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DescriptionMETHOD OF AGGLOMERATING PRINTING INK
AND FORMULATIONS FOR USE THEREINTechnical Field

This invention relates to methods and formulations to de-ink paper containing printed matter that has been applied by non-impact printing methods. More specifically, the invention relates to methods and formulations which separate the ink from paper and agglomerate the separated ink to form particles of a size sufficient that they can be efficiently removed from the paper.

Background Art

In recent years, the growth of environmental consciousness has spurred the increasing use of recycled paper. At the same time, the increased use of non-impact, reprographic printing processes such as electrographic photocopying (e.g. xerography), laser printing, or ink-jet printing has greatly increased the difficulty encountered in the paper recycling process.

For printed paper to be recycled, the ink must be substantially, or preferably completely, removed to permit the manufacture of high quality paper with the recycled or secondary fibers. Conventional de-inking procedures remove conventional water or oil based inks by mechanically repulping the printed paper and then contacting the repulped paper with an aqueous medium containing a surfactant to separate the ink from the pulped fibers. The separated ink is then removed by washing or flotation.

Conventional de-inking techniques, however, cannot be used to satisfactorily recycle paper printed with non-impact printing inks. This deficiency arises from the composition of non-impact printing inks. Generally speaking, non-impact printing inks are formulated with a thermoplastic binder which, during conventional pulping and de-inking, forms particles that are too large to be removed by washing or

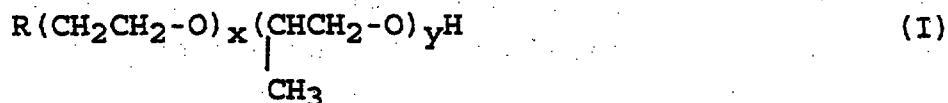
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flotation but too small to be removed satisfactorily by screening or centrifuging.

Several techniques have been tried to agglomerate these polymer-based inks into larger, denser particles that can be removed by screening or centrifuging. For example, U.S. Patent Nos. 4,820,379 and 5,102,500 disclose agglomerating reprographic inks with alkoxy-capped poly(ethylene oxide) additives in the presence of a polymeric material and, optionally, a chelating agent. U.S. Patent No. 5,141,598 discloses de-inking electrostatically printed paper using a mixture of an aliphatic petroleum distillate, an alkylphenoxy (ethyleneoxy) ethanol and an ethoxylated polyoxypropylene glycol. The mixture has a combined HLB less than 10 and a weight ratio of 6:1:3.

Disclosure of the Invention

Accordingly, the present invention is directed to a method of de-inking non-impact printed paper that substantially obviates one or more of the problems due to limitations and disadvantages of currently used de-inking methods. In one aspect, this invention provides a de-inking method where reprographic or non-impact inks are separated from repulped paper fibers and agglomerated to a size sufficient to permit their removal from those fibers. The method comprises the step of contacting repulped fibers containing non-impact printed subject matter with an additive formulation for a time and at a temperature sufficient to separate the ink from the repulped paper fibers and to agglomerate the separated ink into particles of a size sufficient to permit their removal from the fibers. The additive formulation comprises (1) 85 to 10% by weight of at least one petroleum distillate and (2) 15 to 90% by weight of at least one derivatized ethylene oxide/propylene oxide polymer having the structural formula I:



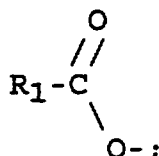
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wherein x and y are each integers from 1 to 20 and R is the derivatizing radical selected from

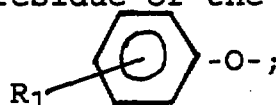
(a) an aliphatic alcohol residue having the formula:



(b) an aliphatic acid residue of the formula:



(c) a phenol residue of the formula:

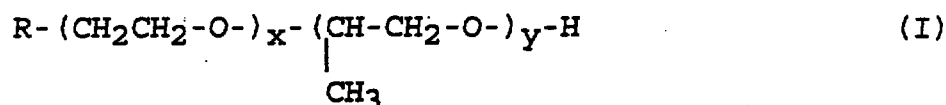


wherein R_1 is a linear or branched, saturated or unsaturated hydrocarbon chain having 1 to 20 carbon atoms.

The invention also provides a formulation useful for carrying out the method. That formulation comprises

(1) 85 to 10% by weight of at least one petroleum distillate; and

(2) 15 to 90% by weight of at least one derivatized ethylene oxide/polypropylene oxide polymer of the formula I:

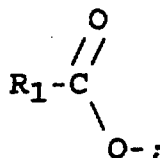


wherein x and y are integers from 1 to 20 and R is the derivatizing radical selected from

(a) an aliphatic alcohol residue having the formula:



(b) an aliphatic acid residue of the formula:



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(c) a phenol residue of the formula:



wherein R_1 is a linear or branched, saturated or unsaturated hydrocarbon chain having 1 to 20 carbon atoms.

DETAILED DESCRIPTION OF THE INVENTION

Typically when de-inking waste paper containing non-impact printed subject matter, the paper is treated in a hydropulper to produce an aqueous slurry of repulped paper fibers. Pulp slurries usually comprise about 3 to 20 and, often, about 4 to 8 weight percent repulped paper fiber based on the total weight of slurry.

Additives commonly used in de-inking operations include surfactants, bleaches, brighteners, softeners, defoamers, dispersants, and chelants. Conventionally used repulping de-inking agents such as ethoxylated alcohols and phenol ethoxylates can also be present. Phenol ethoxylates are particularly useful when the pulp contains a mixture of non-impact printed paper along with conventional, impact printed paper. These additives and the additive formulations can be added to the hydropulps at any time before, during, or after repulping. Since the pulping per se takes only a very short time, the additives are usually added to the hydropulper at the beginning of the pulping operation.

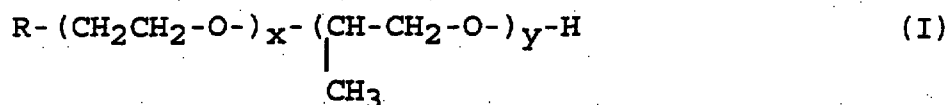
To remove ink from non-impact printed paper according to the present invention, repulped paper fibers are contacted with a formulation comprising at least one petroleum distillate and at least one polymer of formula I, shown below. The formulation comprises, typically, 10 to 85% by weight of a petroleum distillate, preferably 15 to 40%, and 15 to 90% by weight of a derivatized ethylene oxide/propylene oxide polymer of formula I, preferably 60 to 85%, more preferably 65 to 80%. A preferred formulation comprises about 25% petroleum distillate and 75% polymer.

The petroleum distillate is preferably a relatively high boiling hydrocarbon fraction, having a boiling point between about 185° and 275°C. Such a fraction typically contains a mixture of aliphatic and naphthenic hydrocarbons with a low level of aromatics. Petroleum distillates having these characteristics are available commercially, e.g., under the trade names Vista LPA-140 (CAS #64742-47-8), boiling

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range 187-232°C, Vista LPA-210 (CAS #64742-47-8), boiling range 203-278°C, both sold by Vista Chemical Company, and ArcoPrime 55 (CAS #8042-47-5), sold by Lyondell Petrochemical Company.

The polymers employed in the de-inking method of the invention are derivatized ethylene oxide/propylene oxide polymers. These polymers, which may be random or block copolymers, are represented by the following formula I:

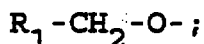


Commercially available polymers of formula I are sold by Chemax, Inc. under the trade names Chemal DA-5P8, by PPG Industries, Inc. under the trade names of Macol LF110 and Macol LF120, and by BASF as Afranilf.

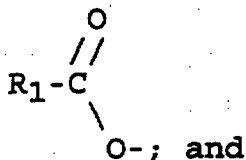
Within the polymer, the ratio of ethylene oxide units to propylene oxide units, $x:y$, can vary from about 1 to 20 to 20 to 1. Preferably, this ratio will be no greater than about 1 to 1 and, more preferably less than about 1 to 1, i.e., the propylene oxide units will preponderate. The ethylene oxide and propylene oxide units can be distributed in random or block configuration within the polymer structure.

As shown in formula I, R, the derivatizing radical, is derived from (a) a linear or branched, saturated or unsaturated, aliphatic alcohol, (b) a saturated or unsaturated aliphatic carboxylic acid or (c) a phenol residue.

The aliphatic alcohol residue (a) has the formula:



The aliphatic acid residue, (b), the formula:



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The phenol residue (c), the formula:



In each formula (a), (b), and (c), R_1 is a linear or branched, saturated or unsaturated hydrocarbon chain having 1 to 20 carbon atoms.

When the derivatizing radical, R, represents an aliphatic alcohol residue (a), the radical R_1 preferably is a saturated radical having 1 to 20 and more preferably 8 to 14 carbon atoms, either in a linear or branched chain. If the residue is branched, it is preferred that it have about 5 to 10 carbon atoms in the longest chain.

When the derivatizing radical, R, represents an aliphatic acid residue (b), R_1 is preferably a linear radical having 5 to 10 and more preferably 8 to 12 carbon atoms. Preferably R_1 , in this case, will be saturated or contain no more than 1 carbon-carbon double bond. In a further preferred embodiment, the aliphatic acid residue (b) is a fatty acid residue. Preferred fatty acid residues include oleic and linoleic fatty acids.

When the derivatizing radical, R, represents a phenol residue (c), the phenol residue may be derived from an ortho, meta-, or para-phenol, preferably a para-phenol. R_1 is preferably a linear saturated aliphatic radical having 1 to 30 and, more preferably, 8 to 14 carbon atoms.

The molecular weight of the polymer of Formula I, including the derivatizing radical, can be between about 400 and 8000. Preferably, the molecular weight is between 400 and 2000 and most preferably, between about 600 and 1400.

In the de-inking method according to the invention, an aqueous pulp slurry is contacted with the additive formulation at a concentration and for a time and at a temperature sufficient to remove ink from the paper fibers and to cause the removed ink to agglomerate into particles sufficiently large to permit their removal from the paper fibers by means known in the art, preferably screening or

centrifuging. The additive formulation may be employed at a level of about 5 to 30 pounds, preferably about 10 to 20 pounds, per ton of fiber, dry weight.

Other additives commonly used in de-inking operations, discussed above, may also be added with or as a part of the additive formulation according to the invention. One of ordinary skill would know the amount of additives commonly used in de-inking operations.

In the de-inking method according to the invention, the paper may first be repulped and then contacted with the additive formulation or the repulping and de-inking may occur simultaneously. A simultaneous method is preferred. In either a sequential or simultaneous method, the pulp slurry may be formed by means known in the art.

The paper to be de-inked may be treated in a hydropulper or other de-inking apparatus with an additive formulation according to the invention to produce an aqueous slurry of about 3 to 20, preferably about 4 to 8, weight percent dry fiber based on the total weight of the slurry. The pulp is preferably contacted with the additive formulation at a temperature above the softening point of the ink, preferably where the ink becomes tacky and agglomeration occurs. For example, the temperature should be about 40 to 100°C, preferably about 65 to 80°C and most preferably about 70°C. The pulp is preferably contacted with the additive formulation at a pH of about 6 to 13, preferably at pH 8 to 11, and most preferably at about pH 11. One of ordinary skill would understand that these conditions may be varied depending upon the particular composition of the ink, or inks, involved in a given de-inking operation.

The ink may be separated from the pulped fibers and agglomerated into particles for removal in a stepwise manner or essentially simultaneously. Again, simultaneous separation and agglomeration is preferred. Generally, at these conditions, about 5 to 60 minutes time is required for

pulping to be complete and for the ink to be removed from the paper.

The ink formulations (frequently referred to as "toners") used in non-impact printing are generally comprised of low molecular weight thermoplastic polymers and pigments, typically carbon black, although colored pigments are also frequently employed. The polymers used are usually low molecular weight polystyrenes, styrene/methacrylate copolymers, butadienes, and polyesters, by way of example. Waxes are sometimes blended into the inks to improve their fixing efficiency. In general, the major requirements for these polymers are: (1) they must have a melting point between 120 and 200°C; (2) they must be stable at temperatures up to about 54°C; (3) they must fuse on paper at about 150°C; and (4) they should have a glass transition temperature (softening point) between about 65 and 75°C.

Preferably, therefore, the pulp is contacted with an additive formulation according to the invention at the temperature where the thermoplastic ink binder becomes tacky and the ink particles more readily agglomerate into tacky particles. The agglomerated particles are preferably at least about 175 microns in diameter and more preferably at least about 200 microns.

After pulping and particle agglomeration are complete, the temperature of the pulp is preferably lowered to a temperature below the softening point of the polymer, preferably to about 55°C or lower. At this point, the agglomerated resin particles harden to a more rigid, non-tacky state which permits ready removal from the pulp by means known in the art. This removal is preferably accomplished by screening or centrifuging. The cooling temperature is not critical, but should be sufficiently low to permit the thermoplastic binder to harden to a sufficient non-tacky state.

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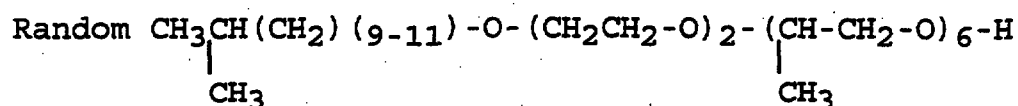
The invention will be demonstrated by the following examples. The examples illustrate but do not limit the present invention.

Example 1

Xerographically printed paper was de-inked using additive formulae according to this invention. Each formulation was made up of 25% of petroleum distillate and 75% by weight of derivatized ethylene oxide/propylene oxide polymer according to the following list.

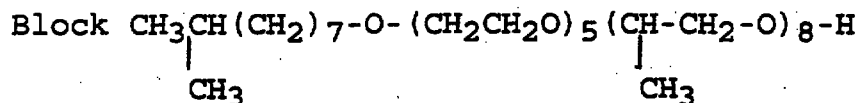
Formulation A

- Petroleum distillate: Vista LPA-140 product
- Derivatized Ethylene Oxide/Propylene Oxide Polymer:



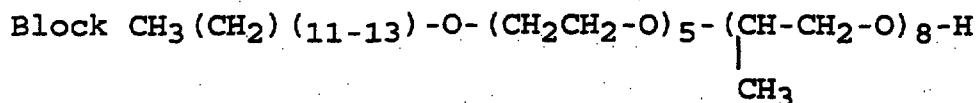
Formulation B

- Petroleum distillate: Vista LPA-140 product
- Derivatized Ethylene Oxide/Propylene Oxide Polymer:



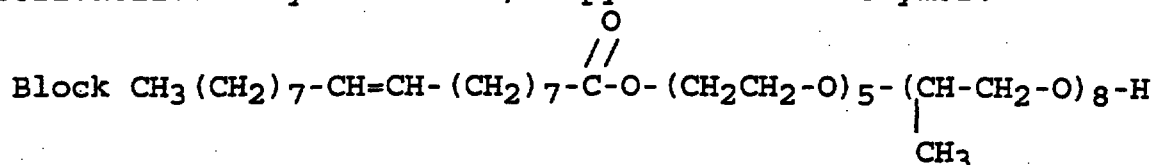
Formulation C

- Petroleum distillate: Vista LPA-140 product
- Derivatized Ethylene Oxide/Propylene Oxide Polymer:



Formulation D

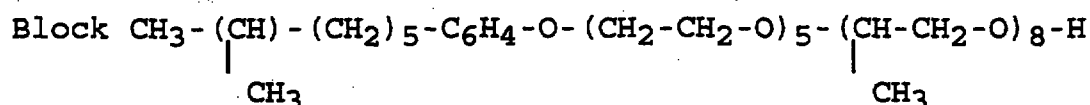
- Petroleum distillate: Vista LPA-140 product
- Derivatized Ethylene Oxide/Propylene Oxide Polymer:



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Formulation E

- Petroleum distillate: Vista LPA-140 product
- Derivatized Ethylene Oxide/Propylene Oxide Polymer:



A slurry of 4% by weight xerographically printed paper was prepared in aqueous alkali at pH 11.0 at 70°C. Each formulation A-E was added to a separate slurry at a concentration of about 20 pounds per ton of slurry. Pulping/de-inking was carried out for 30 minutes at 70°C, after which the temperature was lowered to 40°C to harden the agglomerated ink/resin particles. Controls with no additive formulation and with petroleum distillate only were run simultaneously with the test run.

The fibers were then washed at 0.5% slurry consistency in the water through a 5 mesh screen, then through a 10 mesh screen, and finally through a 20 mesh screen to remove the agglomerated ink particles.

Resin particle size was measured for all runs by a Thomas Optical Image analyzer. It was found that, when using a formulation of this invention, particle size greater than 200 microns was consistently realized, allowing the particles to be removed easily by screening. By contrast, when a formulation according to the invention was not used, a substantial number of particles of less than 200 microns were produced, and could not be removed by screening. These results are set forth in Table I.

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Table I

<u>Formulation</u>	<u>Median Particle Size</u>	<u>Minimum Particle Size</u>	<u>Particle Size Range</u>
A	1300 microns	250 microns	250-2100
B	1200	275	275-1700
C	1400	220	220-2300
D	1200	320	320-1900
E	1400	280	280-1650
Pet. Distill. Only	<100	<50	<50-350
Control	<100	<50	<50-350

Each batch of recycled fibers recovered in this example was made into hand sheets using conventional paper laboratory methods. Brightness was determined on each sheet using a General Electric Brightness Meter, as a quality evaluation.

Each of specimens A through E exhibited paper brightness between 80 and 83 indicating that little or no ink remained in this paper. By contrast, the control run, in which none of the additive formulations of this invention was employed, had a brightness value of 76.3, indicating that significantly more ink remained in this paper than in specimens A through E. The formulation containing petroleum distillate only had a brightness value of 76.5. The brightness of the initial paper in its original state was 84.5. Thus, the present invention successfully recycled the xerographic paper to a state closest to its original brightness by removing the greatest amount of ink.

Example II

Using the same procedures and additive formulations as in Example 1, a batch of laser-printed paper was de-inked.

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The ink/resin particles were removed by screening and their particle size was measured. The results are recorded in Table II.

Table II

<u>Formulation</u>	<u>Median Particle Size (Microns)</u>	<u>Minimum Particle Size (Microns)</u>	<u>Particle Size Range (Microns)</u>
A	1000	230	230-2200
B	900	270	270-1500
C	1100	240	240-1900
D	1000	250	250-1700
E	800	240	240-1200
Pet. Distill. Only	<100	<50	<50-350
Control	<100	<50	<50-350

Handsheet brightness for fibers de-inked according to the invention ranged from about 77.8 to 80.1. This compares to a brightness of 75.4 for the control, 84.5 for the initial paper in its original state, 76.5 for the formulation using only petroleum distillate.



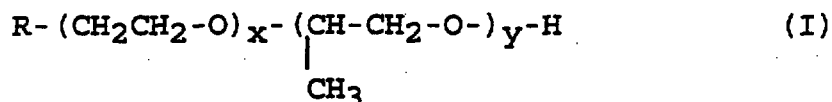
Claims

1. A de-inking method for removing ink from non-impact printed paper, the method comprising the step of contacting repulped paper fibers containing non-impact printed subject matter with an additive formulation for a time and at a temperature sufficient to separate the ink from the repulped paper fibers and to agglomerate the separated ink into particles of a size sufficient to permit their removal from the fibers,

the formulation comprising:

(1) 85 to 10% by weight of at least one petroleum distillate, and

(2) 15 to 90% by weight of at least one derivatized ethylene oxide/propylene oxide polymer of formula I:

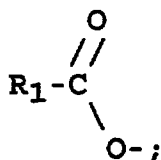


wherein x and y are each integers from 1 to 20 and R is the derivatizing radical selected from

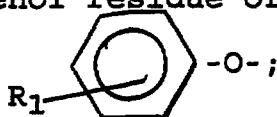
(a) an aliphatic alcohol residue having the formula:



(b) an aliphatic acid residue of the formula:



(c) a phenol residue of the formula:



wherein R_1 is a linear or branched, saturated or unsaturated hydrocarbon chain having 1 to 20 carbon atoms.

2. A method according to claim 1, further comprising the steps of lowering the temperature to render



the agglomerated ink particles solid and non-tacky and removing the agglomerated ink particles from said fibers.

3. A method according to claim 2, wherein the contacting step comprises a first step of separating the ink from the fiber followed by a second step of agglomerating the separated ink into particles of a size to permit their removal for the fibers.

4. A method according to claim 2, wherein the contacting step essentially simultaneously separates the ink from the fibers and agglomerates the separated ink into particles of a size to permit their removal from the fibers.

5. A method according to claim 2, wherein the agglomerated ink is removed by screening.

6. A method according to claim 2, wherein the agglomerated ink is removed by centrifuging.

7. A method according to claim 2 wherein the ratio of ethylene oxide to propylene oxide units in formula I is less than 1 to 1.

8. A method according to claim 2, wherein the contacting step is carried out at a temperature ranging from 65° to 80°C.

9. A method according to claim 8, wherein the ratio of ethylene oxide units to propylene oxide units in formula I is less than 1 to 1.

10. A method according to claim 9, wherein the additive formulation is employed at a level of about 5 to 30 pounds per ton of fiber, dry weight.

11. A method according to claim 2, wherein the additive formulation is employed at a level of about 5 to 30 pounds per ton of fiber, dry weight.

12. A method according to claim 11, wherein the agglomerated ink particles are removed by screening.

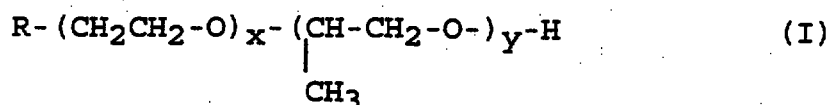
13. A method according to claim 11, wherein the agglomerated ink particles are removed by centrifuging.

14. A formulation for use in de-inking paper containing non-impact printed subject matter comprising:



(1) 85 to 10% by weight of at least one petroleum distillate, and

(2) 15 to 90% by weight of at least one derivatized ethylene oxide/propylene oxide polymer of formula I:

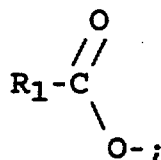


wherein x and y are each integers from 1 to 20 and R is the derivatizing radical selected from

(a) an aliphatic alcohol residue having the formula:



(b) an aliphatic acid residue of the formula:



(c) a phenol residue of the formula:



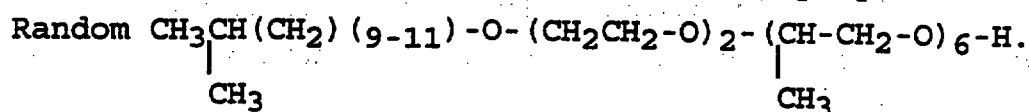
wherein R_1 is a linear or branched, saturated or unsaturated hydrocarbon chain having 1 to 20 carbon atoms.

15. A formulation according to claim 14, wherein the ratio of ethylene oxide to propylene oxide in the polymer is less than 1 to 1.

16. A formulation according to claim 14, wherein the petroleum distillate is a mixture of aliphatic and naphthenic hydrocarbons having a boiling point between about 185 and 275°C.

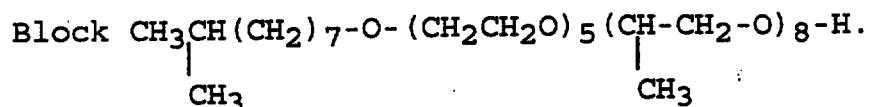
17. A formulation according to claim 16, wherein the petroleum distillate is VISTA LPA-140 product.

18. A formulation according to claim 16, wherein the derivatized ethylene oxide/propylene oxide polymer is

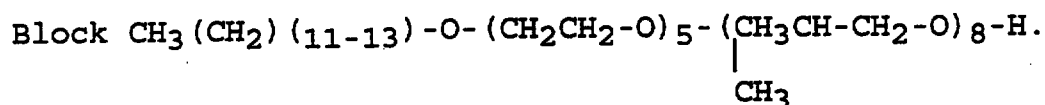




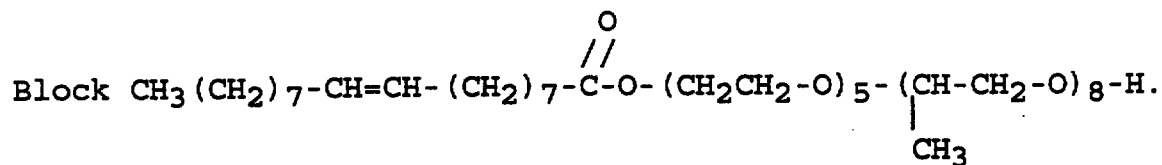
19. A formulation according to claim 16, wherein the derivatized ethylene oxide/propylene oxide polymer is



20. A formulation according to claim 16, wherein the derivatized ethylene oxide/propylene oxide polymer is



21. A formulation according to claim 16, wherein the derivatized ethylene oxide/propylene oxide polymer is



22. A formulation according to claim 16, wherein the derivatized ethylene oxide/propylene oxide polymer is

