

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : D21C 5/02	A1	(11) International Publication Number: WO 97/14844 (43) International Publication Date: 24 April 1997 (24.04.97)
(21) International Application Number: PCT/US96/16389 (22) International Filing Date: 10 October 1996 (10.10.96) (30) Priority Data: 08/544,115 17 October 1995 (17.10.95) US (71) Applicant: WITCO CORPORATION [US/US]; One American Lane, Greenwich, CT 06831-2559 (US). (72) Inventors: RASHEED, Khalid; 2406 Creek Meadows, Missouri City, TX 77459 (US). BERGER, Paul, D.; 3014 Deer Creek, Sugarland, TX 77428 (US). FRIEDMAN, Seymour, K.; 1430 Prospect Avenue, Fairlawn, NJ 07410 (US). (74) Agents: BLACK, Donald, T. et al.; Scully, Scott, Murphy & Presser, 400 Garden City Plaza, Garden City, NY 11530 (US).		(81) Designated States: AU, BR, CA, JP, KR, MX, NO, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: NOVEL SURFACTANT COMPOSITIONS AND THE USE THEREOF IN PAPER DEINKING (57) Abstract Mixtures of C ₈ to C ₂₂ alpha-olefin sulfonates and alkyl ether sulfates of the formula: RO-(CH ₂ CH ₂ O) ₁₋₄ SO ₃ Na where R is C ₈ -C ₁₈ alkyl, with one or more of alkoxylates of C ₁ -C ₁₀ alcohols, dialkoxylates of certain cyclohexenyl diacids, or propoxylated quaternary ammonium compounds; and mixtures of fatty acid alkoxylates, fatty alcohol alkoxylates, and one or more of said cyclohexenyl diacid dialkoxalates and C ₁ -C ₁₀ alcohol alkoxylates, provide enhanced removal of ink when used in the froth flotation deinking of waste paper.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

1

NOVEL SURFACTANT COMPOSITIONS AND THE
USE THEREOF IN PAPER DEINKING

The present invention relates to the treatment of waste paper to remove ink from the paper. More specifically, the present invention relates to novel surfactant compositions useful in the removal of ink from waste paper, and to the use of such novel surfactant compositions in the removal of ink from the paper.

10 The growing interest in recycling of used ("waste") paper as a source in the manufacture of new paper and paper products has increased the demand for effective products and processes which are adaptable to the processing of the many different types of paper
15 currently used in commerce. In particular, there remains a strong interest in processes and reagents which are useful in the removal of ink from the waste paper. Obviously, it is highly desirable to maximize removal of ink from waste paper to permit the recycled
20 waste paper to be as bright and clean as possible. Ideally, such reagents should be able to maximize removal of ink from types of paper currently known in commerce including newsprint, impact printed paper and non-impact printed paper. Such differing types of paper
25 and the differing types of ink that may be used thereon, pose a challenge in the identification of useful, efficient surfactant formulations and processes which can be used in the removal of the ink from the paper. This challenge is particularly seen when the waste paper
30 feedstock comprises a mixture of types of paper, as is

-2-

1 often the case when the paper is obtained from business
and industrial concerns.

The prior art demonstrates that various
surfactants and surfactant combinations have been
5 employed in the deinking of paper. While the techniques
disclosed in the prior art may have been useful,
nonetheless they are less than ideal for various
reasons. Thus, there remains a need for surfactant
formulations which exhibit the effectiveness and
10 efficiency exhibited by the compositions in the present
invention.

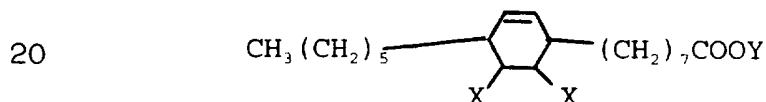
For instance, U.S. Patent No. 4,311,552
discloses deinking waste material, such as waste
newsprint, in a slurring process using a deinking agent
15 which comprises a C_{14} to C_{20} alpha olefin sulfonate,
particularly in combination with a nonionic detergent
such as a 9-mole phenyl ethoxylate.

U.S. Patent No. 4,935,096 discloses deinking
of waste paper, using as the deinking agent an ionic
20 surfactant, alone or in combination with nonionic
surfactants. Among the disclosed ionic surfactants, are
anionic compounds derived from alkylbenzene or
hydrocarbons, such as sodium alkylbenzene sulfonates,
sodium alcohol ether sulfates, sodium alcohol sulfates,
25 and sodium alkyl or dialkyl sulfosuccinates. Among the
disclosed cationic surfactants are mono, di or tri alkyl
quaternary ammonium compounds. Among the nonionic
surfactants disclosed are alkyl phenyl ethoxylates,
ethoxylates of alcohols or fatty acids, and "mixed
30 ethylene/propylene oxide adducts".

- 3 -

1 U.S. Patent No. 4,964,949 discloses deinking
 of waste paper employing a deinking agent which
 comprises a reaction product of one or more alkylene
 oxides with natural oils or fats and polyhydric
 5 alcohols, and also comprises a compound selected from
 the group consisting of alkylene oxide adducts of C₁₂ to
 C₁₈ alcohols, or sulfates of alkylene oxide adducts of C₁₂
 to C₁₈ alcohols, or C₈ to C₂₂ fatty acids or salts
 thereof.

10 U.S. Patent No. 5,158,697 discloses deinking
 of waste paper wherein the deinking agent comprises one
 or more of alkoxyated dimer acids and polymer acids of
 unsaturated fatty acids containing 16 to 20 carbon
 atoms; alkoxyates of partial esters of dimer acids and
 15 polymer acids of unsaturated fatty acids containing 16
 to 20 carbon atoms esterified with alcohol containing 1
 to 18 carbon atoms; or alkoxyated dicarboxylic acids or
 dicarboxylic acid monoesters of the following formula



wherein one of the X groups is COOH and the other is H
 or CH₃, Y is H or R, and R is an alkyl group containing 1
 25 to 18 carbon atoms.

The present invention is directed to a
 deinking composition useful in the froth flotation
 deinking of waste paper, comprising a surfactant mixture
 selected from the group consisting of

30 (A) mixtures of

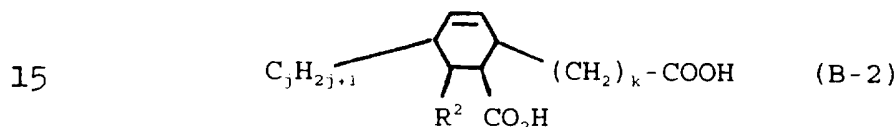
-4-

1 (A.1) an anionic surfactant component selected from the group consisting of alpha-olefin sulfonates containing 8 to 22 carbon atoms, alkyl ether sulfates of the formula $R^1O-(CH_2CH_2O)_nSO_3Na$ wherein n is 1 to 4, R^1 is
 5 C_8-C_{18} alkyl, and mixtures thereof; and

(A.2) a second surfactant component selected from the group consisting of

(A.2.a) alkoxyates of straight and branched C_1-C_{10} alcohols wherein the alkoxyate moiety contains
 10 propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.5:1 to 2.0:1;

(A.2.b) dialkoxyates of diacids of the formula (B-2)



wherein R^2 is H or CH_3 , j is 1-11, k is 1-11 and (j + k) is 10-14, the dialkoxyate containing a total of up to
 20 60 propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.2:1 to 4.0:1; and

(A.2.c) propoxylated quaternary ammonium compounds of the formula $(R^3)_3-N-CH_2CH_2O(PrO)_{9-40}-H^+A^-$ wherein PrO denotes propoxy, each R^3 is independently a
 25 C_1-C_{12} alkyl group, and A is a halide, acetate, phosphate, methylsulfate or ethylsulfate anion; and

(B) mixtures of

(B.1) a mixture of one or more fatty acid alkoxyates wherein the fatty acyl moiety contains 12 to
 30 18 carbon atoms and the alkoxyate portion contains 10-

-5-

1 30 ethoxy units and 5-25 propoxy units, one or more
alkoxylates of C_{12} - C_{20} alcohols with 10-30 ethoxy units
and 5-25 propoxy units; and

(B.2) a third surfactant component selected
5 from the group consisting of

(B.2.a) alkoxyates of diacids as defined in
(A.2.b) and

(B.2.b.) alkoxyates of straight and branched
 C_1 - C_{10} alcohols as defined in (A.2.a).

10 The present invention is also directed to a
process of deinking waste paper, by subjecting the waste
paper to froth flotation in a liquid composition
comprising a surfactant mixture selected from the group
consisting of

15 (A) mixtures of

(A.1) an anionic surfactant component selected
from the group consisting of alpha-olefin sulfonates
containing 8 to 22 carbon atoms, alkyl ether sulfates of
the formula $R^1O-(CH_2CH_2O)_nSO_3Na$ wherein R is C_8 - C_{18} alkyl
20 and n is 1 to 4, and mixtures thereof; and

(A.2) a second surfactant component selected
from the group consisting of

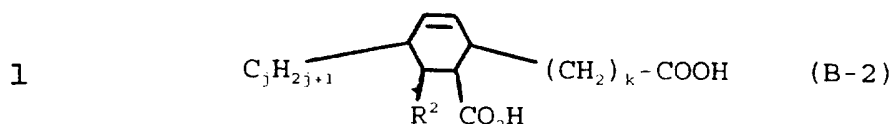
(A.2.a) alkoxyates of straight and branched
 C_1 - C_{10} alcohols wherein the alkoxyate moiety contains
25 propoxy and ethoxy units in a propoxy:ethoxy mole ratio
of 0.5:1 to 2.0:1;

(A.2.b) dialkoxyates of diacids of the
formula (B-2)

30

35

-6-



wherein the R^2 group is CH_3 or H , j is 1-11, k is 1-11 and $(j + k)$ is 10-14, the dialkoxylate containing a total of up to 60 propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.2:1 to 4.0:1; and

(A.2.c) propoxylated quaternary ammonium compounds of the formula $(\text{R}^3)_3\text{-N-CH}_2\text{CH}_2\text{O-(PrO)}_{9-40}\text{-H}\cdot\text{A}^-$ wherein PrO denotes propoxy, each R is independently a $\text{C}_1\text{-C}_{12}$ alkyl group, and A is a halide, acetate, phosphate, methylsulfate or ethylsulfate anion; and

(B) mixtures of (B.1) a mixture of one or more fatty acid alkoxylates wherein the alkoxylate portion contains 10-30 ethoxy units and 5-25 propoxy units, one or more alkoxylates of $\text{C}_{12}\text{-C}_{20}$ alcohols with 10-30 ethoxy units and 5-25 propoxy units; and

(B.2) a third surfactant component selected from the group consisting of

(B.2.a) alkoxylates of diacids as defined in (A.2.b) and

(B.2.b.) alkoxylates of straight and branched $\text{C}_1\text{-C}_{10}$ alcohols as defined in (A.2.a).

In a particularly preferred aspect, waste paper is slurried and subjected to froth flotation in a liquid medium comprising any of the foregoing mixtures of surfactants, whereby ink and the waste paper are separated in the liquid medium, and then separating the slurried waste paper from the liquid medium containing the solubilized ink.

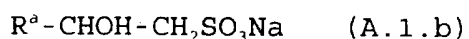
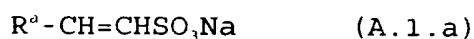
30

35

-7-

1 The compositions of the present invention are particularly useful in removal of ink from waste paper and more particularly from waste paper comprising mixtures comprising two or more distinct types of paper, 5 whether the paper has been imprinted by conventional impact-printing techniques with any of the inks used in that type of printing, or by non-impact printing techniques (such as laser printing) using any of the types of inks used in that kind of printing.

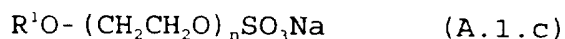
10 One component present in many of the compositions of the present invention is an anionic surfactant component which is an alpha-olefin sulfonate, alkyl ether sulfate, or a mixture thereof. By alpha-olefin sulfonates are meant sulfonates of straight and 15 branched alkenyl groups containing 8 to 22 carbon atoms and containing at least one carbon-carbon double bond, as well as the hydroxylated counterparts thereof, including but not limited to compounds exhibiting either of the following formulas (A.1.a) and (A.1.b), or 20 mixtures thereof,



25 wherein R^a is a straight or branched alkyl group, preferably straight, selected so that the molecule as a whole contains 8 to 20 carbon atoms. Preferred examples of these anionic surfactants include alpha-olefin sulfonates containing 14 to 16 carbon atoms in the 30 molecule.

- 8 -

1 By alkyl ether sulfate is meant compounds of
the formula (A.1.c)



5

wherein n is 1 to 4, and R is C₈-C₁₈ alkyl.

Anionic surfactants of the foregoing formulas
are commercially available and can readily be
synthesized using known industrial chemical techniques.

10 Preferred commercial examples include "Witconate AOS", a
C₁₄-C₁₆ alpha-olefin sulfonate, and "Witcolate ES-3", a
sodium lauryl ether sulfate corresponding to the
foregoing formula (A.1.c) wherein n is 3 and R¹ is
C₁₂-C₁₄ alkyl, both of which are sold by Witco Corp.

15

The foregoing anionic surfactants have been
found to be particularly effective and efficient in the
removal of ink from waste paper, particularly when used
in froth flotation processes as described below, when
the anionic surfactant component is used in combination
20 with any of several second surfactant components, namely
the following.

One such second surfactant component comprises
one or more alkoxyates of straight and/or branched
alcohols, which alcohols contain 1 to 10 carbon atoms.

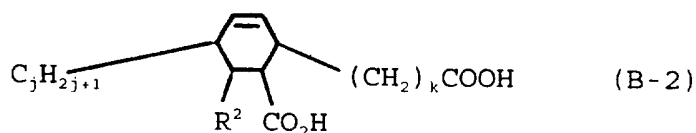
25

The alcohols are alkoxyated with both propoxy and
ethoxy units, such that the resulting alkoxyate has a
mole ratio of propoxy units to ethoxy units of 0.5:1 to
2.0:1. In this and all other alkoxyated compounds
described herein, the ethoxy and propoxy units can be
30 present as poly(ethoxy) and poly(propoxy) blocks, or can

- 9 -

1 be intermingled. It will be understood that useful
 alcohol alkoxylates include any of this formula which
 can form the desired surfactant composition of the
 present invention exhibiting the desired properties
 5 described herein. Thus, the range of molecular weights,
 or chain lengths, of alcohol alkoxylates of the
 foregoing description which are useful in the
 compositions of the present invention vary rather
 widely. An alcohol alkoxylate of the foregoing
 10 description will be effective depending on the other
 components of the composition, but for illustrative
 purposes it should be understood that the molecular
 weight of useful alcohol alkoxylates of the foregoing
 description may generally range from about 1000 to about
 15 10,000, without intending to be bound by the precise
 numerical values. Satisfactory alkoxylated alcohols
 meeting the foregoing descriptions can be readily
 synthesized using established industrial synthesis
 techniques, although numerous examples of satisfactory
 20 alkoxylated alcohols are commercially available. One
 exemplary commercially available alkoxylated alcohol is
 "Witconol NS-500LQ", a high molecular weight alkoxylated
 butanol.

Another class of alkoxylates useful in
 25 combination with the anionic surfactants described
 hereinabove, are dialkoxylates of diacids of the formula
 (B-2)



35

-10-

- 1 wherein R^2 can be H or CH_3 , wherein the diacid is
dialkoxylated, that is, substituted at both -COOH sites
with alkoxylate chains containing propoxy and ethoxy
units in a propoxy:ethoxy mole ratio of 0.2:1 to 2.0:1.
5 The propoxy and ethoxy units can be interspersed or can
be present as blocks formed from each type of unit. The
number of moles of alkoxy units in the dialkoxylated
diacid can fall within the range of chain lengths which
still enable the alkoxylated diacid to function
10 effectively in the surfactant composition as described
herein. For purposes of illustration, however,
satisfactory dialkoxylated diacids will generally
contain up to 75 alkoxy units, and preferably 20 to 60
alkoxy units in total. The compounds can have a
15 molecular weight in the range of about 1200 to about
3000.

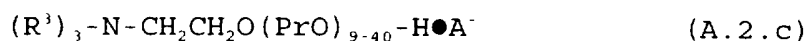
Alkoxylated diacids of this description can be
readily formed by reacting the corresponding diacid,
which is commercially available, with an appropriately
20 chosen number of moles of ethylene oxide and propylene
oxide under conventional alkoxylating conditions.
Satisfactory diacids include "Westvaco Diacid 1550" and
"Westvaco Diacid 1575", available from the Westvaco
Corp. in which the principal diacid component
25 corresponds to formula (B-2) wherein the substituent R^2
is H. These diacids are disclosed more generally in
U.S. Patent No. 3,899,476.

As is shown in the example herein, effective
deinking of paper feedstock has also been obtained using
30 as the surfactant component (even as the sole surfactant

-11-

1 component) one or more dialkoxylates of cyclohexenyl
diacid derivatives of the foregoing formula (B-2).

Another type of surfactant which has been
found to exhibit exemplary results when used in deinking
5 operations in combination with the anionic surfactant
component described herein, is propoxylated quaternary
ammonium compounds of the formula (A.2.c)



10

wherein (PrO) denotes the propoxy unit, each of the R^3
groups is independently C_1 - C_{12} alkyl and A is a halide,
acetate, phosphate, methyl sulfate, or ethyl sulfate
anion. Preferably, one of the R^3 groups is methyl and
15 two R^3 groups are ethyl. More preferably, A represents
chloride.

Propoxylated quaternary ammonium compounds of
the foregoing formula (A.2.c) can readily be
synthesized, and several examples are commercially
20 available. More specifically, compounds known as "Emcol
CC-9" and "Emcol CC-42", which are propoxylated methyl
diethyl quaternary ammonium compounds of the foregoing
formula containing, respectively, 9 and 40 propoxy
units, are commercially available from Witco Corp.
25 Since these compounds are cationic, the ability of these
propoxylated quaternary ammonium compounds to form
together with the foregoing anionic surfactants a
surfactant composition useful in the deinking of waste
paper is particularly surprising in that it is
30 conventionally expected that cationic and anionic

-12-

1 substances would interact with each other (because of
their opposing ionic charges) rather than cooperating
synergistically to function as effectively as they have
been found to function.

5 The anionic surfactant component on the one
hand, and the second surfactant component on the other
hand which as defined hereinabove can be alcohol
alkoxylate, dialkoxylate of cyclohexenyl diacids, or
propoxylated quaternary ammonium compounds, are present
10 together in amounts relative to each other effective to
aid in the removal of ink from the waste paper.
Generally, the weight ratio of the anionic surfactant or
surfactants to the second surfactant (i.e. the nonionic
and/or cationic surfactant or surfactants) present
15 should be from 20:1 to 1:20. More preferably, the
weight ratio of the anionic surfactant component to the
second surfactant component is about 5:1 to 1:1, and
more preferably about 4:1 to about 1.5:1.

 Additionally, surfactant compositions useful
20 in accordance with the present invention comprise
mixtures of fatty acid alkoxylate, a fatty alcohol
alkoxylate, and a third surfactant component. The fatty
acids represent one or a blend of fatty acids containing
12 to 18 carbon atoms. In the fatty acid alkoxylates,
25 the alkoxylate portion contains 10-30 ethoxy units and
5-25 propoxy units. The fatty alcohol alkoxylate is
preferably derived from fatty alcohols containing 16 to
20 carbon atoms, and is substituted with an alkoxylate
chain containing propoxy and ethoxy units in a
30 propoxy:ethoxy mole ratio of 0.5:1 to 2.0:1.

-13-

1 Typically, without intending to be bound hereby, the
fatty alcohol alkoxylate should exhibit a molecular
weight in the range of about 1000 to about 3000.

It has been determined that a mixture of the
5 fatty acid alkoxylate and fatty alcohol alkoxylate with
a third surfactant exhibits exemplary results in the
deinking of waste paper, especially when the third
surfactant is an alkoxylate of a cyclohexenyl diacid as
defined hereinabove with respect to alkoxylates of
10 diacids of the formula (B-2), and when the third
surfactant is an alkoxylate of straight or branched C_1 -
 C_{10} alcohol as described hereinabove.

In those surfactant compositions of the
present invention comprising one or more fatty acid
15 alkoxylates, fatty alcohol alkoxylate, and the indicated
third surfactant component such as dialkoxylates of
cyclohexenyl diacids or alkoxylates of alcohols, the
weight ratio of the fatty acid alkoxylate to the fatty
alcohol alkoxylate is from 1:1 to 10:1, and the ratio of
20 the fatty acid alkoxylate plus fatty alcohol alkoxylate
to the third surfactant component is from 1:20 to 20:1,
but is preferably in the range of 5:1 to 1:1 and more
preferably about 2:1 to 1:1.

The surfactant formulations of the present
25 invention can be produced by simply combining the
indicated surfactant components in the desired relative
amounts, such as by stirring in a suitable tank until
the components are thoroughly and homogeneously
intermixed. Water may be present, in an amount ranging

30

35

-14-

1 from 0.1 wt.% to 90 wt.% depending on the desired final
concentration of active ingredients.

In general, effective deinking is provided by
intimately contacting the waste paper with any of the
5 surfactant formulations of the present invention,
preferably in an aqueous or other liquid medium to
provide desired fluidity and penetration of the
surfactant components to the paper/ink interface.
Preferably, the waste paper is first shredded or
10 otherwise converted to small pieces so as to improve the
contact of the paper and ink with the liquid medium
bearing the surfactants. Of course, appropriate
agitation can be provided to enhance the desired contact
between the surfactant components and the paper/ink
15 interface.

It is preferred to utilize the surfactant
compositions of the present invention in connection with
the froth flotation of ink from the waste paper. The
general conditions of froth flotation deinking
20 techniques are known in this field. The waste paper is
pulped in an aqueous bath, which has preferably been
rendered alkaline by appropriate adjustment of the pH
via the addition of a base such as sodium hydroxide.
Preferably, the pH is about 9 to 11. The desired
25 surfactants are added at amounts calculated to provide
the desired ratio between amounts of the respective
compounds. The overall amount of surfactant is selected
with respect to the quantity of the paper in the cell
and with respect to the general amount of ink product on
30 the paper. Generally, the total amount of surfactant

-15-

1 comprises about 0.1 wt.% to about 5.0 wt.% and
preferably up to about 1.0 wt.% based on the amount of
waste paper present. Lesser amounts of surfactant risk
reducing the efficiency of the deinking, whereas higher
5 amounts of surfactant may assist in the deinking of
waste paper but not necessarily enhance the efficiency
of the deinking in proportion to the additional amounts
of surfactant used. The flow of gas, typically air,
through the flotation cell agitates the liquid medium
10 and the waste paper, provides enhanced contact with the
surfactant, and propels ink particles removed from the
waste paper to the top surface where a froth rich in
removed ink is established. The froth can be removed
continuously or intermittently. After a period of time
15 appropriate for the volume of the cell and the quantity
of waste paper and its ink content, the pulp of deinked
waste paper is removed from the cell for further
processing toward the recovery and reuse in regenerated
paper products.

20 The present invention has been found to
provide improved effectiveness and efficiency in the
deinking of waste paper, particularly waste paper
comprising mixtures of different types of paper. The
enhanced deinking has been determined through analysis
25 for the gain in brightness of the recovered paper
product and for the percentage of ink removed, (in total
and as large particle removal), as well as for the
percentage of fiber recovered in the regenerated
product.

30

35

-16-

1 The following examples demonstrate the
significant and favorable results that are obtained in
the practice of the present invention.

5 EXAMPLES

 The feed material to be deinked was repulped
in a commercial pulping apparatus (Morden Slushmaker).
The feed material comprised about 90 wt.% ledger paper
10 and about 10% copier paper (i.e. that had been printed
on by a conventional photocopying machine). In both
cases the ink formulations present contained hydrocarbon
resins used as binders for pigments. Each batch
contained 4 pounds of paper (dry weight) which was
15 combined with enough water to form a pulp which
comprised about 6 wt.% paper. This pulp was maintained
in this apparatus for thirty minutes at about 120°F at a
pH of 10 to which it had been adjusted with sodium
hydroxide.

20 Each repulped batch was then diluted with
water to 0.8 wt.% consistency and the temperature was
adjusted to 100°F, after which portions of the resulting
pulp were transferred from the pulping tank into a
conventional deinking flotation cell. Once the
25 flotation cell was full and the flow of water through
the cell was adjusted to 15 gallons per minute, each of
the surfactant compositions described below were added
in separate runs. All surfactant compositions used were
diluted to 68.1 grams per liter and were added at either
30 0.3, 0.6 or 0.9 wt.% (based on total dry solids of

-17-

1 surfactants weight). The surfactants added were allowed
to mix for five minutes in the cell prior to starting
air flow through the cell. Then, air flow upwards
through the cell was started and adjusted to 8 cubic
5 feet per minute and the cell was operated for an
additional 10 minutes.

Samples of each pulp batch were collected
before and after flotation, and were analyzed for
brightness and dirt count measurements. Six air dry
10 filter pads were produced from the deinked paper, and
were used for brightness measurements. Also, the "dirt
count" (large ink particles remaining) was measured with
an image analyzer at 25X magnification. In addition,
the froth was collected and weighed, for yield
15 calculations.

The various surfactant combinations tested
are described in Tables 1-A and 1-B. The results of the
testing are set forth in Table 2.

The results in Table 2 and Table 3-B
20 demonstrate that the surfactant components of the
present invention provide superior deinking of waste
paper.

25

30

35

-18-

1

TABLE 1-A

<u>Surfactant</u>	<u>Description</u>
A	A dialkoxylate of "Westvaco Diacid
5	1575" with a total of 13.5 moles of ethylene oxide ("EO") and 7.5 moles of propylene oxide ("PO") per mole of diacid
B	A (60:40) (wt.)) mixture of fatty acid alkoxylate with a
10	blend of alkoxylates of C ₁₆ -C ₂₀ alcohols (with 15 moles of EO and 7 moles of PO)
C	A dialkoxylate of "Westvaco Diacid
15	1575" with a total of 7.5 moles of EO and 7.5 moles of PO per mole of diacid
D	A dialkoxylate of "Westvaco Diacid
20	1575" with a total of 2.5 moles of EO and 7.5 moles of PO per mole of diacid
E	Sodium C ₁₄ -C ₁₆ olefin sulfonate ("Witconate AOS")
F	Polyoxypropylene (9) methyl diethyl ammonium chloride ("Emcol CC-9")
G	Polyoxypropylene (40) methyl diethyl ammonium chloride ("Emcol CC-42")
25	H
H	Butoxy alkoxylate with 60 moles of EO and 55 moles of PO ("Witconol NS-500 LQ")
I	Sodium laureth-3 sulfate
30	J
J	Lauryl dimethylamine oxide("Emcol LO")

35

1

TABLE 1-B

<u>Surfactant (s)</u> <u>Mixture No.</u>		<u>Description</u>
5	1	40 wt.% A 60 wt.% B
	2	100 wt.% B
10	3	40 wt.% C 60 wt.% B
	4	40 wt.% D 60 wt.% B
15	5	80 wt.% E 20 wt.% F
	6	80 wt.% E 20 wt.% G
20	7	80 wt.% E 20 wt.% H
	8	60 wt.% E 40 wt.% H
25	9	80 wt.% I 20 wt.% J
	10	80 wt.% I 20 wt.% G
30		
35		

-20-

- 1 11 80 wt.% I
20 wt.% F
- 12 100 wt.% A
- 5 13* 100 wt.% L727
("Lionsurf 727")
- 14* 100 wt.% "DI600"
- 10 *commercial products used as standards.

TABLE 2

	<u>Surfactant Mixture</u>	<u>% Active</u>	<u>Increase In Brightness</u>	<u>% Fiber Yield</u>	<u>% Ink Removal</u>
15	1	0.3	4.1	98.2	75.9
		0.6	5.2	98.9	90.5
		0.9	4.3	99.4	79.3
20	2	0.3	5.6	97.8	87.2
		0.6	7.4	98.5	87.5
		0.9	6.8	99.1	87.5
25	3	0.3	8.7	96.5	88.1
		0.6	8.3	98.3	67.6
		0.9	9.2	98.8	81.2
30	4	0.3	4.4	98.3	49.6
		0.6	6.5	98.7	75.4
		0.9	4.7	99.4	85.4

35

- 21 -

1	5	0.3	4.0	98.5	86.5
		0.6	4.0	99.2	85.9
		0.9	3.4	99.6	75.9
5	6	0.3	4.3	98.4	89.4
		0.6	2.2	99.6	91.2
		0.9	2.1	99.7	91.7
10	7	0.3	4.1	98.4	90.4
		0.6	4.5	99.1	84.5
		0.9	2.9	99.6	86.4
15	8	0.3	3.7	98.5	93.9
		0.6	3.3	99.3	27.2
		0.9	2.7	99.6	81.1
20	9	0.3	3.6	98.6	90.0
		0.6	3.9	99.2	88.9
		0.9	2.6	99.7	82.3
25	10	0.3	2.9	98.8	92.8
		0.6	2.0	99.6	89.6
		0.9	1.7	99.8	93.0
30	11	0.3	3.2	98.6	85.0
		0.6	2.0	99.6	81.4
		0.9	0.3	100.0	82.3
35	12	0.3	4.5	98.2	81.3
		0.6	3.3	99.3	76.3
		0.9	3.1	99.6	76.5
	13	0.3	5.2	97.9	90.0
		0.6	4.9	99.0	72.9
		0.9	3.7	99.5	92.7

-22-

1 14	0.3	3.0	98.8	91.8
	0.6	2.8	99.4	77.6
	0.9	2.8	99.6	82.5

5

10

15

20

25

30

35

-23-

1 In addition, the same procedure was carried
 out using as the surfactant various
 ethoxylated/propoxylated derivatives of the cyclohexenyl
 diacid "Westvaco Diacid 1575" defined hereinabove. The
 5 various alkoxyates are identified in Table 3-A, and the
 test results are set forth in Table 3-B.

TABLE 3-A

10

<u>Surfactant</u>	<u>Alkoxylation (moles of EO/moles of PO)</u>
K	13.5 EO/7.5 PO
L	25 EO/25 PO (block) (formulated)
M	25 EO/25 PO (random) (formulated)
N	25 EO/25 PO (random) (unformulated)
15 O	25 EO/7.5 PO (block) (formulated)
P	25 EO/7.5 PO (block) (neat)
Q	13.5 EO/7.5 PO (block) (formulated)
R	13.5 EO/7.5 PO (block) (neat)
S	"DI600" as standard
T	"Lionsurf 727" as standard

20

TABLE 3-B

<u>Surfactant</u>	<u>% Active</u>	<u>Increase In Brightness</u>	<u>% Fiber Yield</u>	<u>% Ink Removal</u>
25 L	0.3	3.8	85.6	91.5
	0.6	3.2	85.0	84.2
	0.9	3.2	86.2	60.7
M	0.3	3.4	93.2	95.0
	0.6	2.8	88.9	85.2
30	0.9	2.9	88.6	77.7

35

- 24 -

1	N	0.3	3.5	92.5	92.7
		0.6	2.5	89.5	83.5
		0.9	2.7	87.2	80.2
5	O	0.3	2.6	92.9	91.3
		0.6	2.5	89.2	77.4
		0.9	1.5	88.8	15.9
10	P	0.3	2.4	93.9	92.2
		0.6	1.8	90.1	56.7
		0.9	1.9	86.0	56.2
10	Q	0.3	0.9	97.8	73.3
		0.6	1.2	97.8	76.7
		0.9	0.9	98.0	44.3
15	R	0.3	0.3	97.8	82.6
		0.6	0.9	97.0	67.0
		0.9	1.3	98.2	44.9
20	S	0.3	1.8	95.6	82.6
		0.6	1.6	96.9	79.8
		0.9	1.5	98.1	40.5
20	T	0.3	1.7	96.2	91.8
		0.6	1.3	96.3	75.1
		0.9	0.9	90.8	55.6

25

30

35

-25-

1 WHAT IS CLAIMED IS

1. A deinking composition useful in the froth
flotation deinking of waste paper, comprising a
5 surfactant mixture selected from the group consisting of

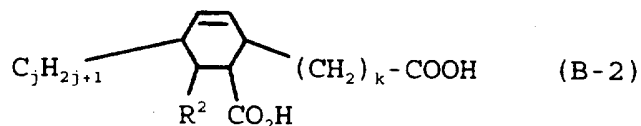
(A) mixtures of

(A.1) an anionic surfactant component selected
from the group consisting of alpha-olefin sulfonates
containing 8 to 22 carbon atoms, alkyl ether sulfates of
10 the formula $R^1O-(CH_2CH_2O)_nSO_3Na$ wherein n is 1 to 4, and R^1
is alkyl containing 8 to 18 carbon atoms, and mixtures
thereof; and

(A.2) a second surfactant component selected
from the group consisting of

15 (A.2.a) alkoxyates of straight and branched
 C_1 - C_{10} alcohols wherein the alkoxyate moiety contains
propoxy and ethoxy units in a propoxy:ethoxy mole ratio
of 0.5:1 to 2.0:1;

(A.2.b) dialkoxyates of diacids of the
20 formula (B-2)



25 wherein R^2 is H or CH_3 , j is 1-11, k is 1-11, and $(j + k)$
is 10-14, the dialkoxyate containing a total of up to
60 propoxy and ethoxy units in a propoxy:ethoxy mole
ratio of 0.2:1 to 4.0:1; and

(A.2.c) propoxylated quaternary ammonium
30 compounds of the formula $(R^3)_3\text{---}N\text{---}CH_2CH_2O(PrO)_{9-40}\text{---}H^+A^-$

-26-

1 wherein PrO denotes propoxy, each R³ is independently C₁-
C₁₂ alkyl, and A is a halide, acetate, phosphate,
methysulfate or ethylsulfate anion; and

(B) mixtures of (B.1) a mixture of one or more
5 fatty acid alkoxylates wherein the fatty acyl moiety
contains 12 to 18 carbon atoms and the alkoxylate
portion contains 10-30 ethoxy units and 5-25 propoxy
units, one or more alkoxylates of C₁₂-C₂₀ alcohols with
10-30 ethoxy and 5-25 propoxy units; and

10 (B.2) a third surfactant component selected
from the group consisting of

(B.2.a) dialkoxylates of diacids as defined in
(A.2.b) and

(B.2.b.) alkoxylates of straight and branched
15 C₁-C₁₀ alcohols as defined in (A.2.a).

2. A deinking composition according to Claim
1 comprising a surfactant mixture selected from the
group consisting of mixtures of

20 (A.1) an anionic surfactant component selected
from the group consisting of alpha-olefin sulfonates
containing 8 to 22 carbon atoms, alkyl ether sulfates of
the formula R¹O-(CH₂CH₂O)_nSO₃Na wherein n is 1 to 4, and R¹
is alkyl containing 8 to 18 carbon atoms, and mixtures
25 thereof; and

(A.2) a second surfactant component selected
from the group consisting of

(A.2.a) alkoxylates of straight and branched
C₁-C₁₀ alcohols wherein the alkoxylate moiety contains
30

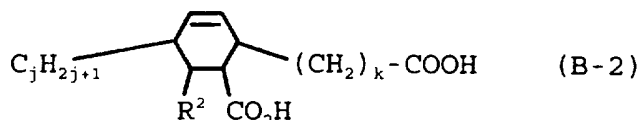
35

-27-

1 propoxy and ethoxy units in a propoxy:ethoxy mole ratio
of 0.5:1 to 2.0:1;

(A.2.b) dialkoxylates of diacids of the
formula (B-2)

5



wherein R^2 is H or CH_3 , j is 1-11, k is 1-11, and $(j + k)$
10 is 10-14, the dialkoxylate containing a total of up to
60 propoxy and ethoxy units in a propoxy:ethoxy mole
ratio of 0.2:1 to 4.0:1; and

(A.2.c) propoxylated quaternary ammonium
compounds of the formula $(\text{R}^3)_3\text{-N-CH}_2\text{CH}_2\text{O}(\text{PrO})_{9-40}\text{-H}\bullet\text{A}^-$

15 wherein PrO denotes propoxy, each R is independently C_1 -
 C_{12} alkyl, and A is a halide, acetate, phosphate,
methylsulfate or ethylsulfate anion.

3. A deinking composition according to Claim
20 2 comprising a surfactant mixture of (A.1) an alpha-
olefin sulfonate containing 8 to 22 carbon atoms; and

(A.2.a.) an alkoxyate of straight or branched
 $\text{C}_1\text{-C}_{10}$ alcohol wherein the alkoxyate moiety contains
propoxy and ethoxy units in a propoxy:ethoxy mole ratio
25 of 0.5:1 to 2.0:1.

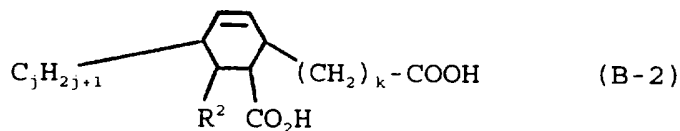
4. A deinking composition according to Claim
2 comprising a surfactant mixture of (A.1) an alpha-
olefin sulfonate containing 8 to 22 carbon atoms; and

30

35

-28-

1 (A.2.b.) a dialkoxylate of a diacid of the
formula (B-2)



wherein R^2 is H or CH_3 , j is 1-11, k is 1-11, and $(j + k)$
is 10-14, the dialkoxylate containing a total of up to
60 propoxy and ethoxy units in a propoxy:ethoxy mole
10 ratio of 0.2:1 to 4.0:1.

5. A deinking composition according to Claim
2 comprising a surfactant mixture of (A.1) an alpha-
olefin sulfonate containing 8 to 22 carbon atoms; and
15 (A.2.c) a propoxylated quaternary ammonium
compound of the formula $(R^3)_3-N-CH_2CH_2O(PrO)_{9-40}-H \bullet A^-$
wherein PrO denotes propoxy, each R is independently
 C_1-C_{12} alkyl, and A is a halide, acetate, phosphate,
methylsulfate or ethylsulfate anion.

20

6. A deinking composition according to Claim
2 comprising a surfactant mixture of (A.1) an alkyl
ether sulfate of the formula $R^1O-(CH_2CH_2O)_nSO_3Na$ wherein n
is 1 to 4, and R^1 is alkyl containing 8 to 18 carbon
25 atoms; and

(A.2.a) an alkoxylate of straight or branched
 C_1-C_{10} alcohol whereih the alkoxylate moiety contains
propoxy and ethoxy units in a propoxy:ethoxy mole ratio
of 0.5:1 to 2.0:1.

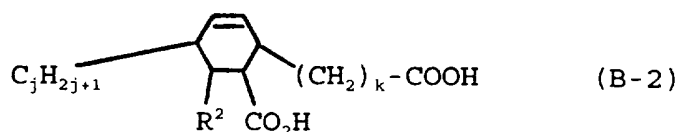
30

35

-29-

1 7. A deinking composition according to Claim
2 comprising a surfactant mixture of (A.1) an alkyl
ether sulfate of the formula $R^1O-(CH_2CH_2O)_nSO_3Na$ wherein n
is 1 to 4, and R^1 is alkyl containing 8 to 18 carbon
5 atoms; and

(A.2.b) a dialkoxylate of a diacid of the
formula (B-2)



wherein R^2 is H or CH_3 , j is 1-11, k is 1-11, and $(j + k)$
is 10-14, the dialkoxylate containing a total of up to
60 propoxy and ethoxy units in a propoxy:ethoxy mole
15 ratio of 0.2:1 to 4.0:1.

8. A deinking composition according to Claim
2 comprising a surfactant mixture of (A.1) an alkyl
ether sulfate of the formula $R^1O-(CH_2CH_2O)_nSO_3Na$ wherein n
20 is 1 to 4, and R^1 is alkyl containing 8 to 18 carbon
atoms; and

(A.2.c) a propoxylated quaternary ammonium
compound of the formula $(R^3)_3-N-CH_2CH_2O(PrO)_{9-40}-H\bullet A^-$
wherein PrO denotes propoxy, each R is independently C_1 -
25 C_{12} alkyl, and A is a halide, acetate, phosphate,
methylsulfate or ethylsulfate anion.

9. A deinking composition according to Claim
1 comprising a surfactant mixture selected from the
30 group consisting of mixtures of

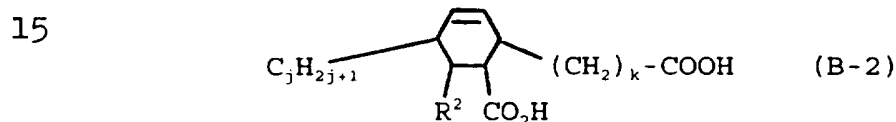
-30-

1 (B.1) a mixture of one or more fatty acid
alkoxylates wherein the fatty acyl moiety contains 12 to
18 carbon atoms and the alkoxyate portion contains 10-
30 ethoxy units and 5-25 propoxy units; one or more
5 alkoxyates of C_{12} - C_{20} alcohols with 10-30 ethoxy and 5-25
propoxy units; and

(B.2) a third surfactant component selected
from the group consisting of

(B.2.a) alkoxyates of straight and branched
10 C_1 - C_{10} alcohols wherein the alkoxyate moiety contains
propoxy and ethoxy units in a propoxy:ethoxy mole ratio
of 0.5:1 to 2.0:1; and

(B.2.b) dialkoxyates of diacids of the
formula (B-2)



wherein R^2 is H or CH_3 , j is 1-11, k is 1-11, and $(j + k)$
20 is 10-14, the dialkoxyate containing a total of up to
60 propoxy and ethoxy units in a propoxy:ethoxy mole
ratio of 0.2:1 to 4.0:1.

10. A deinking composition according to Claim
25 9 comprising

(B.2.a) an alkoxyate of straight or branched
 C_1 - C_{10} alcohol wherein the alkoxyate moiety contains
propoxy and ethoxy units in a propoxy:ethoxy mole ratio
of 0.5:1 to 2.0:1.

30

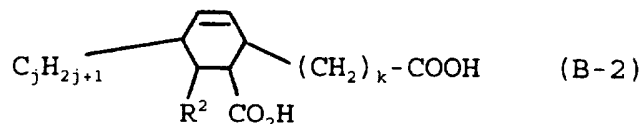
35

-31-

1 11. A deinking composition according to Claim
9 comprising

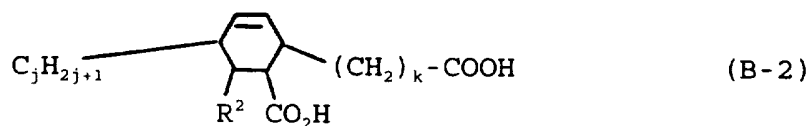
(B.2.b) a dialkoxylate of a diacid of the
formula (B-2)

5



wherein R^2 is H or CH_3 , j is 1-11, k is 1-11, and $(j + k)$
10 is 10-14, the dialkoxylate containing a total of up to
60 propoxy and ethoxy units in a propoxy:ethoxy mole
ratio of 0.2:1 to 4.0:1.

12. A deinking composition useful in the
15 froth flotation deinking of waste paper, comprising one
or more dialkoxylates of diacids of the formula (B-2)



20

wherein R^2 is H or CH_3 , j is 1-11, k is 1-11, and $(j + k)$
is 10-14, the dialkoxylate containing a total of up to
60 propoxy and ethoxy units in a propoxy: ethoxy mole
ratio of 0.2:1 to 4.0:1.

25 13. The method of deinking waste paper
comprising subjecting said waste paper to froth
flotation in an aqueous medium comprising a composition
in accordance with any of claims 1 to 12.

30

35

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/16389

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :D21C 5/02

US CL :162/5; 510/174

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)

U.S. : 162/5; 510/174

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

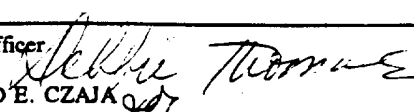
Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,311,552 A (BRUCATO et al) 19 January 1982, see entire document.	1-12
Y	US 5,158,697 A (KAWAMORI et al) 27 October 1992, see entire document.	1-12
Y	US 4,964,949 A (HAMAGUCHI et al) 23 October 1990, see whole document.	1-12
A	US 4,935,096 A (GALLAGHER et al) 19 June 1990, column 2, line 6 through column 3, line 34.	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier document published on or after the international filing date	"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
"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)	"G" document member of the same patent family
"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	

Date of the actual completion of the international search 03 JANUARY 1997	Date of mailing of the international search report 03 FEB 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer  DONALD E. CZAJKA Telephone No. (703) 308-0651

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/16389

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS, DIALOG, STN

search terms: deink?, alkyl ether sulfates, alkoxylate? alcohol?, dialkoxylate? diacids, propoxylated quaternary ammonium, fatty acid alkoxylate?