267,064, Nov. 4, 1988, Pat. No. 4,908,063.**[51] **Int. Cl.⁵ C08L 91/06**[52] **U.S. Cl. 106/271; 106/270; 427/416; 427/258; 524/276**[58] **Field of Search 524/275, 277, 381, 524, 524/322, 376, 276, 106/270, 271**[56] **References Cited****U.S. PATENT DOCUMENTS**2,928,752 3/1960 Felletschin 106/268
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Primary Examiner—Mark L. Bell*Assistant Examiner*—Deborah Jones*Attorney, Agent, or Firm*—Pravel, Hewitt, Kimball & Krieger[57] **ABSTRACT**

An overprint aqueous varnish has improved properties by having incorporated therein a small amount of an aqueous mixture of a finely divided hydrocarbon and certain high molecular weight oxyalkylated primary alcohols.

20 Claims, No Drawings

OVERPRINT AQUEOUS VARNISH

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

REFERENCE TO RELATED APPLICATIONS

The present application is a continuation-in-part application of co-pending U.S. Patent Application Ser. No. 267,064, filed 1988 Nov. 04, now U.S. Pat. No. 4,908,063.

FIELD OF THE INVENTION

1. Background of the Invention

This invention relates to a new and useful additive composition for water-based inks and overprint aqueous varnishes. More particularly, this invention relates to an aqueous dispersion for use as a water-based ink and overprint varnish formulation additive for improving the performance of such inks in terms of gloss, adhesion, slip and the like and the performance of such varnishes in terms of gloss, toughness, heat resistance, lubricity and the like. Also, new additive compositions useful as a clear protective coating of a substrate, such as a film or paper product, bearing on its surface printed indicia are provided.

There are four (4) general classes of printing inks. There are letter press and lithographic inks, also known as oil inks or paste inks, and there are flexographic and rotogravure inks, also known as solvent or liquid inks. This invention is concerned with a particular class of flexographic and rotogravure inks which are water-based. Although these inks have certain characteristics in common with inks used in other printing processes, they form a distinct class because of the character of the printing processes in which they are used, their applications and their formulations. The main distinction of flexographic and rotogravure inks is that they are normally of low viscosity compared to other classes of printing inks.

Flexographic and rotogravure inks have, in the past, been prepared by dispersing pigments or other colorants in volatile organic solvents such as alcohols, ketones and hydrocarbons. Due to environmental problems associated with the use of inks formulated with volatile organic solvents, water-based flexographic and rotogravure inks are becoming more important.

In flexographic printing, a form of rotary letter press uses a flexible plate, such as rubber, and fluid inks. Originally, flexographic printing was primarily used for paper bag printing but subsequently proved suitable for printing almost any kind of flexible packaging material. Flexographic inks generally consist of pigment dispersed in a vehicle made by dissolving one or more resins in a solvent, such as a volatile organic solvent or water. The water-based flexographic inks are widely used on paper and paper board. The vehicles for water-based inks are usually made from acrylic copolymers, acidic rosin esters, shellac, acidic styrene copolymers and various additives, such as waxes. The advantages of water-based inks include good press stability and printability, absence of fire hazard and volatile organic solvent emissions, convenience and the economy of water as a diluent and for wash-up. Since the water-based inks

do not use volatile organic solvents, their use is gaining favor over the use of organic solvent-based inks.

Rotogravure inks normally comprise a pigment, a resin, a polymer or wax additive and a solvent. As in flexographic inks, water-based rotogravure inks are gaining favor over organic solvent-based inks because of environmental and worker hazard considerations.

In general, water-based inks are a mixture of water, resin, emulsifier or dispersing agent, a pigment and a polymer or wax additive. There exists a need to improve water-based inks in terms of gloss, maintenance, rub resistance, adhesion, slip, water resistance and other desirable properties.

In general, overprint varnishes are aqueous emulsions of polymers, such as acrylic and styrenic polymers which may also contain a hydrocarbon wax. Overprint varnishes are used to improve the properties of printed products which have been printed with relatively low-grade (and low cost) inks. Thus, for products for which very high quality printing is not necessary (e.g., cereal boxes, cracker boxes, tissue boxed, pet food bags, etc.), overprint varnishes offer an economical means of "upgrading" the appearance and other properties of products printed with low cost inks. Overprint varnishes are also used to improve the appearance and tactile qualities of higher grade products, such as lithographic magazine covers. There exists a need to improve the overprint varnishes in terms of toughness, gloss, heat resistance, lubricity and other desirable properties.

2. Prior Art

U.S. Pat. No. 2,925,349 discloses a polish which utilizes alcohols having up to 20 carbon atoms as dispersants. Such alcohols may be oxyethylated.

U.S. Pat. No. 3,533,811 discloses a water-based printing ink comprising a water-missible organic solvent, film forming resins which are soluble in the water-missible solvent, pigment, soluble protein, a polymer latex and a volatile base. The water-missible organic solvents which are used are lower aliphatic alcohols and the lower alkylene glycols and their esters and ethers.

U.S. Pat. No. 3,563,910 disclosed oxyalkylated alcohols having up to 38 carbon atoms as emulsifiers for water/hydrocarbon mixtures.

U.S. Pat. No. 3,884,707 discloses a water-based ink comprising a basic dye, water, an organic solvent and a resin. The organic solvents employed are, for example, ethylene glycol and its esters.

U.S. Pat. No. 4,686,260 discloses a process for preparing a polymer emulsion for a water-based ink which contains colloiddally suspended polymer. The emulsifiers used are anionic, cationic or nonionic, emulsifiers or mixtures thereof such as a variety of alcohols and ethylene oxide derivatives of long-chained carboxylic acids such as lauric, myristic, palmitic oleic and stearic acids. Also, analogous ethylene oxide condensates of long-chained alcohols, such as octyl, decyl, stearyl and cetyl alcohols are disclosed.

U.S. Pat. No. 4,499,225 discloses a coating composition composed of an aqueous mixture of polyethylene and a surfactant which may be a cationic, anionic or nonionic type. The composition can be used for coating for baking on various electrical and automobile parts. No nonionic surfactant was specifically identified from a chemical standpoint except by the use of the trade name of Surfynol No. 104. It is understood that Surfynol surfactants are proprietary mixtures containing 2,4,7,9-tetramethyl-5-decyl-4,7-diol surfactant.

U.S. Pat. No. 3,563,910 discloses an emulsifier composition consisting of a mixture of at least two straight and branched chain polyoxyalkylated alcohols useful in formulating insecticides, fungicides, defoliant and the like, as well as in the preparation of paraffinic waxes or coatings, such as paints.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been found that an aqueous dispersion of certain high molecular weight oxyalkylated primary alcohols, a finely divided mostly linear aliphatic hydrocarbon having a molecular weight of about 300-3,000 and/or partially oxidized or similarly modified mostly linear aliphatic hydrocarbon having a molecular weight of about 300-3,000 improves the print characteristics of water-based inks and coating characteristics of overprint aqueous varnishes. The water-based inks to which the additive compositions of the present invention are incorporated have improved adhesion, gloss, slip properties and other desirable characteristics. The overprint aqueous varnishes to which the additive compositions of the present invention are incorporated impart improved properties to paper products coated therewith.

In accordance with another aspect of the present invention, an improved substrate, such as a film or paper product, bearing ink indicia printed thereon is provided by overlaying such substrate with a clear protective polymer coating having a formulation enhancing additive comprising a mixture of certain high molecular weight oxyalkylated primary alcohols and a finely divided mostly linear aliphatic hydrocarbon having a molecular weight of about 300-3,000 and/or partially oxidized or similarly modified mostly linear aliphatic hydrocarbon having a molecular weight of about 300-3,000. The coated product has improved rub resistance, slip, water spotting prevention, water spot blocking, adhesion over water-based inks, and clarity and other properties.

Accordingly, an object of this invention is to prepare a new and useful water-based ink additive composition containing water, the described oxyalkylated alcohol, and the described aliphatic hydrocarbon and/or modified hydrocarbon. Such dispersions are imminently suitable as ink additive systems can be used to significantly improve the performance of water-based inks.

Another object of the invention is to prepare a water-based ink of improved performance, containing an ink additive composition which includes water, the described oxyalkylated primary alcohol and the described hydrocarbon and/or modified hydrocarbon.

Another object of the invention is to provide a method of coating a substrate, such as a film or paper product, bearing printed ink indicia thereon with a clear overprint aqueous varnish containing the additive composition of the present invention. The composition includes water, an oxyalkylated primary alcohol and a hydrocarbon and/or modified hydrocarbon.

Another object of the invention is to provide an improved substrate, such as a film or paper product, having printed ink indicia thereon protected by a clear overprint paper varnish containing the additive composition comprising the previously described oxyalkylated primary alcohol and the previously described hydrocarbon and/or modified hydrocarbon.

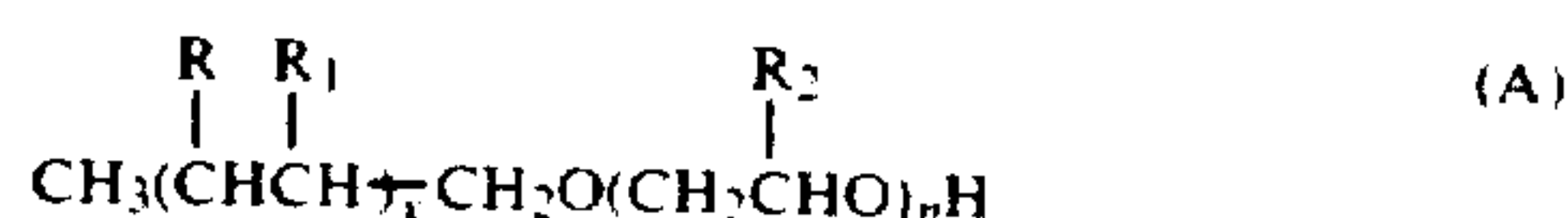
Another object of this invention is to provide a clear overprint aqueous varnish having a formulation enhancing additive incorporated therein, said additive com-

prising a finely divided hydrocarbon and certain high molecular weight oxyalkylated primary alcohols.

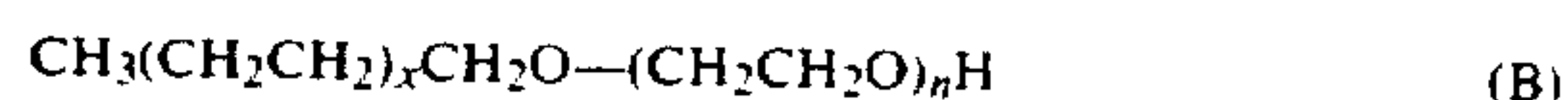
DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that aqueous dispersions of a high molecular weight oxyalkylated alcohol having an average chain length in the hydrocarbon portion of the alcohol of from about 18 to about 150 carbon atoms, preferably from about 40 to about 90 carbon atoms, especially about 25 to about 60 carbon atoms, and a finely divided mostly linear aliphatic hydrocarbon having a molecular weight of about 300-3,000 and/or partially oxidized or similarly modified mostly linear aliphatic hydrocarbon having a molecular weight of about 300-3,000 are useful in water-based inks and as an additive for use in compositions protecting printed paper products and for use in clear overprint aqueous varnishes.

The dispersants used in formulating the water-based ink additive systems of the invention and in additive varnish compositions for protecting a paper product bearing printed indicia are represented by oxyalkylated alcohols of the formula:



wherein R and R₁ individually represent hydrogen or the same or different lower alkyl groups of from 1 to about 10 carbon atoms; R₂ represents hydrogen or a methyl group; x represents a number of from about 8 to about 75 and preferably from about 19 to about 44, and indicates the average number of carbon atoms in the hydrocarbon portion of the chain; and n represents the average number of oxyalkylene groups present in the molecule and is a number of 2 to about 65 and preferably about 4 to about 50. The most preferred oxyalkylated alcohols are essentially linear alcohols represented by the formula



where x and n are integers having the same values as just mentioned. The average molecular weight of the oxyalkylated alcohols of Formula (A) may range from about 400 to about 8,000. The relative efficiency of the hydrophilic and lipophilic portions of the molecular can be controlled by the addition of varying amounts of ethylene oxide.

The dispersants are prepared by oxyalkylation of alcohols represented by the formula:



wherein R, R₁ and x are defined above. Oxyalkylating agents include ethylene oxide, propylene oxide and mixtures thereof. The starting materials can be readily oxyalkylated with the just described alkylene oxides using typical base catalysts, such as potassium hydroxide, sodium hydroxide, sodium ethoxide, potassium t-butoxide, sodium hydride or sodium or potassium metals. The reaction is normally conducted under pressures of 0 to 60 psig and at temperatures of 212° to 356°

F. (100° to 180° C.). Higher temperatures are normally avoided to minimize side reactions and color formation.

By varying the molecular weight of the starting alcohol and the amount of oxyalkylation, a variety of compounds of varying molecular weights can be prepared. Thus, the molecular weight of the starting alcohol may be chosen to have an average molecular weight of from about 270 to about 2,000.

A family of primary linear polymeric alcohols to be oxyalkylated are commercially available under the trade name UNILIN™ alcohols from Petrolite Corporation, Specialty Polymers Group, Tulsa, Okla.

Also included in the aqueous dispersions of the present invention is a finely divided mostly linear saturated aliphatic hydrocarbon having a molecular weight of between about 300 and about 3,000.

Such hydrocarbons include various polyethylenes. The polyethylene used in preparation of the dispersions of the present invention may be described as having a molecular weight of about 700–3,000. The polyethylene may be linear or may have a number of branch formations in its molecular structure. When branched the polyethylenes preferably have one or two branches per molecule on the average and the branches may have 1 to 6 carbons, preferably C₁–C₆ alkyl group. For brevity the polyethylenes and their respective molecular weights are identified by the term "PE" followed by a number indicating the molecular weight.

In addition to the polyethylenes, the aliphatic saturated hydrocarbon component of the dispersion of the present invention may comprise petroleum-derived waxes, such as paraffin and microcrystalline waxes. The paraffin waxes are mostly linear alkanes having about 20–36 carbon atoms per molecule on the average and a molecular weight of about 280–500 and may include C₁₈–C₃₆ isoalkanes and cycloalkanes. The microcrystalline waxes have molecular weights of about 500–700 with somewhat more branching than the paraffin waxes.

Furthermore, the aliphatic saturated hydrocarbon component of the dispersion of the present invention includes Fischer-Tropsch waxes. Such waxes are polymethylenes. Polymethylene wax production is based on the Fischer-Tropsch synthesis, which is basically the polymerization of carbon monoxide under high pressure to produce the wax. The polymethylene waxes useful herein preferably may have an average molecular weight of 600–1,000.

Also contemplated in the present invention are the above described hydrocarbons which may have been chemically modified without sacrificing the ink and/or overprint varnish enhancing properties of the dispersions of the present invention. These include the partially oxidized polyethylenes, polymethylenes and the petroleum-derived waxes. The oxidized low molecular weight mostly linear hydrocarbons of a molecular weight of 300–3,000 have multiple functional groups, such as carboxylic acid, ketones, alcohols, esters, etc., distributed along their chains. The functional groups are the result of the oxidation of these hydrocarbons by an oxygen-containing gas at elevated temperatures, as is well known in the art.

The functional groups of the oxidized hydrocarbons may be generally quantified by determination of an acid number which is the amount of potassium hydroxide in milligrams required to neutralize one gram of the oxidized polymer. The oxidized hydrocarbons will nor-

mally have an acid number in the range of from about 5 to about 25.

Also, the polyethylenes, besides being homopolymers, may be copolymers of ethylene with propylene, butylene, etc. and oxygen-containing units such as vinyl acetate, acrylic acid, etc., as long as the ink and/or overprint varnish enhancing properties are retained. Other closely related material that can be used include the natural waxes, such as beeswax, carnauba and candelilla waxes.

It is important that the hydrocarbon and/or modified hydrocarbon components of the dispersion of the present invention be finely divided particles. For best results, these components should have an average particle size of less than 20 microns and preferably less than 15 microns and more than 1 micron. Such particle sizes may be obtained by micronizing larger particles of the hydrocarbon and/or modified hydrocarbon component or may be attained by precipitation from solutions thereof. It is desirable that they have a broad particle size distribution which may best be achieved directly, for example, by precipitation, or may be achieved by blending micronized products of different particle sizes.

One method of preparing of the aqueous dispersion of the present invention is by the following procedure:

1. The final solids content of the dispersion which is desired is determined. The maximum solids content attainable will vary with the molecular weight and the amount of oxyalkylation of the described dispersants.

2. The amount of water needed is weighed into an agitated dispersion vessel and the amount of dispersant needed is added to a separate container.

3. The dispersant is heated to 15°–20° F. (8°–11° C.) above its melting point which may range from about 180°–250° F. (82°–121° C.); and, at the same time, the water is heated to about 190° F. (88° C.).

4. When both components are heated to the appropriate temperatures, the dispersant is slowly poured into the heated water which is at the same time vigorously stirred.

5. When all of the dispersant has been added to the water, the heat source is removed and stirring is continued for 2 to 3 additional minutes.

6. The dispersion is slowly stirred, cooling at the rate of about 2°–4° F. (1°–2° C.) per minute. When the temperature reaches about 140° F. (60° C.), the cooling rate may be increased or held constant until the desired pour temperature is reached. A stable dispersion results.

7. The finely divided hydrocarbon and/or modified hydrocarbons is thereafter incorporated in the resulting dispersion.

The addition of a small amount of the dispersion of the present invention in inks and overprint varnishes notably improves the performance of such inks and varnishes in regard to gloss, immediate adhesion, delayed adhesion, coefficient of friction (COF), wet rub, dry rub and water resistance. Gloss can be determined using conventional glossmeters, adhesion can be determined by adhesive tape pull tests, slip can be determined using conventional slide angle/slip and friction testers, rub resistance can be determined using a Sutherland Rub Tester and water resistance can be determined by a water drop test at 10, 30 and 60 second application intervals. These are standard tests conventionally employed by the industry.

The preferred additive composition of the present invention is an aqueous dispersion having a solids content of at least 8.0% by weight. Normally, the solids

content of the dispersion may be lower or much higher in the range of at least 20% by weight and as high as 70% by weight. Dispersions useful for adding to water-based inks or paper protective coating compositions in accordance with the present invention may contain about 30-92% by weight water, about 2-40% by weight oxyalkylated alcohol and about 1-60% by weight of hydrocarbon and/or modified hydrocarbon. The amount of hydrocarbon to modified hydrocarbon may range from 0 to 100% hydrocarbon. Preferably, the dispersion will comprise about 40-80% by weight water, 2-20% by weight alcohol and 1-40% by weight of hydrocarbon and/or modified hydrocarbon.

It has been found that excellent results are obtained when a mixture of oxidized and unoxidized polyethylenes as the hydrocarbon mixture are used. The most preferred composition is 50-85% water, 2-15% oxyalkylated alcohol and 10-35% of oxidized plus unoxidized polyethylene. It is preferred for the oxidized polyethylene portion of the mixture to be about 50-95% and the unoxidized polyethylene portion of the mixture to be about 5-50%. Excellent results have been obtained where the composition contains 70-80% oxidized polyethylene and 20-30% unoxidized polyethylene.

Water-based inks and paper protecting varnish compositions containing about 0.5 to about 10% by weight of the dispersion of the present invention have improved properties. The preferred amount of the dispersion in the inks is about 1-8% by weight.

The additive formulation of the present invention may be incorporated in conventional clear overprint aqueous varnishes containing a polymer and a solvent system. Typically, the polymer may be a styrene/acrylic copolymer. Any polymer suitable for use in clear overprint aqueous varnishes are useful.

In the following examples, all percentages are on a weight/weight basis unless otherwise indicated.

The following examples will illustrate the practice of the present invention in its preferred embodiments. Other embodiments within the scope of the claims herein will be apparent to one skilled in the art from consideration of the specification and practice of the invention as disclosed herein. It is intended that the specification, together with the examples, be considered exemplary only, with the scope and spirit of the invention being indicated by the claims which follow.

EXAMPLE I

This example illustrates preparation of the oxyalkylated alcohol component which serves as the dispersant of the composition of the present invention.

A primary linear alcohol of the following formula was prepared by oxidation of a corresponding polyethylene precursor:



wherein x is about 23.

This olefin-derived linear polymeric alcohol was oxyethylated in a conventional manner to provide an oxyethylated alcohol having 16 ethylene oxide units per mole of polymer on the average and a molecular weight of about 1,400 and melting about 224° F. (107° C.).

EXAMPLE II

This example illustrates the preparation of an aqueous dispersion of the oxyethylated alcohol prepared in Example I.

Using the formulating procedure as described above, a suitable quantity of water was heated to 190° F. (88° C.). In a separate vessel the alcohol was heated to a molten condition. Then, molten oxyethylated alcohol was added to the hot water under high shear conditions to yield a 25% by weight aqueous dispersion of the oxyethylated alcohol and cooled. This dispersion was designated Composition 1.

EXAMPLE III

This example illustrates the preparation of the micronized low molecular weight polyethylenes.

Linear polyethylene of an average molecular weight of about 2,000 was used in the following examples. Oxidized polyethylene used in the following examples was prepared by air oxidizing a linear polyethylene of a molecular weight of 1,500 to an acid number of 18. The unoxidized polyethylene portion and the oxidized polyethylene portion separately were comminuted using conventional micronizing equipment. Portions of each polyethylene were comminuted to average sizes of 6 microns and 10 microns.

EXAMPLE IV

This example illustrates the preparation of an aqueous dispersion containing the oxyethylated alcohol and a mixture of oxidized and unoxidized micronized low molecular weight linear polyethylenes.

To 100 parts by weight of the aqueous dispersion prepared in accordance with Example II, 1.9 parts by weight of the oxidized polyethylene (MW=1,500) and 0.6 parts by weight of the unoxidized polyethylene (MW=2,000) were added and vigorously blended into the dispersion. The unoxidized polyethylene had an average size of 10 microns and the oxidized polyethylene had an average size of 6 microns. The resulting composition was given the designation of Composition 2.

EXAMPLE V

In this example, an aqueous dispersion was prepared by mixing at a temperature of 250° F. (121° C.) under pressure water, the oxyalkylated alcohol of Example I and unoxidized linear polyethylene wax having a molecular weight of 2,000 to produce a dispersion composed of 60% by weight water, 19% by weight oxyalkylated alcohol and 21% by weight polyethylene. Upon cooling the polyethylene precipitated as finely divided particles having an average size of 2 microns. The resulting dispersion was designated Composition 3.

EXAMPLE VI

In this example, a dispersion of 60% water and 40% solids was prepared. Of the solids 80% was composed of the oxyalkylated alcohol of Example I and 10% by weight of oxidized polyethylene (MW=1,500) having a 6 micron size and 10% by weight of unoxidized polyethylene (MW=2,000) having a 10 micron size was prepared. The resulting dispersion was designated Composition 4.

EXAMPLE VII

This example illustrates the preparation of a water-based ink.

The following ink composition was prepared:

TABLE 1

Ingredient	Weight %	Supplier
Joncryl 61-LV	13.0	S. C. Johnson
Water	2.5	—
Isopropanol (95%)	4.5	—
Foamburst 320CT	1.0	Ross Chemical
Neocryl A-1054	55.0	ICI Resins
Flexiverse BCD5103	24.0	Sun Chemical

This preparation was accomplished by weighing Joncryl 61-LV acrylic emulsion and water into a mixing tub. Then, Foamburst 320CT antifoam, isopropanol and Neocryl A-1054 acrylic resin dispersion were added to the tub and mixed thoroughly with the other ingredients therein. Finally, the Flexiverse BCD5103 blue pigment was added to the tub and mixed thoroughly with the ingredients therein to form a well dispersed ink composition. This ink composition was blended with ink additive compositions as described in Example VIII.

EXAMPLE VIII

Water-based blue surface inks containing compositions of the present invention were applied to various substrates at different levels of compositions based on oxyethylated alcohols and the micronized polyethylene polymers of low molecular weight and were tested for gloss, 90° degree delayed adhesion, static coefficient of friction (slide angle) and dynamic coefficient of friction (slide angle) using a four color, flexographic press. Composition 5 was an aqueous dispersion of Example II containing a surfactant coated micronized branched polyethylene of about 700 molecular weight.

Higher gloss readings and higher adhesions are desirable properties and lower coefficients of friction are also desirable properties in the following table:

TABLE 2

Gloss on Low Density Polyethylene Substrate		
Ink Additive	Ink Additive %	Glossmeter Reading
Composition 2	3	77
Composition 2	6	76
Composition 3	1.25	80
Composition 3	3.75	74
Composition 5	5	80

TABLE 3

Gloss on Polypropylene Film		
Ink Additive	Ink Additive %	Glossmeter Reading
Composition 2	3	87
Composition 2	6	79
Composition 3	1.25	86
Composition 3	3.75	68
Composition 5	5	80

TABLE 4

90° Delayed Adhesion on Low Density Polyethylene Substrate		
Ink Additive	Ink Additive	Rating
Composition 2	3	10.0
Composition 2	6	10.0
Composition 3	1.25	9.0
Composition 3	3.75	7.5
Composition 5	5	8.0

TABLE 5

90° Delayed Adhesion on Polypropylene Film		
Ink Additive	Ink Additive %	Rating
Composition 2	3	1.0
Composition 2	6	10.0
Composition 3	1.25	4.5
Composition 3	3.75	8.0
Composition 5	5	6.5

TABLE 6

Static COF* on Low Density Polyethylene Substrate		
Ink Additive	Ink Additive %	COF
Composition 2	3	0.43
Composition 2	6	0.49
Composition 3	1.25	0.48
Composition 3	3.75	0.47
Composition 5	5	0.47

*Coefficient of Friction as measured using slide angle test employing Testing Machines, Inc., Model No. 32-25-00.

TABLE 7

Static COF on Polypropylene Film		
Ink Additive	Ink Additive %	COF
Composition 2	3	0.58
Composition 2	6	0.57
Composition 3	1.25	0.59
Composition 3	3.75	0.50
Composition 5	5	0.47

TABLE 8

Dynamic COF on Low Density Polyethylene Substrate		
Ink Additive	Ink Additive %	COF
Composition 2	3	0.31
Composition 2	6	0.34
Composition 3	1.25	0.32
Composition 3	3.75	0.37
Composition 5	5	0.34

TABLE 9

Static COF on Polypropylene Film		
Ink Additive	Ink Additive %	COF
Composition 2	3	0.38
Composition 2	6	0.33
Composition 3	1.25	0.38
Composition 3	3.75	0.26
Composition 5	5	0.31

In this example, the speed of the printer was held constant at 200 feet/minute and each run was about a minute long. The wet temperature on the drier was held at 170° F. (77° C.) for all the runs. This example shows that the water-based printing aid compositions of the present invention are useful in the formulation of water-based inks.

EXAMPLE IX

This example illustrates the results of using compositions of the present invention wherein different combinations of unoxidized polyethylene and oxidized polyethylene in different finely divided sizes were employed.

In each of the following compositions various linear polyethylene species were added to an aqueous dispersion prepared in accordance with Example II. The total amount of added polyethylene was 2.5% by weight of the resulting composition.

The first species of polyethylene was a mixture of 50% unoxidized polyethylene of 2,000 molecular weight and a particle size of 6 microns and 50% unoxidized polyethylene of 2,000 molecular weight and a particle size of 10 microns.

The second species of polyethylene was a mixture of 50% by weight oxidized polyethylene of 1,500 molecular weight and a particle size of 6 microns and 50% by weight of oxidized polyethylene of 1,500 molecular weight and a particle size of 10 microns.

The third species of polyethylene was a mixture of 50% by weight of unoxidized polyethylene of 2,000 molecular weight and a particle size of 6 microns and 50% by weight oxidized polyethylene of 1,500 molecular weight and a particle size of 10 microns.

The fourth species of polyethylene was a mixture of 50% by weight of oxidized polyethylene of 1,500 molecular weight and a particle size of 6 microns and 50% by weight of unoxidized polyethylene of 2,000 molecular weight and a particle size of 10 microns.

The fifth species of polyethylene was a mixture of 50% by weight of unoxidized polyethylene (MW = 700; 6 micron size) and 50% polyethylene added as a 30% solids aqueous dispersion by weight of a commercially available aqueous dispersion of polyethylene (30% solids). This fifth species was not made in accordance with Example II mentioned above; it is a stand alone product.

The sixth species of polyethylene was a mixture of 75% by weight of oxidized polyethylene of 1,500 molecular weight and a particle size of 6 microns and 25% by weight of unoxidized polyethylene of 2,000 molecular weight and a particle size of 10 microns.

The compositions of the various species of polyethylene mixtures and the oxyethylated alcohol of the present example were added to a standard water-based blue ink in an amount of 3.0% by weight. The resulting ink composition was applied to aluminum foil and polypropylene film and tested for various properties including gloss, slip, rub and adhesion. The results of such tests are summarized in Table 10 and 11.

TABLE 10

Comparison on Aluminum Foil				
Composition	Gloss	Slip	Rub	Adhesion Ranking
PE Species 1	77	.41/.21	.09	2
PE Species 2	72	.42/.19	.07	6
PE Species 3	73	.36/.20	.07	2
PE Species 4	73	.38/.20	.07	2
PE Species 5	71	.44/.23	.08	5
PE Species 6	79	.42/.18	.05	1

TABLE 1

Comparison on Polypropylene Film				
Composition	Gloss	Slip	Rub	Adhesion Ranking
PE Species 1	71	.44/.23	.08	2
PE Species 2	68	.39/.20	.06	6
PE Species 3	66	.45/.20	.07	2
PE Species 4	68	.32/.20	.07	2
PE Species 5	62	.48/.21	.07	5
PE Species 6	65	.39/.15	.06	1

From the Tables 10 and 11, it is noted that the combination of the use of oxidized polyethylene of 6 micron size and unoxidized polyethylene of 10 micron size when added to the aqueous dispersion of oxyethylated alcohol provides markedly better gloss, slip and adhesion in water-based inks as compared to the use of the standard additive when added to the same dispersion and slightly better properties over other tested combinations of oxidized and unoxidized polyethylenes.

EXAMPLE X

A second oxyethylated alcohol having a molecular weight of about 865 and an ethylene oxide content of 10 moles per mole of polymer was prepared.

EXAMPLE XI

In this example, an aqueous dispersion containing a mixture of paraffin wax and essentially linear unmodified polyethylene was prepared for form a 50% solids composition. Of the solids 10% by weight was composed of the oxyalkylated alcohol of Example X and 90% by weight of paraffin wax (MP = 147° F. (63.9° C.)). The dispersion was added to printing ink at an additive level of 3.0% by weight. The resulting ink when applied to various surfaces showed improved characteristics.

When used in small amounts by weight of the ink composition in water-based inks, the aqueous dispersions prepared in accordance with this example improve such inks in terms of gloss maintenance and rub resistance without sacrifice of adhesion of the inks to a substrate, of slip of the inks from the substrate and of water spot resistance of inks applied to a variety of substrates.

EXAMPLE XII

This example illustrates the improvements in the finely divided polyethylene in water using the long chain oxyalkylated alcohol dispersants as compared to the use of other tested nonionic surfactants.

In various tests the use of long chain oxyalkylated alcohol dispersants as used in the present invention was compared with the use of other nonionic dispersants with regard to the ability of each to form stable dispersions of finely divided polyethylene having a molecular weight of 500 (PE-500).

The dispersants tested as follows:

Surfactant	Description
a	The oxyalkylated alcohol prepared generally in accordance with Example I of the instant application but having an average molecular weight of 900 and 10 ethylene oxide units
b	T Maz 81, Mazer, Inc., HLB 10.0 (POE-5-sorbitan monooleate)
c	T Max 61, Mazer, Inc., HLB 9.6 (POE-5-sorbitan monostearate)
d	Tween 81, ICI Americas, Inc., HLB 10.0 (POE-5-sorbitan oleate)
e	Tween 61, ICI Americas, Inc., HLB 9.6 (POE-4-sorbitan monostearate)
f	Brig 30, ICI Americas, Inc., HLB (POE-4-lauryl ether)
g	Hodag 20-LT, Hodag Inc., HLB 10.0 (PEG-200-monolaurate)
h	Hodag 40-LT, Hodag Inc., HLB 12.8 (PET-400 monolaurate)
i	Triton N-57, Rohm-Haas, HLB 10.0 (nonylphenol + 5EO)
j	Surfynol 104-E, Air Products Co.,

-continued

Surfactant	Description
	(2,4,7,9-tetramethyl-5-decyl-4,7-diol)

Dispersions of PE-500 were made by melting various amounts of PE-500 and various amounts of the tested surfactants by heating and stirring the PE-500 and surfactants together to about 225° F. Then, each of the resulting melts was poured into various amounts of water at 200° F. with vigorous stirring. While still being stirred, each of the resulting aqueous dispersions was quickly cooled to room temperature. Then, the stability of each dispersion was visually noted. The results of these tests have been set forth in the following table wherein the weights of the components are given in grams:

Surfactant	Wt. of Surfactant	Wt. of H ₂ O	Wt. of PE-500	Observation
a	5	450	45	White stable dispersion of extremely fine particles
b	5	450	45	White dispersion with quick separation of particles
c	5	450	45	White dispersion with quick separation of particles
d	5	450	45	White dispersion with quick separation of particles
e	5	450	45	White dispersion with quick separation of particles
f	5	450	45	White dispersion with some large particles and with quick separation of particles
g	5	450	45	White dispersion with quick separation of particles
h	5	450	45	White dispersion with many large particles and quick separation of particles
i	5	450	45	White dispersion with many large particles and quick separation of particles
j	5	450	45	White dispersion with quick separation of particles
b	10	450	40	White dispersion with quick separation of particles
b	15	450	35	White dispersion with many large particles and quick separation of particles
b	20	450	30	White dispersion of small particles and quick separation of particles
e	15	450	35	White dispersion with many large particles and quick separation of particles

From the above data, it can be seen that the stability of aqueous dispersions of polyethylene of low molecular weight is greater when the dispersants used in the ink composition of the present invention is used as compared to the use of other tested nonionic surfactants.

EXAMPLE XIII

Various compositions of the present invention were tested as property enhancing additives in clear overprint aqueous varnishes conventionally used to protect paper products having ink indicia printed thereon. In the tests, 8×5½ inch paper cards obtained from the Leneta Company were employed. One half of each card was blank and the other half had black lithographic ink printed on it. The cards had a very light coating of lacquer on both the blank portion and the black portion.

To a standard overprint varnish, additives of the present invention were incorporated in a series of tests

and a standard additive presently in use in the industry was incorporated in a comparative test. The enhancement of the tested varnishes in terms of gloss, rub resistance and slip angle slide was determined using conventional and known procedures.

In each of the tests the standard overprint protecting varnish had the following composition as set forth in Table 12:

TABLE 12

Ingredient	Parts/hundred (pph)
Styrene/acrylic copolymer	90
Surfynol 104-E emulsifier	0.3
Water	9.7

The effectiveness of the additive compositions of the present invention in enhancing the properties of the just described clear overprint aqueous paper varnish as compared to the effectiveness of a standard additive conventionally used in the trade to assist formulators of clear paper coating systems as above described was determined. In all the tests the black portion of the cards was used as surface on which the properties were determined.

The standard additive known as Jonwax 26 and obtained from S. C. Johnson Co. is identified as a 25% solid aqueous dispersion of polyethylene wax containing 6% fatty acid soap as the dispersant.

Additive Composition 6 was composed of 21% polyethylene of 2,000 molecular weight (PE-2000), 19% of the oxyethylated alcohol dispersant of Formula B above where x averages 49 and n averages 16, and 60% water.

Additive Composition 7 was composed of 1.8% oxidized PE-1500, 0.6% unoxidized PE-2000, 24% of the oxyethylated alcohol dispersant of Formula B above where x averages 49 and n averages 16, and 73.6% water.

Additive Composition 8 was composed of 45% of a paraffin wax (Citco Pacemaker 53), 5% of the oxyethylated alcohol dispersant of Formula B above where x averages 29 and n averages 10, and 50% water.

Additive Composition 9 was composed of 50% of Composition 8 and 50% of Composition 3.

The test data of the various tests have been tabulated in Table 13:

TABLE 13

Additive	%	Rub Resistance Relative Rating (0→4 best)	Slide Angle Static Slip Resistance	Slide Angle Dynamic Slip Resistance	Gloss
Blank	0.0	0.0	34	32	68
Standard	6.0	1.0	23	16	70
No. 6	3.8	4.0	23	14	65
No. 7	6.0	2.0	24	13	68
No. 8	3.0	3.6	14	9	72
No. 9	3.3	4.0	16	9	68

As can be seen from the above table, the additives of the present invention consistently provide better relative rub resistance even at lower amounts as compared to the use of the standard additive. Improvements are also noted in both static slip resistance and dynamic slip resistance with the use of the additives of the present invention without sacrifice of gloss.

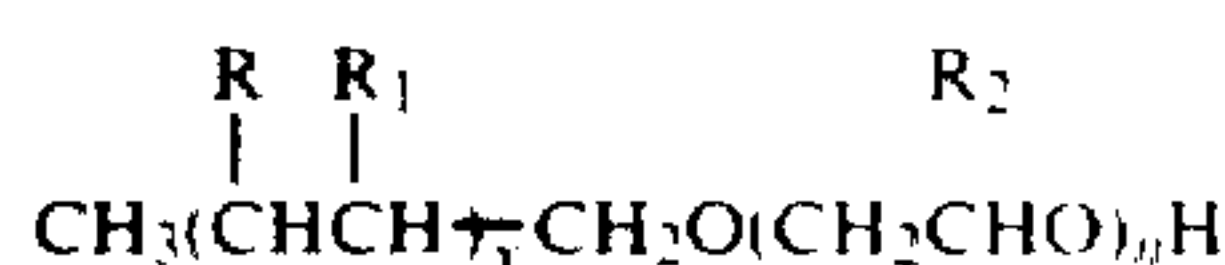
While the illustrative embodiments of the invention have been described with particularity, it will be under-

stood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention as herein disclosed, including all features which would be regarded as equivalents thereof by those skilled in the art to which the present invention pertains.

What is claimed is:

1. **[A product bearing print ink indicia protected by an]** *An overprint aqueous varnish having formulation enhancing additive comprising a mixture of*

- a. *A finely divided mostly linear aliphatic hydrocarbon [and/or] or a modified hydrocarbon or mixtures thereof having a molecular weight of about 300-3,000 selected from the group consisting of (i) a copolymer of ethylene and either propylene, butylene, vinyl acetate or acrylic acid; (ii) petroleum-derived waxes; (iii) Fischer-Tropsch waxes; (iv) natural wax; and (v) partially oxidized hydrocarbon; and*
- b. *a compound represented by the formula:*



wherein R and R₁ are independently hydrogen or C₁-C₁₀ alkyls; R₂ is hydrogen or methyl, x is about 8 to about 75; and n is about 2 to about 65.

2. The **[product]** *varnish* of claim 1 wherein x is about 19 to about 44.

3. The **[product]** *varnish* of claim 1 wherein n is about 4 to about 50.

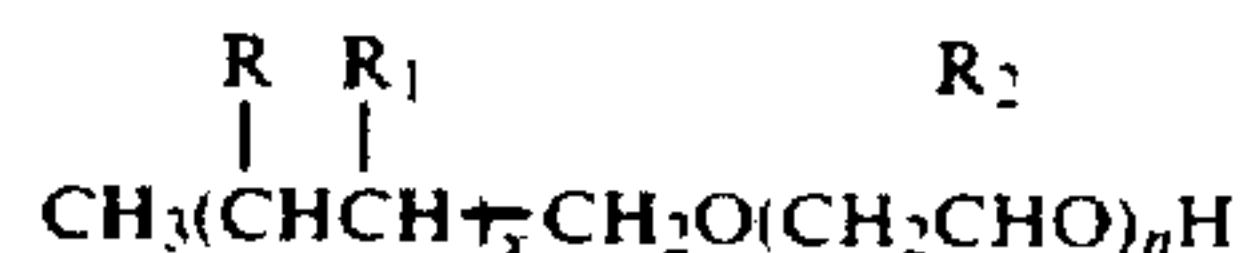
4. The **[product]** *varnish* of claim 2 where n is about 4 to about 50.

5. The **[product]** *varnish* of claim 1 wherein the hydrocarbon is **[a mixture of unoxidized polyethylene and]** oxidized polyethylene.

6. The **[product]** *varnish* of claim **[5]** *19* wherein the oxidized polyethylene **[mixture]** comprises about 55-95% by weight of the **[polyethylene mixture]** *hydrocarbon*.

7. A method of coating a product comprising the steps of forming an aqueous mixture of

- a. *a finely divided mostly linear aliphatic hydrocarbon [and/or] or a modified hydrocarbon or mixtures thereof having a molecular weight of about 300-3,000 selected from the group consisting of (i) a copolymer of ethylene and either propylene, butylene, vinyl acetate or acrylic acid; (ii) petroleum-derived waxes; (iii) Fischer-Tropsch waxes; (iv) natural wax; and (v) partially oxidized hydrocarbon; and*
- b. *a compound represented by the formula:*



wherein R and R₁ are independently hydrogen or C₁-C₁₀ alkyls; R₂ is hydrogen or methyl, x is about 8 to about 75; and n is about 2 to about 65; adding the thus-formed aqueous mixture to an overprint aqueous varnish; mixing the aqueous mixture and varnish; and applying the resulting mixture to a product bearing printing ink indicia.

8. The method of claim 7 wherein x is about 19 to about 44.

9. The method of claim 7 wherein n is about 4 to about 50.

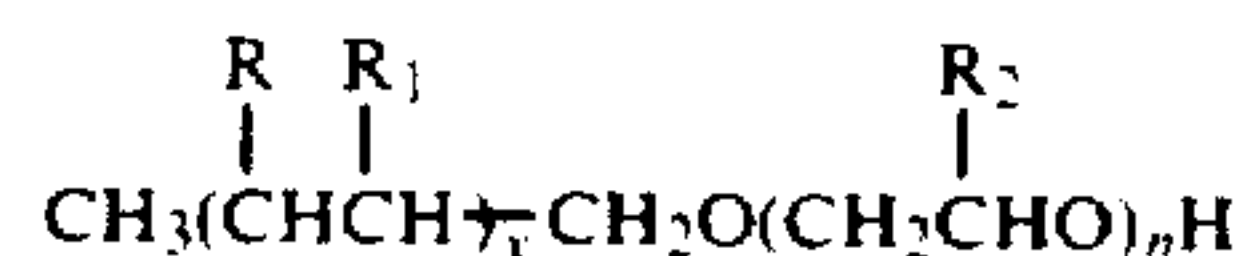
10. The method of claim 8 wherein n is about 4 to about 50.

11. The method of claim 7 wherein the hydrocarbon is **[a mixture of unoxidized polyethylene and]** oxidized polyethylene.

12. The method of claim 8 wherein the **[oxidized polyethylene mixture]** *hydrocarbon further* comprises **[about 55-95% by weight of the polyethylene mixture]** *unoxidized polyethylene*.

13. An aqueous varnish having incorporated therein a formulation enhancing additive comprising a mixture of

- a. *a finely divided mostly linear aliphatic hydrocarbon [and/or] or a modified hydrocarbon or mixtures thereof having a molecular weight of about 300-3,000 selected from the group consisting of (i) a copolymer of ethylene and either propylene, butylene, vinyl acetate or acrylic acid; (ii) petroleum-derived waxes; (iii) Fischer-Tropsch waxes; (iv) natural wax; and (v) partially oxidized hydrocarbon; and*
- b. *a compound represented by the formula:*



wherein R and R₁ are independently hydrogen or C₁-C₁₀ alkyls; R₂ is hydrogen or methyl, x is about 8 to about 75; and n is about 2 to about 65.

14. The varnish of claim 13 wherein x is about 19 to about 44.

15. The varnish of claim 13 wherein n is about 4 to about 50.

16. The varnish of claim 14 wherein n is about 4 to about 50.

17. The varnish of claim 13 wherein the hydrocarbon is **[a mixture of unoxidized polyethylene and]** oxidized polyethylene.

18. The varnish of claim **[17]** *20* wherein the oxidized polyethylene mixture comprises about 55-95% by weight of the polyethylene mixture.

19. *The varnish of claim 5 wherein the hydrocarbon further contains unoxidized polyethylene.*

20. *The varnish of claim 17 wherein the hydrocarbon further contains unoxidized polyethylene.*

* * * * *