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(71) Applicant: **BETZ EUROPE, INC.**
Somerton Road
Trevose, PA 19053-6783(US)

(72) Inventor: **Ling, Tien-Feng**
2563 Stonebridge Drive
Jacksonville, Florida 32223(US)
Inventor: **Dreisbach, David Dale**
3331 Valpariso Way
Jacksonville, Florida 32223(US)

(74) Representative: **W.P. Thompson & Co.**
Coopers Building,
Church Street
Liverpool L1 3AB (GB)

(54) Control of deposition of organic contaminants.

(57) Methods for inhibiting deposition of organic contaminants from pulp in pulp and papermaking systems or from secondary fiber during repulping which comprises treating the pulp and papermaking system with hydrophobically modified associative polymer.

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The present invention relates to methods for inhibiting the deposition of organic contaminants. More particularly, it relates to inhibiting such deposition from pulp in pulp and papermaking systems and from secondary fiber during repulping.

The deposition of organic contaminants in the pulp and paper industry can cause both quality and efficiency problems in pulp and papermaking systems. Some components occur naturally in wood and are released during various pulping and papermaking processes. The term "pitch" can be used to refer to deposits composed of organic constituents which may originate from these natural resins, their salts, as well as coating binders, sizing agents, and defoaming chemicals which may be found in the pulp. In addition, pitch frequently contains inorganic components such as calcium carbonate, talc, clays, titanium, and related materials.

Stickies is a term that has become increasingly used to describe deposits that occur in systems using recycled fibre. These deposits often contain the same material found in "pitch" deposits in addition to adhesives, hot melts, waxes, and inks. All of the aforementioned materials have many common characteristics including: hydrophobicity, deformability, tackiness, low surface energy, and the potential to cause problems with deposition, quality, and efficiency in the process. Diagram 1 shows the complex relationnship between pitch and stickies discussed here.

Diagram 1

	Pitch	Stickies
Natural Resins (fatty and resin acids, fatty esters, insoluble salts, sterols, etc.)	X	X
Defoamers (oil, EBS*, silicate, silicone oils, ethoxylated compounds, etc.)	X	X
Sizing Agents (Rosin size, ASA*, AKD*, hydrolysis products insoluble salts, etc.)	X	X
Coating Binders (PVAC*, SBR*)	X	X
Waxes		X
Inks		X
Hot Melts (EVA*, PVAC*, etc)		X
Contact Adhesives (SBR*, vinyl acrylates, polyisoprene, etc.)		X

*

EBS Ethylene bis stearamide
ASA alkenyl succinic anhydride
AKD alkyl ketene dimer
PVAC polyvinyl acetate
SBR styrene butadiene rubber
EVA ethylene vinyl acetate

The deposition of organic contaminants can be detrimental to the efficiency of a pulp or paper mill causing both reduced quality and reduced operating efficiency. Organic contaminants can deposit on process equipment in papermaking systems resulting in operational difficulties in the systems. The deposition of organic contaminants on consistency regulators and other instrument probes can render these components useless. Deposits on screens can reduce throughput and upset operation of the system. This deposition can occur not only on metal surfaces in the system, but also on plastic and synthetic surfaces such as machine wires, felts, foils, Uhle boxes and headbox components.

Historically, the subsets of the organic deposit problems, "pitch" and "stickies" have manifested themselves separately, differently and have been treated distinctly and separately. From a physical standpoint, "pitch" deposits have usually formed from microscopic particles of adhesive material (natural or man-made) in the stock which accumulate on papermaking or pulping equipment. These deposits can readily be found on stock chest walls, paper machine foils, Uhle boxes, paper machine wires, wet press felts, dryer felts, dryer cans, and calendar stacks. The difficulties related to these deposits included direct interference with the efficiency of the contaminated surface, therefore, reduced production, as well as holes, dirt, and other sheet defects that reduce the quality and usefulness of the paper for operations that follow like coating, converting, or printing.

From a physical standpoint, "stickies" have usually been particles of visible or nearly visible size in the stock which originate from the recycled fiber. These deposits tend to accumulate on many of the same surfaces that "pitch" can be found on and cause many of the same difficulties that "pitch" can cause. The most severe "stickies" related deposits however tend to be found on paper machine wires, wet felts, dryer felts, and dryer cans.

Methods of preventing the build up of deposits on the pulp and papermill equipment and surfaces are of great importance to the industry. The paper machines could be shut down for cleaning, but ceasing operation for cleaning is undesirable because of the consequential loss of productivity, poor quality while partially contaminated and "dirt" which occurs when deposits break off and become incorporated in the sheet. Preventing deposition is thus greatly preferred where it can be effectively practiced.

In the past stickies deposits and pitch deposits have typically manifested themselves in different systems. This was true because mills usually used only virgin fiber or only recycled fiber. Often very different treatment chemicals and strategies were used to control these separate problems.

Current trends are for increased mandatory use of recycled fiber in all systems. This is resulting in a co-occurance of stickies and pitch problems in a given mill. It is desirable to find treatment chemicals and strategies which will be highly effective at eliminating both of these problems without having to feed two or more separate chemicals. The materials of this invention have clearly shown their ability to achieve this goal.

Pitch control agents of commerce have historically included surfactants, which when added to the system, can stabilize the dispersion of the pitch in the furnish and white water. Stabilization can help prevent the pitch from precipitating out on wires and felts.

Mineral additives such as talc have also found use and can reduce the tacky nature of pitch by adsorbing finely dispersed pitch particles on their surfaces. This will reduce the degree to which the particles coagulate or agglomerate.

Polyphosphates have been used to try to maintain the pitch in a finely dispersed state. Alum has also been widely used to reduce deposition of pitch and related problems.

Both chemical and non-chemical approaches to stickies control are employed by papermakers. Non-chemical approaches include furnish selection, screening and cleaning, and thermal/mechanical dispersion units.

Chemical treatment techniques for stickies control include dispersion, detackification, wire passivation and cationic fixation. Chemicals used included talc, polymers, dispersants and surfactants.

Surfactants, anionic polymers and copolymers of anionic monomers and hydrophobic monomers have been used extensively to prevent pitch deposition of metal soap and other resinous pitch components. See "Pulp and Paper", by James P. Casey, Vol. II, 2nd Edition, pp.1096-7.

US-A- 4 871 424, (Dreisbach et al., October 1989) teaches the use of polyvinyl alcohol and copolymers of vinyl alcohol to inhibit pitch deposition from pulp in paper-making systems.

US-A- 3 081 219, (Drennan et al., March 1963) teaches the use of a polymeric N-vinyl lactam to control pitch in the making of paper for sulfite pulps.

US-A- 3 154 466, (Nothum, October 1964), teaches the use of xylene sulfonic acid-formaldehyde condensates and salts thereof as pitch dispersants in papermaking.

USA- 3 992 249, (Farley, November 1976) discloses the use of certain anionic vinyl polymers carrying hydrophobic-oleophilic and anionic hydrophilic substituents when added prior to the beating operation in the range of about 0.5 parts to 100 parts by weight of the fibrous suspension to inhibit the deposition of adhesive pitch particles on the surfaces of pulp-mill equipment.

US-A- 4 846 933, (Dreisbach et al., July 1989) teaches the use of a water soluble polymer containing polymerized units of methyl vinyl ether having methyl ether groups to control pitch deposition from pulp.

US-A- 4 822 452, (Tse et al., April 1989) teaches the use of urethane block copolymers, as nonionic associative thickeners. These copolymers act as thickeners in the preparation of a fibrous web of textile length fibres.

"The Influences of washing, defoamers and dispersants on pitch deposition from unbleached Kraft pulps", N. Dunlop-Jones and L.H. Allen, Journal of Pulp and Paper Science: Vol. 15 No. 6, November 1989 teaches the use of nonylphenol ethoxylate compounds to inhibit pitch deposition in papermaking systems.

US-A- 4 781 794, (Moreland, November 1988) teaches methods for detackifying adhesive materials contained in secondary fibre. The methods comprise adding an unsubstituted methyl ether cellulose derivative to the secondary fibre. Methyl cellulose is a representative compound.

US-A- 4 886 575, (Moreland, December 1989) teaches the use of polyvinyl alcohol to inhibit the deposition and adherence of stickies to the repulping equipment.

US-A- 4 923 566, (Shawki et al., May 1990) teaches methods for pacifying stickies by applying urea between the drying rolls and the finished produce reel.

US-A- 4 643 800, (Maloney et al., February 1987) teaches removing and dispersing contaminant from secondary fibre during repulping. Nonionic surfactants and dispersants are used to separate the contaminant from the fibre.

According to the present invention there is provided a method for inhibiting the deposition of organic contaminants from pulp in pulp and papermaking systems which comprises treating the pulp and papermaking systems with a hydrophobically modified associative polymer.

According to the present invention there is also provided a method for inhibiting the deposition of organic contaminants from secondary fiber during repulping which comprises treating the secondary fiber with a hydrophobically modified associative polymer.

These associative polymers act to inhibit the deposition when adsorbed onto contaminants or contaminant prone surfaces. Common organic contaminants include constituents which occur in the pulp (virgin, recycle or combinations) having the potential to deposit and reduce paper machine performance or paper quality. This will include natural resins such as, for example as fatty acids, resin acids, their insoluble salts, fatty esters, sterols and other organic constituents, like ethylene bis-stearamide, waxes, sizing agents, adhesives, hot melts, inks, defoamers, and latexes that may be found to deposit in papermaking systems.

This inhibition may be achieved by continuous or batch addition to the stock (virgin, recycled and/or combination) prior to the site of concern or by continuous application directly to the site of primary contamination (i.e. the wire) prior to the accumulation of the deposit. The term hydrophobically associative polymer relates to polymers which have two or more hydrophobic regions giving them the capacity to form associative networks by the attraction/interaction of the hydrophobic regions.

Hydrophobically associating water-soluble polymers possess unusual rheological characteristics which are thought to arise from the intermolecular association of neighbouring hydrophobic substituents. The hydrophobic substituents are incorporated onto the polymer through chemical grafting or a suitable copolymerization procedure. The hydrophobic groups are incorporated to a level so as to not render the final modified polymer water insoluble. These polymers have found use in industrial fields such as enhanced oil recovery and in the formulation of latex based paints. See Carbohydrate Polymers 12 (1990) 443-459, R. Tanaka et al.

These polymers are widely used as rheology modifiers where their unique associative capabilities are very important. In this application they are often referred to as "associative thickeners". They are very different in behaviour from typical high molecular weight water-soluble polymers. They also behave very differently from dispersants which are low molecular weight and highly charged.

Associative thickeners are water-soluble polymers containing hydrophobic groups which are capable of non-special hydrophobic association, similar to surfactants. See Polymers as Rheology Modifiers, Chapter 12. page 207, Systems Approach to Rheology Control, P.R.Howard, E.L. Leafure, S.T. Rosier and E.J. Schaller.

One group of these hydrophobically modified associative polymers are the hydrophobically modified hydroxyethyl cellulose associative polymers. These polymers are available from Aqualon Company as Natrosol Plus 330 and Plus 430 and previously from Hercules as WSP-D-330. (Natrosol is a Trade Mark.) The hydrophobically modified hydroxyethyl cellulose associate polymers are described by K.G. Shaw and D.P. Liepold, Journal of Coatings Technology 57, No. 727, pp. 63-72 (August, 1985).

Another family of hydrophobically modified associative polymers are the hydrophobically modified associative water-soluble anionic polymers which are derived from ethylenically unsaturated acids such as acrylic acid and methyacrylic acid; ethylenically unsaturated monomers such as 2-acrylamido-2-propane sulfonic acid(AMPS) and 1-allyloxy-2-hydroxypropyl sulfonate and unsaturated acid monomers in general. Acrylate-based monomers are the preferred monomers in deriving these polymers. Representatives of these polymers are available from Rohm & Haas as Acrysol TT615, Acrysol ICS 1; Polyphobe 107 available from Union Carbide and the Alcogum SL70 and 296W polymers available from Alco Chemical Corporation. Polymers based on maleic acid copolymers and naphthalene sulfonate condensates have not been effective in this invention. It is thought that this is due to their inability to achieve high enough molecular weight to be effective. (AMPS and Acrysol are Trade Marks).

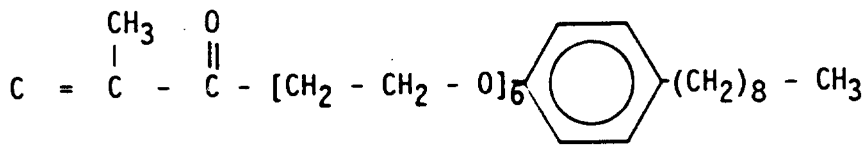
Alcogum SL70 is thought to be a terpolymer of methacrylic acid, ethyl acrylate, and a nonionic monomeric surfactant. The nonionic surfactant monomer consists of a poly(oxyethylene) compound and an alkyl hydrocarbon segment. The components are consistent with the patent literature in an approximate ratio of 40:50:10. The Alcogum 296W polymer is the sodium salt of poly(acrylic acid) prepared by the hydrolysis of poly(methyl acrylate) and was found to contain approximately 16 mole percent residual methyl acrylate units.

In another embodiment, the modified associative polymers are hydrophobically substituted acrylamide copolymers. These copolymers result from substitution of an acrylamide monomer to some extent to result in a copolymer. These copolymers can possess the comonomers other than acrylamide with the following structures:

$$C = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - O - (CH_2 - CH_2 - O)_{24} - C_{22}H_{45} \qquad \text{(I)}$$

$$C = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - O - (CH_2 - CH_2 - O)_{10} - O - (CH_2)_8 - CH_3 \qquad \text{(II)}$$

$$C = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - [O - C - \underset{\underset{\displaystyle CH_3}{|}}{C}]_{4,5} - [O - C - \underset{\underset{\displaystyle CH_3}{|}}{C}]_{3,6} - OH \qquad \text{(III)}$$



(IV)

Other representative modified polymers used in the present invention are hydrophobically substituted polyethylene oxide polymers. These multihydrophobically substituted polymers indicate that two or more hydrophobic groups are desirable for optimum efficiency. These polymers can have hydrophobic groups which are combined to the polyethylene oxide polymer by ester linkages. Preferred polyethylene oxide polymers include polyethylene oxide dioleate esters. Mapag 6000 available from PPG/Mazer is a representative polyethylene oxide polymer. (Mapag is a Trade Mark).

other hydrophobically associative thickener polymers based on modified ethylene oxide are also effective deposition control polymers as defined for use in the present invention. Pluracol TH922 and TH916 available from BASF are polymers useful in accordance with the present invention.

A further embodiment of the present invention utilizes associative water-soluble urethane polymers. These polymers have alternating blocks of hydrophobic groups and hydrophilic groups. These polyethylene glycol/ethylene oxide based urethane block polymers may have molecular weights in the range of (10,000 to 2,000,000) and are disclosed in US-A- 4 079 028 and US-A-4 155 892 as paint thickeners. Commercial formulations of these copolymers are available as Acrysol RM-825 and Acrysol RM-1020 from Rohn and Haas. These polymers comprise urethane block copolymers in different carrier fluids. For instance, Acrysol RM-825 is a 25 percent solids grade of polymer in a mixture of 25 percent butyl carbitol (a diethylene glycol monobutyl ether) and 75 percent water. Similar copolymers are available from Union Carbide Corporation as UCAR SCT 200 and UCAR SCT 275. These compounds are discussed in US-A- 4 496 708. Similar compounds are also available from Henkel Corporation under the trade names DSX 1514 and DSX 1550. These compounds are discussed in US-A- 4 438 225.

The polymers used in the present invention are effective at controlling the deposition of organic contaminants in papermaking systems. This may include Kraft, acid sulfite, mechanical pulp and recycled fiber systems. For example, deposition in the brown stock washer, screen room and decker system in Kraft papermaking processes can be controlled. The term "papermaking system" is meant to include all pulp processes. Generally, it is thought that these polymers can be utilized to prevent deposition on all surfaces from the beginning of the pulp mill to the reel of the papermachine under a variety of pH values and conditions. More specifically, these polymers effectively decrease the deposition not only on metal surfaces but also on plastic and synthetic surfaces such as, for example, machine wires, felt, foils, Uhle boxes and headbox components.

The polymers may be added to the papermaking system along with other papermaking additives. These can include other polymers, starch and sizing aids.

The polymers used in the present invention can be added to the pulp at any stage of the papermaking system. They may be added directly to the pulp furnish or sprayed on wires, felts, press rolls or other deposition-prone surfaces. They may be added to the papermaking system neat, as a powder, slurry or in solution; the preferred primary solvent being water but is not limited to such. They may be added specifically and only to a furnish identified as contaminated or may be added to blended pulps. The polymers may be added to the stock at any point prior to the manifestation of the deposition problem and at more than one site when more than one deposition site occurs. Combinations of the above additive methods may also be employed by way of feeding the pulp millstock, feeding to the papermachine furnish, and spraying on the wire and felt simultaneously. The effective amount of these polymers to be added to the papermaking system depends on a number of variables, including the pH of the system, hardness of the water, temperature of the water, additional additives, and the organic contaminant type and content of the pulp. Generally, 0.5 parts per million to about 150 parts per million is added to the paper making system. Preferably, from about 10 parts per million to about 50 parts per million is added to the system.

There are several advantages anticipated with the present invention as compared to prior processes. These advantages include: an ability to function without being greatly affected by hardness of the water in the system; an ability to function with lower foaming than surfactants, an ability to function while not adversely affecting sizing, fines retention, and an ability to function at very low dosages, reduced environmental impact, and improved biodegradability. Also, the ability of these agents to function in spite of dilution has been clearly shown.

Further these agents have proven effective against both the pitch and stickies manifestation of organic deposition problems providing for an effective reduction of these problems in mills employing a variety of virgin and recycled fiber sources.

The data set forth below were developed to demonstrate the unexpected results occasioned by use of the present invention. The following examples are included as being illustrations of the present invention and should not be construed as limiting the scope thereof.

It was found that pitch (natural resins, etc.) could be made to deposit from a 0.5% consistency fiber slurry containing approximately 2000 parts per million of a laboratory pitch preparation by placing the slurry into a metal pan suspended in a laboratory ultrasonic cleaner water bath. The slurry contained 0.5% bleached hardwood Kraft fiber, approximately 2000 parts per million of the potassium salt of a fatty acid blend, approximately 200 parts per million calcium from calcium chloride and approximately 300 parts per million sodium carbonate. The slurry was maintained at 50°C and at a pH of 11.

It was stirred gently by an overhead stirrer and subjected to ultrasonic energy for 10 minutes. The deposit weight was determined by subtracting the starting weight of the pan from the weight of the pan plus the deposit after completion of the test. This was converted to percent control of deposit using the formula:

$$\%\ \text{control of deposit} = \frac{\text{untreated weight} - \text{treated weight}}{\text{untreated weight}} \times 100$$

A high percent control of deposit is indicative of good deposit inhibiting qualities. Studies of this type were conducted using hydrophobically modified associative polymers of the type described in this invention. Results of this testing is reported in Table I.

TABLE I

Treatment Agent	% Control	
	50 ppm	10 ppm
Unmodified Hydroxyethyl Cellulose[1]	60	1
Hydrophobically modified Hydroxyethyl cellulose[2]	97	23
Hydrophobically modified Hydroxyethyl cellulose[3]	96	62
Hydrophobically modified Hydroxyethyl cellulose[4]	94	--

[1] available commercially as Natrosol H4BR
[2] available commercially as Natrosol Plus 330
[3] available commercially as Natrosol Plus 430
[4] available commercially as Hercules WSP-D-330

These results indicate that the hydrophobically modified associative polymers are more efficient deposit inhibitors than the unmodified polymers of a related type. These results further indicate that the polymers used in the present invention are effective at controlling deposition on metal surfaces and under alkaline conditions and specifically referred to typically as "pitch".

Further studies of the testing described in respect of Table I were conducted using hydrophobically modified associative anionic polymers and anionic dispersants disclosed as being preferred in the prior art. These results appear in Table II.

TABLE II

Treatment Agent	% Control 100 ppm	50 ppm	10 ppm
Hydrolysed Styrene Maleic Anhydride Copolymer [1]	82	12	17
Hydrolysed Diisobutylene Maleic Anhydride Copolymer [2]	13	13	0
Hydrophobically Associative Anionic Polymer [3]	--	88	28
Hydrophobically Associative Anionic Polymer [4]	--	93	18
Hydrophobically Associative Anionic Polymer [5]	--	95	22
Hydrophobically Associative Anionic Polymer [6]	--	98	14
Hydrophobically Associative Anionic Polymer [7]	--	93	25

1. Available commercially as Alco SMA 1000, see also US-A- 3 992 249 (Farley)
2. Available commercially as Tamol 731, see also US-A- 3 992 249 (Farley)
3. Available commercially as Alcogum SL70
4. Available commercially as Alcogum 296W
5. Available commercially as Acrysol TT615
6. Available commercially as Acrysol ICS 1
7. Available commercially as Polyphobe 107

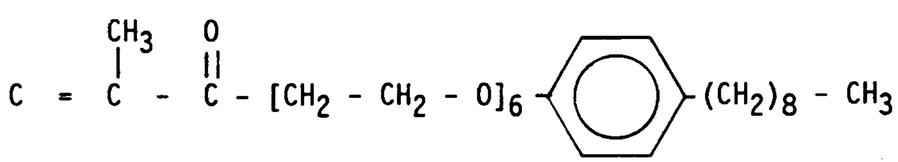
These results illustrate that the polymers used in the present invention are surprisingly more effective for deposition control than known deposition inhibitors specifically, they show efficacy at controlling pitch deposition.

Further testing as described in respect of Table 1 was conducted using hydrophobically substituted acrylamide copolymers. The hydrophobic comonomers possess the structures:

$$C = \overset{CH_3}{\overset{|}{C}} - \overset{O}{\overset{\|}{C}} - O - (CH_2 - CH_2 - O)_{24} - C_{22}H_{45} \qquad (I)$$

$$C = \overset{CH_3}{\overset{|}{C}} - \overset{O}{\overset{\|}{C}} - O - (CH_2 - CH_2 - O)_{10} - O - (CH_2)_8 - CH_3 \qquad (II)$$

$$C = \overset{CH_3}{\overset{|}{C}} - \overset{O}{\overset{\|}{C}} - [O - C - \underset{CH_3}{\underset{|}{C}}]_{4,5} - [O - C - \underset{CH_3}{\underset{|}{C}}]_{3,6} OH \qquad (III)$$



(IV)

The results of their testing appear in Table III.

TABLE III

Treatment Agent	Mole % Hydrophobe	Molar Ratio AMD/IPA	% Control		
			50 ppm	20 ppm	10 ppm
I	0.0	11:1	20	0	0
I	0.3	11:1	--	--	--
I	0.6	11:1	31	39	--
I	1.0	11:1	48	41	--
I	2.0	11:1	54	24	--
I	2.0	34:1	72	49	23
I	2.0	No IPA	68	49	32
I	3.0	11:1	66	45	20
I	4.0	17:1	66	16	16
II	2.0	11:1	72	--	12
II	3.0	11:1	81	--	13
II	4.0	11:1	84	--	35
II	5.0	11:1	87	--	32
II	0.5	No IPA	15	--	0
II	1.0	No IPA	48	--	13
II	2.0	No IPA	77	--	6
II	3.0	No IPA	75	--	13
II	4.0	No IPA	83	--	30
III			60	--	0
III			65	--	2
IV	2.0	11:1	46	--	0
IV	3.0	11:1	58	--	6
IV	4.0	11:1	70	--	39
IV	5.0	11:1	79	--	11
IV	0.5	No IPA	16	--	6
IV	1.0	No IPA	26	--	5
IV	2.0	No IPA	49	--	21
IV	3.0	No IPA	60	--	0
IV	4.0	No IPA	67	--	25

The results of Table III indicate that the hydrophobically modified associative polymers used in the present invention are effective at inhibiting deposition. The results illustrate that substituted acrylamides used in the present invention are more efficient at inhibiting deposition broadly and pitch deposition specifically than unsubstituted acrylamides.

Additional testing was performed as described in respect of Table I using hydrophobically substituted polyethylene oxides. These results are reported in Table IV.

TABLE IV

Treatment Agent	% Control	
	50 ppm	10 ppm
Nonyl Phenol Ethoxylate (Surfonic N-95)	81	9
Polyethylene oxide dioleate (Mapeg 6000)	85	36
Talloweth-60 Myristal glycol (Dapral 282)	88	46
(Surfonic is a Trade Mark)		

The results indicated in Table IV are further indicative that the multi-hydrophobically substituted polyethylene oxides are effective for inhibiting deposition. They were also shown to be more effective than the known mono-hydrophobically substituted deposition inhibitors.

Hydrophobically modified ethylene oxide polymers were also tested according to the procedure described in respect of Table I. The results of this testing appear in Table V.

TABLE V

Treatment Agent	% Control	
	50 ppm	10 ppm
Hydrophobically modified Associative Ethylene Oxide[1] Copolymer	95	88
Hydrophobically Modified Associative ethylene oxide[2] Copolymer	95	86

[1] Available commercially as Pluracol TH922
[2] Available commercially as Pluracol TH916
(Pluracol is a Trade Mark)

The results presented in Table V further show that the polymers used in the present invention provide highly effective and efficient deposition control and more specifically, pitch control.

Further studies of the testing described in respect of Table I were conducted using commercially available associative water-soluble urethane polymers. These testing results appear in Table VI.

TABLE VI

Treatment Agent	Percent Control of Pitch		
	100 ppm	50 ppm	10 ppm
Nonylphenol ethoxylate[1]		81	9
Sodium lignosulfate[2]	0	4	11
Hydrolyzed styrene maleic anhydride[3]	82	12	17
Diisobutene maleic anhydride[4]	13	13	0
Water-soluble urethane polymer[5]		83	58
Water-soluble urethane polymer[6]		87	72
Water-soluble urethane polymer[7]		81	31
Water-soluble urethane polymer[8]		87	49
Water-soluble urethane polymer[9]		94	49
Water-soluble urethane polymer[10]		96	75

[1] commercially available as Surfonic N-95
[2] commercially available as Lignosol XD
[3] commercially available as Alco SMA 1000
[4] commercially available as Tamol 731
[5] commercially available as Acrysol RM 1020
[6] commercially available as Acrysol RM 825
[7] commercially available as DSX 1514
[8] commercially available as DSX 1550
[9] commercially available as UCAR SCT 200
[10] commercially available as UCAR SCT 275

These results indicate that the associative water-soluble urethane polymers used in the present invention were more effective for inhibiting deposition than the known deposition inhibitors. These results further indicate that these polymers are effective at controlling deposition on the metal surfaces of papermaking systems.

Further studies of the testing described in respect of Table I were conducted using water-soluble urethane polymers synthesized using a wide variety of reactive isocyanates, water-soluble dios, branching agents, and terminating groups. These polymers constitute polyethylene oxide/polyethylene glycol polymers with urethane linkages. They are synthesized utilizing isocyanate compounds such as, for example, hexamethylene, diisocyanate, toluene diisocyanate, isophorone diisocyanate, and other dihydroxyl reactive

materials. These polymers are also synthesized utilizing water-soluble diol compounds and can be selected from polyethylene glycol compounds with molecular weights from about 400 to about 1450 and ethylene oxide/propylene oxide block copolymers. The isocyanates included hexamethylene diisocyanate, toluene diisocyanate, isophorone diisocyanate and other dihydroxyl reactive materials. The water-soluble diols included PEG (Polyethylene Glycol) 400, PEG 600, PEG 1000, PEG 1450, Pluronic L-35 and Pluronic 10R5. (Pluronic is a Trade Mark). The branching agents included glycerol and pentaerythritol. The terminating groups (monohydroxy compounds) included 2-ethyl hexanol, nonyl phenol, nonyl phenol ethoxylates with 40 and 70 moles E0, and secondary alcohol ethoxylates with 30 moles E0.
These testing results appear in Table VII.

TABLE VII

Urethane Polymer Components				Percent Control of Deposition	
Diol	Isocyanate	Branching Agent	Termination Agent	50 ppm	10 ppm
PEG 400	HMDI	---------	2-EH	63	5
PEG 400	HMDI	Glycerol	2-EH	91	21
PEG 600	TDI	----	2-EH	82	0
Pluronic L-35	TDI	----	2-EH	91	24
PEG 1000	HMDI	----	2-EH	89	23
PEG 1000	HMDI	----	N PH	--	9
PEG 1000	HMDI	Penta	2-EH	--	23
Pluronic 10R5	HMDI	----	2-EH	--	54
PEG 1450	ISOPH	----	NP-70	89	25
PEG 1450	ISOPH	----	NP-40	88	12
PEG 1450	ISOPH	----	NP-70	92	21
PEG 1450	ISOPH	----	15-S-30	97	62
PEG 1450	HMDI	----	15-S-30	96	64
PEG 1450	ISOPH	----	NP-70	84	18
PEG 1450	ISOPH	----	15-S-30	93	76
--------	ISOPH	Glycerol	NP-40	92	12
--------	ISOPH	Glycerol	15-S-30	94	19
PEG 1450	ISOPH	Glycerol	15-S-30	78	12

PEG (MW) = polyethylene Glycol
Pluronic L-35 = EO/PO/EO Block Copolymer
Pluronic 10R5 = PO/EO/PO Block Copolymer
HMDI = Hexamethylene diisocyanate
TDI = Toluene Diisocyanate
ISOPH = Isophorone Diisocyanate
PENTA = Pentaerythritol
2-EH = 2-Ethyl Hexanol
N-pH = Nonyl Phenol
NP-70 = Nonyl Phenol with 70 moles EO
NP-40 = Nonyl Phenol with 40 moles EO
15-S-30 = Secondary Alcohol with 30 moles EO

These results indicate that water-soluble urethane polymers used in the present invention having a widely varying character with respect to branching, end groups, and character of the backbone (diols and isocyanates used) can be highly effective for controlling pitch deposition.

In order to establish the efficacy of the materials used in the present invention as deposition control agents, on plastic surfaces and specifically for adhesive contaminants of the sort found in recycled fiber, a laboratory test was devised utilizing adhesive-backed tapes as stickie coupons. The stickie coupon can be fabricated from any type of adhesive tape that will not disintegrate when placed in water. For the study, tapes made from a styrenebutadiene rubber and vinylic esters were used. Both of these potential organic contaminants are known to cause problems "stickies" in secondary fiber utilization. A second coupon was fabricated from polyester film such as the product marketed as MYLAR by the DuPont Chemical Company. This material was chosen because papermachine forming fabrics are frequently made of polyester which is susceptible to considerable problem caused by stickies.

500 mL of solutions in 600 mL beakers containing various deposit control agents are placed in a water bath heated to 50°C. The tape and the polyester film coupons are placed in the test solution so the adhesive side of the coupon faces away from the polyester film coupon. After 1 hour of immersion, the adhesive side of the stickie coupon is placed in contact with the polyester coupon and pressed to 1000 pound force.

The average peel strength of the bond formed between the tape coupon and the polyester coupon was measured with an Instron tensile tester. The peel strength of the bond formed between the stickie tape coupon and the polyester coupon was interpreted as a measure of the tendency for an organic contaminant to attach to components of a paper-machine and cause runnability or product quality problems. More specifically, this indicates the tendency of a stickies deposit to form on a plastic surface.

The results of this testing appear in Table VIII.

TABLE VIII
% Detackification

Treatment Agent	Dosage (ppm)						
	0.2	0.5	1.0	2.0	5.0	10.0	25.0
1. Octylphenoxy Poly-(ethyleneoxy) ethanol			2.8	9.4	18.7	47.3	93.7
2. Nonylphenolethoxylate	-	-	4.7	29.1	64.2	86.3	100
3. Dodecylphenoxy Poly (ethyleneoxy) ethanol	-	-	31.2	56.0	94.7	100	100
4. Block Copolymer of Ethyleneoxide/propylene oxide	-	-	5.0	27.1	60.0	80.4	83.7
5. Sodium Salt of Condensed Naphthalene Sulfonic Acid	-	-	0	0	0	0	1.4
6. Water Soluble Urethane Polymer	67.9	80.9	89.4	100	100	-	-
7. Water Soluble Urethane Polymer	71.1	89.2	100	100	100	-	-
8. Water Soluble Urethane Polymer	69.0	80.9	93.9	100	100	-	-
9. Water Soluble Urethane Polymer	85.3	95.9	100	100	100	-	-

[1] is commercially available as Triton X-114
[2] is commercially available as Surfonic N-95
[3] is commercially available as Igepal RC-520
[4] is commercially available as Pluronic F-108
[5] is commercially available as Tamol SN
[6] is commercially available as Acrysol RM 825
[7] is commercially available as Acrysol QR-708
[8] is commercially available as DSX 1514
[9] is commercially available as DSX 1550

(Triton is a Trade Mark)

The results shown in Table VIII further support the efficacy of the present invention (examples 6-9 of Table VIII) for deposit control on plastic surfaces. They showed better efficacy relative to prior art deposit control agents (examples 1-5 of Table VIII). This demonstrates the effectiveness of nonionic polymers used in the present invention for stickies deposition control.

Further studies of the testing described in Table VIII were conducted using commercially available water-soluble anionic polymers. These test results appear in Table IX.

TABLE IX
% Detackification

Treatment Agent	Dosage (ppm) 0.5	1.0	2.0	5.0	10.0	50.0	100.0
1. Hydrolysed diisobutylene maleic anhydride copolymer	-	0	-	2.7	8.2	0	3.5
2. Hydrophobically associative anionic polymer	63.1	98.6	98.2	97.8	-	-	-
3. Hydrophobically associative anionic polymer	12.7	97.6	98.5	98.7	-	-	-
4. Hydrophobically associative anionic polymer	80.0	97.9	98.0	98.9	-	-	-
5. Hydrophobically associative anionic polymer	96.4	97.6	97.4	98.7			

[1] commercially available as Tamol 731
[2] commercially available as Acrysol® TT615
[3] commercially available as Acrysol® ICS 1
[4] commercially available as Alcogum SL-70
[5] commercially available as Alcogum SL-78

These results indicate that water-soluble anionic associative polymers used in the present invention can be effective for controlling organic contaminant deposition (examples 2-5 of Table IX). They further indicate the efficacy of these anionic polymers at controlling stickies deposition. These results further illustrate how surprisingly more effective this invention is than prior art use of anionic dispersant deposition control agents (example 1 of table IX).

Papermaking consists of various processes which can be affected by sudden changes in pH, temperature, dilution (i.e., concentration), shear force, etc. Severe changes in these parameters can cause system shock which adversely impact paper production. Deposit control agents that can strongly adsorb onto the organic contaminant surface and resist the desorbing effects of dilution are highly desirable. Not only will deposition control be improved, but also the required dosage will be reduced, while negative side effects, such as forming and wet-end interferences, will be reduced or eliminated. The procedure outlined in Table VIII was modified to examine the effect of dilution on deposition control. Dilution was accomplished by immersing the adhesive tape and MYLAR in distilled water for 30 minutes after the initial immersion. This can be repeated as many times as desired. The results of the testing are tabulated in Table X.

TABLE X

Sample	Concen. (ppm)	No Dilution	1st Dilution	2nd Dilution	3rd Dilution	4th Dilution
1	50	100	5	0	0	0
2	50	100	8	2	0	0
3	50	100	34	16	5	0
4	50	88	86	81	62	40
5	10	100	95	95	94	95
6	10	100	100	100	94	95
7	10	100	94	93	89	89
8	10	100	95	95	95	96

Sample 1 = octylphenoxy poly(ethyleneoxy)ethanol
Sample 2 = nonylphenol ethoxylate
Sample 3 = dodecylphenoxypoly(ethyleneoxy) ethanol
Sample 4 = block copolymers of ethylene oxide and propylene oxide
Sample 5 = water soluble associative polymer available as Acrysol® RM-825
Sample 6 = water soluble associative polymer available as QR-708
Sample 7 = water soluble associative polymer available as DSX-1514
Sample 8 = water soluble associative polymer available as DSX-1550

As shown in Table X, the associative polymers used in the present invention (samples 5-8 of Table X) in this test were very effective after the fourth dilution. They showed better performance relative to prior art deposit control agents (samples 1-4 of Table X). This demonstrates a strong adsorbing power and good resistance to the desorbing effects of dilution.

Claims

1. A method for inhibiting the deposition of organic contaminants from pulp in pulp and papermaking systems which comprises treating the pulp and papermaking systems with a hydrophobically modified associative polymer.

2. A method for inhibiting the deposition of organic contaminants from secondary fiber during repulping which comprises treating the secondary fiber with a hydrophobically modified associative polymer.

3. A method according to claim 1 or 2, wherein the hydrophobically modified associative polymer is a hydrophobically modified nonionic associative polymer.

4. A method according to claim 3, wherein the hydrophobically modified nonionic associative polymer is a hydrophobically modified hydroxyethyl cellulose associative polymer.

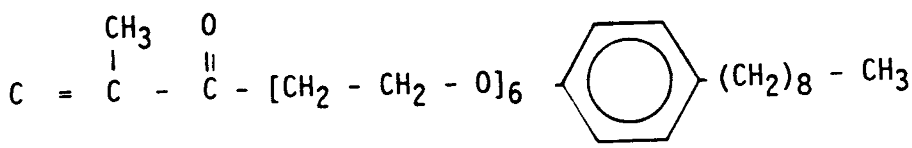
5. A method according to claim 3, wherein the hydrophobically modified nonionic associative polymer is a hydrophobically substituted acrylamide copolymer.

6. A method according to claim 5, wherein the hydrophobically substituted acrylamide copolymer has a structure including one selected from:-

$$C = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - O - (CH_2 - CH_2 - O)_{24} - C_{22}H_{45}$$

$$C = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - O - (CH_2 - CH_2 - O)_{10} - O - (CH_2)_8 - CH_3$$

$$C = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - [O - C - \underset{\underset{\displaystyle CH_3}{|}}{C}]_{4,5} - [O - C - \underset{\underset{\displaystyle CH_3}{|}}{C}]_{3,6} OH$$



7. A method according to claim 3, wherein the hydrophobically modified nonionic associative polymer is a hydrophobically substituted polyethylene oxide polymer.

8. A method according to claim 7, wherein the hydrophobically substituted polyethylene oxide polymer has hydrophobic groups which are combined to the polyethylene oxide polymer by ester linkages.

9. A method according to claim 8, wherein the hydrophobically substituted polyethylene oxide polymer is a polyethylene oxide dioleate ester.

10. A method according to claim 7, wherein the hydrophobically substituted polyethylene oxide polymer is an associative water-soluble polyethylene oxide polymer with urethane linkages.

11. A method according to claim 10, wherein the associative water-soluble polyethylene oxide polymer with urethane linkages is synthesized from isocyanate compounds or water-soluble diol compounds.

12. A method according to claim 11, wherein isocyanate compounds are selected from hexamethylene diisocyanate, toluene diisocyanate, isophorone diisocyanate, and other dihydroxyl reactive compounds, or the water-soluble diols are selected from polyethylene glycol compounds, and ethylene oxide/propylene oxide block copolymers.

13. A method according to claim 12, wherein the polyethylene glycol compounds have the molecular weight from about 400 to about 1450.

14. A method according to any of claims 10 to 13, wherein the associative water-soluble polyethylene oxide polymer further comprises synthesis utilizing a branching agent.

15. A method according to claim 14, wherein the branching agent is selected from glycerol and pentaerythritol.

16. A method according to any of claims 10 to 15, wherein the associative water-soluble polyethylene oxide polymer with urethane linkages has a molecular weight from about 10,000 to about 2,000,000.

17. The method according to claim 1 or 2, wherein the hydrophobically modified associative polymer is hydrophobically modified nonionic associative polymer derived from an ethylenically unsaturated acis, an ethylenically unsaturated monomer or an unsatruated acid monomer.

18. A method according to any of claims 1 to 17, wherein the hydrophobically modified associative polymer is delivered to the pulp and papermaking system or to the secondary fiber in a carrier solvent.

19. A method according to claim 18, wherein the carrier solvent is water.

20. A method according to any of claims 1 to 17, wherein the hydrophobically modified associative polymer is delivered to the pulp and papermaking system or to the secondary fiber as a powder or a slurry.

21. A method according to any of claims 1 to 20, wherein the hydrophobically modified associative polymer is added to the pulp and papermaking system or to the secondary fiber by spraying.

22. A method according to claim 21, wherein the hydrophobically modified associative polymer is sprayed onto the paper machine wire, paper machine felt, paper machine press roll or other surfaces prone to deposition.

23. A method according to any of claims 1 to 21, wherein the hydrophobically modified associative polymer is added to the pulp and papermaking system or to the secondary fiber with the furnish.

24. A method according to any of claims 1 to 23, wherein the deposition of organic contaminants occurs on the metal surfaces of the pulp and papermaking systems or of the repulping systems.

25. A method according to any of claims 1 to 23, wherein the depositions of organic contaminants occurs on the plastic surfaces of the pulp and papermaking systems or of the repulping systems.

26. A method according to any of claims 1 and 3 to 25, wherein the hydrophobically modified associative polymer is added to the papermaking systems with other papermaking treatments.

27. A method according to any of claims 1 and 3 to 26, wherein the organic contaminant is selected from one or more of a pitch deposit and a stickies deposit.

28. A method according to any of claims 1 and 3 to 27, wherein the polymer is added to the paper machine stock or added directly to the contamination prone surface.

29. A method according to claim 28, wherein the surface is selected from paper machine wire and paper machine wet felt.

30. A method according to any of claims 1 and 3 to 29, wherein the pulp and papermaking system is experiencing the effects of dilution.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 3007

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A,D	US-A-3 992 249 (FARLEY) ---		D21H21/02 D21C9/08
A	US-A-4 861 429 (BARNETT ET AL.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D21H D21C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 AUGUST 1993	SONGY Odile

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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