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(71) **Applicant:** BUCKMAN LABORATORIES INTERNATIONAL, INC. [US/US]; 1256 North Mclean Boulevard, Memphis, TN 38108-0305 (US).

(72) **Inventors:** BAN, Weiping; C/o Buckman Laboratories International, Inc., 1256 North Mclean Boulevard, Memphis, TN 38108-0305 (US). THOMAS, George, S.; C/o Buckman Laboratories International, Inc., 1256 North Mclean Boulevard, Memphis, TN 38108-0305 (US).

(74) **Agent:** KILYK, Luke, A.; Kilyk & Bowersox, P.L.L.C., 400 Holiday Court, Suite 102, Warrenton, VA 20186 (US).

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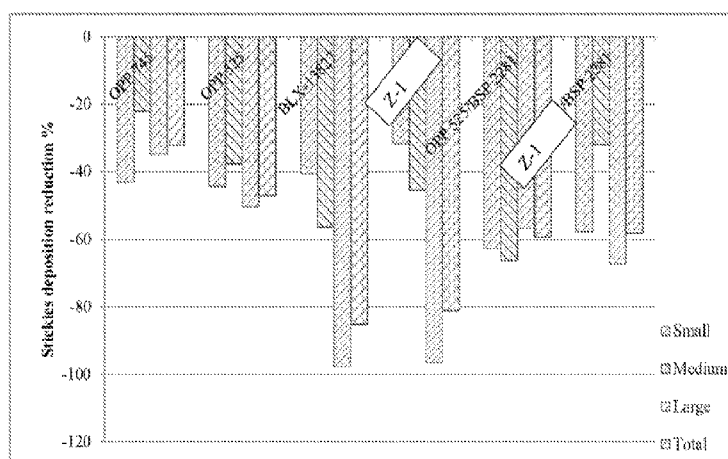


Fig 1.

(57) **Abstract:** Methods to control organic contaminants in fibers are described. One method involves contacting the fibers with a) at least one zeolite and optionally b) detackifier, or an ester hydrolyzing enzyme, or both, for a sufficient time and in a sufficient amount to control the organic contaminants present in the fibers. This method is effective to reduce stickies in paper mill furnish formed with recycled fibers. A method for pitch control in paper mill furnish formed with virgin fibers is also provided. Resulting paper products formed from the processed fibers are also described as well as methods to make them.

METHODS TO CONTROL ORGANIC CONTAMINANTS IN FIBERS USING ZEOLITES

BACKGROUND OF THE INVENTION

[0001] This application claims the benefit under 35 U.S.C. §119(e) of prior U.S. Provisional Patent Application No. 61/867,644, filed August 20, 2013, which is incorporated in its entirety by reference herein.

[0002] The present invention relates to papermaking processes and more particularly relates to controlling the organic contaminants present in certain types of fibers used to make paper or similar types of fiber containing products.

[0003] Organic contaminants are present in paper pulp that tends to deposit on processing surfaces and equipment, causing maintenance problems and production inefficiencies. Organic contaminants of significant concern in this regard include "stickies" and pitch, with the former generally associated with recycled pulp sources while the latter with virgin pulp supplies.

[0004] Conventional recycling of old paper products such as old newsprint, old corrugated containers, and mixed office waste is an important aspect of paper mills today due to environmental demands that many paper containing products have a portion of recycled fibers contained within the paper product. Thus, paper mills are in a situation where the recycling of paper products is a necessity. However, the recycling of the paper products generally requires additional processing steps in order to lead to fibers which can be useable in paper products.

[0005] Conventional recycling of old newspapers to obtain fibers comparable to the type of fibers used to originally make the newsprint is known in the art as "de-inking," and typically involves pulping, washing, usually with surfactants, screening, solubilizing insoluble contaminants usually by strong caustic treatments, washing, and bleaching of the fibers to

counteract the yellowing effects of caustic treatments.

[0006] Generally, the first step in conventional recycling is to separate the paper into individual fibers with water to form a pulp slurry followed by removing ink and contaminants from the fibers by a combination of various process steps, such as screening, centrifugal cleaning, washing, flotation, and the like. The screening and centrifugal cleaning step removes large contaminants, such as paperclips, staples, plastics, and the like. The primary purpose of washing and flotation steps is to solubilize and/or suspend contaminants in the water and to remove the contaminants from the water. Surfactants and caustic agents are added to facilitate the solubilization and separation of contaminants from the fibers. Once caustic agents are used, some yellowing of the fibers can occur which may result in a need to bleach the fibers. The fibers are blended with, typically, virgin fibers and then used in the paper making process for which the fiber properties are suitable. Recent developments in waste paper de-inking make use of enzymes to aid in the detachment and removal of inks from the fibers. These processes describe the use of particular types of enzymes to facilitate ink removal without the negative effects of caustic treatment on brightness along with the use of flotation to remove the agglomerated ink particles.

[0007] In the past, chemical additives such as caustic agents have been added to remove organic contaminants, known as "stickies." Stickies are generally adhesives, glues, hot melts, coatings, coating binders, ink residues, de-inking chemicals, wood resins, rosin, and unpulped wet strength resins that typically are present with the fiber to be recycled. These organic contaminants typically must be removed in substantial quantities so that they do not affect the subsequent processing steps. There is always a desire in the paper making industry to develop new methods to remove such organic contaminants in more effective and environmentally

friendly ways.

[0008] "Stickies" can be generally described as tacky, hydrophobic, pliable organic materials found in recycled paper systems. Stickies have a broad range of melting points and different degrees of tackiness dependent upon the composition of the stickies. Temperature, pH, concentration, size, and composition can affect the tackiness of stickies. The variable nature of stickies is one of the reasons that controlling or removing them can be difficult and unpredictable. Also, the use of recycled fiber has been increasing and is expected to continue growing, making stickies a more significant problem.

[0009] Recycled paper fibers contain many components that when repulped in recycle fiber plants become stickies. Recycled furnishes may have as many as a dozen different types of stickies, each having its own characteristics. Sources of stickies may include any of the following: adhesives, hot melts, coating binders, ink residues, deinking chemicals, wood resins, rosin, pitch, and wet strength resins. The actual tacky deposits found on paper machines may be a combination of several of these organic contaminants as well as inorganic particles such as talc, clay, or calcium carbonate.

[0010] Stickies deposit on machine surfaces, fabrics, wires, felts, rolls and dryers lead to problems such as wet end breaks, pressroom breaks, dryer section breaks, holes, sheet defects, and high dirt counts. These deposits and associated problems lead to a significant amount of downtime yearly. The cost of stickies has been estimated at over 500 million dollars annually in the U.S., when considering the cost of downtime, chemical costs, production losses, rejected materials, and customer complaints.

[0011] There are various methods of removing stickies, mechanical and chemical. Mechanical methods include screening, cleaning, washing, floating, and dispersing, with each

method designed to remove a different size contaminant. Screening typically removes larger or macro stickies (>0.004 inch or 100 microns). Forward and reverse cleaners can be used. Based on density differences using centrifugal force, forward cleaners remove contaminants heavier than water and reverse cleaners remove particles lighter than water. This method removes more macro stickies than micro stickies. Floating removes intermediate size stickies (50-300 microns), which are troublesome, because they are small enough to be accepted by screening and cleaning but too large to be removed by washing. In dispersing, the stock is thickened, passed through a device at high temperature, pressure, and shear, which breaks organic contaminants, including stickies, into smaller pieces.

[0012] Various chemical methods can be used. For instance, in pacification, additives like talc, clay, nonionic organic polymers, and other inorganic particles are used to render the stickies less tacky. In dispersion, dispersants, surfactants, and solvents are used to make stickies smaller. Other methods use certain enzymatic treatments for pitch/stickies removal.

[0013] In fixation, the stickies are attached to the paper sheet by using a cationic water soluble polymer, which adds charge to the stickies. In disperse and fix, a dispersant is added first to reduce the size of the stickies and then a cationic polymer is used to fix the stickies onto the sheet. With passivation, the use of dispersants, solvents, and low molecular weight cationic polymers makes the paper machine less susceptible to stickies.

[0014] In the past, the favored approach to remove stickies was to keep the stickies large in the stock prep area, so that the mechanical cleaning equipment can remove as many "stickies" as possible. Then, all remaining stickies should be dispersed either mechanically or chemically and fixed to the fiber, so that they can be sent out with the sheet.

[0015] Once as many stickies as possible are removed mechanically, the rest have in the

past been dispersed mechanically, chemically, or by using a combination of the two. Once dispersed, polymer addition to stabilize these particles in their smallest state has been used, so that the particles will be retained on the sheet.

[0016] Measuring and controlling stickies in a recycled paper manufacturing process has always been a challenge. Variations in recycled paper quality and the trend to increase the amount of waste paper incorporated into each ton of pulp produced are each contributing factors that make this challenge even more difficult to address. (Pulp and Paper Fact Book, 2000). These variations make predicting the amount of stickies that are entering a mill's system troublesome. Once these stickies are in the system, the larger contaminants, or macrostickies, are often removed mechanically. However, additional stresses on the screens and cleaner banks such as high furnish consistency, improper in-screen dilution, improper reject rates, and differential pressure control problems will facilitate the acceptance of formed macrostickies (Gallagher, 1997). Macrostickies are defined as stickies that are retained on a 0.10 mm screen plate (Heise, 1998). These contaminants which come from adhesives, coatings, binders, and other materials are incorporated into the furnish during the pulping process, and will deposit on forming fabrics, press felts, dryer fabrics, press section rolls, Uhle boxes, and calendar stacks (Douek, 1997). These materials remain tacky in the paper making process, leading to the "stickies" label (Doshi, 1997). Once the materials are incorporated into the furnish, they are difficult to remove, since they are deformable in nature and are often close to the specific gravity of water. These physical characteristics present a different screening and cleaning challenge as these contaminants slip through screens and cleaners (Scholz, 1997) that are designed to allow water and fiber to be accepted. The consequence of this fact is the acceptance of macrostickies into the post screening process.

[0017] Even if the cleaning and screening systems do perform properly and do remove most of the macrostickies, the remaining microstickies may cause problems. The agglomeration of microstickies, stickies not retained on a 0.1 mm screen, can lead to the formation of macrostickies which will then deposit onto the machine and onto fabric surfaces (Doshi, 1997). Microstickies are not problematic as long as they remain small. However, they often agglomerate in the paper making process leading to macrostickies formation

[0018] The cost of stickies deposition is a significant one. One source estimates the cost of the stickies problem to the industry in terms of machine downtime to be over \$500 million annually for major recycled paper grades (Friberg, 1997). Once macrostickies are present in the furnish after the screening and cleaning systems, mechanical means of removing stickies have been exhausted. Preventing the agglomeration of microstickies is also an issue in addition to the microstickies problem. In order to address each of these problems, a chemical control solution is often required.

[0019] U.S. Patent No. 6,471,826 B2 describes the use of a composition comprising at least one esterase or lipase to reduce the concentration of stickies in pulp and paper mill systems. U.S. Patent No. 4,698,133 describes the use of water-soluble cellulose derivatives to inhibit the deposition of stickies on paper mill process equipment.

[0020] Pitch deposition on process equipment in paper making systems using virgin pulp supplies also can result in operational problems and production inefficiencies. Pitch is a naturally occurring matter in wood pulp. Pitch can deposit, for instance, on screens used in the process line to reduce their throughput, and/or on process control devices, rendering them inoperable, such as instrument probes. Deposition of the pitch 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. Pitch deposits may also break off resulting in spots and defects in the final paper product which decrease the quality of the paper. 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. U.S. Patent No. 5,074,961 describes the use of methylcellulose derivatives to inhibit the deposition of pitch on paper mill process equipment.

SUMMARY OF THE INVENTION

[0021] A feature of the present invention is to provide methods to control organic contaminants present in fibers that contain organic contaminants. A further feature of the present invention is to provide a method to process recycled and/or virgin pulp fibers in a manner such that the organic contaminants present in the recycled and/or virgin pulp fibers are controlled.

[0022] Additional features and advantages of the present invention will be set forth in part in the description which follows, and in part will be apparent from the description, or may be learned by practice of the present invention. The objectives and other advantages of the present invention will be realized and obtained by means of the elements and combinations particularly pointed out in the written description and appended claims.

[0023] To achieve these and other advantages and in accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention relates to a method to control organic contaminants present in fibers containing organic contaminants. The method involves contacting fibers with a) at least one zeolite and optionally b) at least one detackifier or at least one type of ester hydrolyzing enzyme, or both, for a sufficient time and

in a sufficient amount to control organic contaminants present in the fibers.

[0024] In the present invention, a method can involve contacting recycled fibers with a) at least one zeolite and optionally b) at least one detackifier, or at least one ester hydrolyzing enzyme, or both, for a sufficient time and in a sufficient amount to control stickies present in the recycled fibers. As an example, the combination of a) at least one zeolite and optionally b) at least one detackifier, such as a water-soluble cellulose derivative, and/or an ester hydrolyzing enzyme, such as lipase, yields synergistic reductions in sticky amounts from recycled fibers, such as compared to the use of clay alone, detackifier alone, and/or clay with same detackifier.

[0025] Amongst other benefits and advantages, the combination of a) at least one zeolite and optionally b) at least one detackifier, or at least one ester hydrolyzing enzyme, or both, gives improved control of stickies. The method is effective to reduce stickies in paper mill furnishes, e.g., which utilize old newspapers, old corrugated containers, and mixed office waste, and the like.

[0026] Also, in the present invention, a method can involve contacting virgin fibers with a) at least one zeolite and optionally b) at least one detackifier, such as at least one type of water-soluble cellulose derivative, or at least one type of ester hydrolyzing enzyme, or both, and optionally at least one type of lipoxygenase, for a sufficient time and in a sufficient amount to control the pitch present in the virgin fibers.

[0027] The present invention further relates to controlling organic contaminants from fibers in papermaking systems. The method includes treating water in a clarifier, or, immediately prior to the clarifier in a papermaking system, with a) at least one zeolite and optionally b) at least one detackifier, or at least one ester hydrolyzing enzyme, or both, for a sufficient time and in sufficient amounts to control the organic contaminants present in the water.

[0028] The benefits of the methods of the present invention include, for example, reduced downtime, increased machine runnability, reduced furnish cost, improved converting efficiency, increased brightness, improved effective residual ink concentration, improved sheet quality, and/or reduced solvent usage. The methods can be cost effective as compared to conventional stickies or pitch control programs.

[0029] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are only intended to provide a further explanation of the present invention, as claimed. The accompanying drawings, which are incorporated in and constitute a part of this application, illustrate several features of the present invention and together with the written description, serve to explain the principles of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] Fig. 1 is a bar graph depicting the reduction in organic contaminants, based on ppm organic contaminants for a variety of formulations including a control and comparative formulations, and formulations of the present invention.

[0031] Fig. 2 is a bar graph depicting the ppm of stickies for large stickies, medium stickies, and small stickies for several formulations and a control using Pulmac testing.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0032] The present invention relates to methods to control organic contaminants present in fiber containing organic contaminants by treating fibers with a) at least one zeolite and optionally b) at least one detackifier, or at least one ester hydrolyzing enzyme, or both, and

optionally also lipoxxygenase. The fiber can be cellulose fibers, such as recycled fibers, virgin wood cellulose fibers, or combinations thereof.

[0033] Processing of Recycled Fibers. A method is provided for contacting fibers, e.g., recycled fibers, with a combination of a) at least one zeolite, and optionally b) at least one detackifier or at least one ester hydrolyzing enzyme(s), or both, which has been found to provide improved stickies control. Synergistic levels of stickies reduction may be achieved where at least one zeolite, and at least one detackifier, and/or at least one ester hydrolyzing enzyme, such as a lipase, are used. The method reduces the amount of stickies in paper mill furnish and/or detackifies the remaining stickies so the deposition of the remaining stickies is inhibited.

[0034] The recycled fibers may be obtained from a variety of paper products or fiber containing products, such as paperboard, newsprint, sanitary and other paper products. These products may comprise, for example, old corrugated containers (OCC), old newsprint (ONP), mixed office waste (MOW), or combinations thereof. These types of paper containing products typically contain large amounts of organic contaminants which are present in the paper products. When these types of paper products are recycled, these organic contaminants are present along with the fibers formed during the pulping stage of a paper making process. These organic contaminants, if not substantially removed, can severely interfere with subsequent stages in the paper making process by affecting the quality of the resulting sheets of paper formed and/or effecting the machinery used to form the paper. Accordingly, the removal of such organic contaminants is important to the paper making process when such organic contaminants are present in fibers.

[0035] For purposes of the present invention, examples of organic contaminants include

what is known in the industry as "stickies" and include, but are not limited to, synthetic polymers resulting from adhesives and the like, glues, hot melts, coatings, coating binders, ink residues, de-inking chemicals, wood resins, rosin, pressure sensitive binders and unpulped wet strength resins. These type of materials are typically found in paper containing products, such as newsprint, corrugated container, and/or mixed office waste. These organic contaminants can have polymers present, such as styrene butadiene rubber, vinyl acrylates, polyisoprene, polybutadiene, natural rubber, ethyl vinyl acetates, polyvinyl acetates, ethylvinyl alcohols, polyvinyl alcohols, styrene acrylates, and/or other synthetic type polymers.

[0036] In the present invention, these organic contaminants can be controlled by contacting the fiber containing the organic contaminants with at least one zeolite and optionally at least one detackifier and/or at least one ester hydrolyzing enzyme for a sufficient time and in a sufficient amount to control the organic contaminants present in the fiber. The at least one zeolite, and optionally at least one detackifier and/or at least one enzyme can disperse or convert the organic contaminants to organic species that do not affect the paper making process. For instance, the polyvinyl acetates can be dispersed and/or converted to polyvinyl alcohols, which do not affect the paper making process. This manner that the compositions achieve control of organic contaminants is quite different from collecting contaminants by flotation.

[0037] **Zeolite.** In the methods of the present invention, one or more types of at least one zeolite are used. The at least one zeolite is in particle or particulate form. The at least one zeolite can be present in a liquid suspension. The liquid suspension can contain the at least one zeolite alone or it can contain one or more of the other treatment chemicals used in the methods of the present invention, such as the detackifier(s) and/or enzyme(s), and can have other

optional components. The at least one zeolite can have any particle size distribution. For instance, the at least one zeolite can have an average or median particle size of 100 microns or less, such as 80 microns or less, 60 microns or less, 50 microns or less, 40 microns or less, 30 microns or less, 25 microns or less, 20 microns or less, 15 microns or less, 10 microns or less, 7 microns or less, or 5 microns or less. For instance, the at least one zeolite can have a median particle size of from about 5 microns to about 50 microns, from about 5 microns to about 45 microns, from about 5 microns to about 40 microns, from about 5 microns to about 20 microns, and the like. The at least one zeolite is commercially available from a variety of sources including, but not limited to, ZEO Inc. More specific brands are Z-Ultra and the like. The at least one zeolite can be used in a natural or synthetic particulate form milled to the desired particle size, or it can be calcined, or otherwise treated. The at least one zeolite can be used in the present invention in a treatment amount of from about 0.1 kg to about 20 kg per metric ton of dried pulp fiber.

[0038] The zeolite can be natural or synthetic (for instance from a sol-gel process). The zeolite can be considered a molecular sieve. The classical definition of a zeolite is a crystalline, porous aluminosilicate. However, zeolite can include some relatively recent discoveries of materials virtually identical to the classical zeolite, but having oxide structures with elements other than silicon and aluminum. Zeolites thus include porous oxide structures that have well-defined pore structures with a degree of crystallinity.

[0039] As an option, the zeolite, such as natural zeolite, can be modified through crosslinking, and/or grafting, and/or surface coating, and/or impregnation and/or adsorption, or any combinations thereof. For example, a zeolite, can be treated with a cationic surfactant, which can optionally improve its adsorption properties.

[0040] The zeolite can be considered a particular microporous, aluminosilicate mineral. Examples include, but are not limited to, analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, natrolite, and stilbite. Further examples include, Zeolite A and faujasite. Other examples include, using the zeolite structural group (Nickel-Strunz classification):

- 09.GA. - Zeolites with T_5O_{10} units – the fibrous zeolites
 - Natrolite framework (NAT): gonnardite, natrolite, mesolite, paranatrolite, scolecite, tetranatrolite
 - Edingtonite framework (EDI): edingtonite, kalborsite
 - Thomsonite framework (THO): thomsonite-series
- 09.GB. - Chains of single connected 4-membered rings
 - Analcime framework (ANA): analcime, leucite, pollucite, wairakite
 - Laumontite (LAU), yugawaralite (YUG), goosecreekite (GOO), montesommaite (MON)
- 09.GC. - Chains of doubly-connected 4-membered rings
 - Phillipsite framework (PHI): harmotome, phillipsite-series
 - Gismondine framework (GIS): amicitte, gismondine, garronite, gobbinsite
 - Boggsite (BOG), merlinoite (MER), mazzite-series (MAZ), paulingite-series (PAU), perlialite (linde type L framework, zeolite L, LTL)
- 09.GD. - Chains of 6-membered rings – tabular zeolites
 - Chabazite framework (CHA): chabazite-series, herschelite, willhendersonite and SSZ-13
 - Faujasite framework (FAU): faujasite-series, linde type X (zeolite X, X zeolites), linde type Y (zeolite Y, Y zeolites)

- Mordenite framework (MOR): maricopaite, mordenite
- Offretite–wenkite subgroup 09.GD.25 (Nickel–Strunz, 10 ed): offretite (OFF), wenkite (WEN)
- Bellbergite (TMA-E, Aiello and Barrer; framework type EAB), bikitaite (BIK), erionite-series (ERI), ferrierite (FER), gmelinite (GME), levyne-series (LEV), dachiardite-series (DAC), epistilbite (EPI)
- 09.GE. - Chains of $T_{10}O_{20}$ tetrahedra
 - Heulandite framework (HEU): clinoptilolite, heulandite-series
 - Stilbite framework (STI): barrerite, stellerite, stilbite-series
 - Brewsterite framework (BRE): brewsterite-series
- Others
 - Cowlesite, pentasil (also known as ZSM-5, framework type MFI), tschernichite (beta polymorph A, disordered framework, BEA), linde type A framework (zeolite A, LTA).

[0041] There are no limitations to the molecular structure, surface area, surface charge density, and/or cation exchange capacity (CEC) of the zeolite to be used in the present invention. Some useful parameters include, but are not limited to:

Specific gravity: 0.7 to 1, such as about 0.85 s.g.

Appearance: Grey to green

Melting point: >1200 C

Particle size: avg size of 1 to 10 microns, such as 2 to 7 microns, or 3 to 6 microns, such as about 4.5 micron average.

CEC: 2.0~5.6

Void volume (pore space): 15-50%.

Any one, two, three, four, or more of these parameters in any combination can be present in the zeolite used in the present invention, as an option.

[0042] For purposes of the present invention, the at least one zeolite is not a clay or kaolinite or bentonite, montmorillonite, wollastonite, or talc or similar types of minerals.

[0043] **Detackifiers.** The methods of the present invention can use optionally at least one detackifier, which can be or include one or more derivatives of cellulose as one of the co-ingredients. The materials that are effective for this application are water soluble derivatives of cellulose. Lower and higher alkyl (e.g., C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, or C₁₀ and higher) ether derivatives of cellulose and/or alkyl linkages other than ethers can be used so long as they are water soluble. Water-soluble derivatives of cellulose are commercially available, e.g., as methyl cellulose, hydroxyethyl methyl cellulose, hydroxypropyl methyl cellulose, cetyl hydroxyethylcellulose and hydroxybutyl methyl cellulose. Non-substituted or substituted forms of these celluloses may be used.

[0044] Methyl ether derivatives (or alkyl ether derivatives) of cellulose can be made by reacting cellulose with the appropriate reagent in the presence of caustic soda. Methyl cellulose can be made using methyl chloride, hydroxyethyl methyl cellulose can be made using ethylene oxide and methyl chloride, hydroxypropyl methyl cellulose can be made using propylene oxide and methyl chloride and hydroxybutyl methyl cellulose can be made using butylene oxide and methyl chloride. Among these three types, there are variations in molecular weight ranging from about 10,000 to about 246,000 which corresponds to a degree of polymerization of from about 53 to about 1,280 anhydroglucoside units. The number of substitution groups on the anhydroglucoside units of the cellulose polymer can affect the solubility properties, but all

levels of substitution that are water soluble are part of this invention. The cellulose derivatives may contain methyl ether substitution, or hydroxyl ethyl ether substitution, or hydroxyl propyl methyl ether substitution or hydroxyl butyl ether substitution or cetyl hydroxyethyl or other groups may be added that do not affect the efficacy of the cellulose derivative for this purpose. Commercially available water-soluble celluloses that can be used in compositions of the present invention include Methocel products, such as Methocel F50, which is hydroxypropylmethylcellulose, Methocel F15AV, which is methyl cellulose, and Cellosize QP-1500-H hydroxyethyl cellulose, which is hydroxyethyl methyl cellulose, all available from Dow Chemical Co., Midland MI and Natrosol 330 Plus which is cetyl hydroxyethylcellulose, available from Ashland Inc., Wilmington, DE, and is described in U.S. Published Patent Application No. 2004/0231816. The water-soluble cellulose derivatives as encompassed by the present invention are generally nonionic in nature and the alkyl group of the alkyl ether moiety can be unsubstituted or substituted. Preferred amounts of the water-soluble cellulose derivatives are from about 0.002 lbs. to about 2 lbs. per ton of dry fiber treated, and more preferably from about 0.004 to about 1 lb. per ton of dry fiber treated, and most preferably from about 0.01 to about 0.4 lbs. per ton of dry fiber treated. Alkyl ether celluloses can be made in the same manner. More than one type of methyl (or alkyl) ether cellulose derivative can be used, such as two, three, or four types. The methyl (or alkyl) ether cellulose derivatives can be pre-combined beforehand or added separately or introduced in any order in forming the composition and/or introducing the composition (or components thereof) in the papermaking process. In the alternative or in addition, other detackifiers can be used. The amount of the detackifiers that can be used in the present invention would be the same amounts as set forth above for the water-soluble cellulose derivatives.

[0045] Ester Hydrolyzing Enzymes. In the methods of the present invention, at least one ester hydrolyzing enzyme can be optionally used, and can be used at a high concentration of ester hydrolyzing enzymes. Esterase, lipase, and cutinase are non-limiting examples of ester hydrolyzing enzymes that may be used singly or in any combinations thereof in the methods of the present invention. Esterases are enzymes that cleave triglycerides (viz., fats or lipids) or esters into carboxylic acids (fatty acids) and mono- and di-glycerides. Lipases are hydrolytic enzymes that act upon the ester bond of neutral lipids and phospholipids. Lipases hydrolyze triglycerides, or fats, to glycerol and fatty acids. Cutinases are hydrolytic enzymes that degrade cutin, the cuticular polymer of higher plants, which is a polyester composed of hydroxy and epoxy fatty acids. Fatty acids of cutin are usually *n*-C₁₆ and *n*-C₁₈ and contain one to three hydroxyl groups.

[0046] Lipase can be derived or isolated from pancreatic sources (e.g., pancreatic lipase) or from various fungi and/or bacteria, and/or other microorganisms. Examples include, but are not limited to, triacylglycerol acylhydrolase and triacyl glycerol lipase. Also, any lipase or esterase capable of hydrolyzing triglycerides to glycerol and fatty acids can be used. Commercially available products containing esterase or lipase can be used. For instance, Optimize®, Optimize Plus, Buzyme® 2528, Buzyme® 2515 and Buzyme® 2517 can be used which are products available from Buckman Laboratories International, Inc. These products can combine the lipase or esterase enzyme with solvents and surfactant for stability. Products containing such enzymes as Resinase HT, Resinase A2X, Novocor ADL, Pancreatic Lipase 250, Lipase G-1000, Greasex 50L, and Greasex 100L products can be used in the methods of the present invention. Such products are available from such commercial sources as Genencor, Novo Nordisk, and Novozymes, Inc. Esterase sources are available as products designated as

NS51032 or NS51060, which are commercially made by Novozymes Inc. The esterase or lipase described in U.S. Patent Nos. 5,507,952 and 5,356,800 and in U.S. Patent Application Publication Nos. 2003/0051836 and 2004/0226672 can be used in the present invention and these patents are incorporated in their entirety along with any other patent publications mentioned in this application, by reference herein. A lipolytic enzyme can be used in the present invention. The ester hydrolyzing enzymes can generally be used in any form, such as liquid form or solid form. Preferably, the amount of ester hydrolyzing enzyme used in the methods of the present invention are a sufficient amount to control the organic contaminants present in the fiber. The enzyme used in the present invention can have any amount of activity. For instance, the activity can be at least 5.0 LU/Gm/min, such as at least 10 LU/Gm/min, or at least 15 LU/Gm/min, for instance from 15.0 to 30.0 LU/Gm/min defined as lipase units per gram per minute (LU/gm/min). The lipases used in the present invention can have this activity, for instance, the triacylglycerol lipase and other lipases. For instance, Resinase A2X lipase from Novozyme has activity of about 15.0 to 20.0 LU/Gm/min defined as lipase units per gram per minute (LU/gm/min). As another example, a cutinase can be evaluated based on its vinyl acetate esterase activity for de-esterifying polyvinylacetate. Therefore, the cutinase can be assayed as its ability to liberate or produce millimoles of acetic acid per gram per minute. This activity can be equal to at least 10 mmol/gm/min, or at least 15 mmol/gm/min, or at least 20 mmol/gm/min of liberated acetic acid. For example, Optimize activity can be equal to 21.0 to 23.0 mmol/gm/min of liberated acetic acid. Preferred (total) amounts of ester hydrolyzing enzyme are from about 0.005 lbs. to about 4 lbs. per ton of dry fiber treated, and more preferably from about 0.01 to about 2 lbs. per ton of dry fiber treated, and most preferably from about 0.05 to about 0.5 lbs. per ton of dry fiber treated. More than one enzyme can be used,

such as two, three, four, or more. The one or multiple enzymes can be added as part of a pre-mixture, added separately, or added in any order in the methods of the present invention.

[0047] The ester hydrolyzing enzyme may be stabilized esterase and/or lipase compositions using the formulations described in U.S. Patent Nos. 5,356,800 and 5,780,283, incorporated in their entirety by reference herein. At least one polymer can be added together with the composition containing the water-soluble cellulose derivative and ester hydrolyzing enzyme at about the same time. Alternatively or additionally, one or more polymers can be added before or after the introduction of the enzyme(s). For instance, the polymer(s) can be added one hour or less before or after introduction of the enzyme(s) to the fiber. The polymer can be a water soluble polymer, such as a cationic water soluble polymer. Examples of such polymers include, but are not limited to, epichlorohydrin/dimethylamine polymers (EPI-DMA) and cross-linked solutions thereof, polydiallyl dimethyl ammonium chloride (DADMAC), DADMAC/acrylamide copolymers, ionene polymers, and the like. Examples of ionene polymers include, but are not limited to, those set forth in U.S. Patent Nos. 5,681,862 and 5,575,993, both incorporated in their entireties by reference herein. Further, the polymers set forth in U.S. Patent No. 5,256,252 can be used as well and this patent is incorporated in its entirety by reference herein. The polymer if used in the methods of the present invention can be used in any amount and preferably in dosage ranges of from about 0.1 to about 15 pounds per ton of dry fiber treated, more preferably from about 0.25 pounds to about 10 pounds per ton of dry fiber treated, and more preferably from about 1 pound to about 5 pounds per ton of dry fiber treated.

[0048] For purposes of the present invention, controlling organic contaminants present in fibers having organic contaminants is understood as one or more of the following: reducing the

size of contaminant particles, reducing the number or amount of measurable particles present, and/or reducing the tackiness of the organic contaminants. Preferably, when controlling organic contaminants using the methods of the present invention, all of these reductions occur. Preferably, the reduction of the size of contaminant particles is by at least about 5%, more preferably by from about 10% to about 75% as compared to when no treatment is used, or compared to clay used alone or clay with detackifier. Similarly, the reduction in the number or amount of organic contaminants present in the fiber is reduced by at least about 5%, and more preferably by from about 10% to about 75% when compared to fibers which have not been treated at all. Also, the reduction of tackiness of the organic contaminants is preferably reduced by at least about 5%, and more preferably by from about 10% to about 75% when compared to fibers which have not been treated at all.

[0049] As an option, conventional paper treatment chemicals or ingredients such as, but not limited to, one or more surfactants, solvents, suspension aids, fillers, chelants, preservatives, buffers, water, and/or stabilizers, and the like can be used. These additional ingredients can be present in conventional amounts.

[0050] In the methods of this present invention, the at least one zeolite and optionally at least one detackifier and/or at least one ester hydrolyzing enzyme can be introduced at any point in the processing of the fiber containing organic contaminants as part of a paper making process. Generally, the at least one zeolite and optionally at least one detackifier and/or ester hydrolyzing enzyme is introduced or brought into contact with the fiber containing the organic contaminants in any fashion. For instance, if the fiber containing the organic contaminants originates from products to be recycled, the at least one zeolite and optionally at least one detackifier and/or ester hydrolyzing enzyme can be introduced prior to the pulping stage,

during the pulping stage, and/or after the pulping stage. If introduced prior to the pulping stage, typically, they will be introduced such as by spraying or other means, onto the paper containing product which are going to be introduced into the pulper. Also, or alternatively, they can be present or introduced into the pulper during the pulping stage which can be by any conventional pulping technique such as mechanical pulping, full chemical pulping, or combinations thereof. They can be introduced during the stock preparation stage of the paper making process. The contact time with the fibers containing organic contaminants can be maximized. The at least one zeolite and at least one detackifier, and/or at least one ester hydrolyzing enzyme generally are used in a manner providing sufficient reaction time, minimal concentration of oxidizers, and a suitable pH and temperature ranges. There is no need to denature the enzymes. The optimum pH for enzyme activity may vary for different enzymes. In general, the at least one zeolite with or without at least one detackifier and/or ester hydrolyzing enzyme is generally effective over a pH range of about 6.8 to about 9.5, and a temperature range of between about 4 and about 65°C. Preferably, the contact time should be sufficient to control the organic contaminants present with the fibers such that organic contaminants are substantially controlled. Preferably, the contact time is from about 1 min. to about 8 hours, more preferably from about 10 min. to about 4 hours, and most preferably from about 20 min. to about 2 hours.

[0051] The at least one zeolite and optionally at least one detackifier and/or ester hydrolyzing enzyme can be introduced or brought into contact with the fiber containing organic contaminants at the thick stock storage stage and/or prior to the flotation de-inking stage. The at least one zeolite with or without at least one detackifier and/or ester hydrolyzing enzyme can be introduced after the flotation stage in the paper making process. The at least one zeolite with or

without at least one detackifier and/or ester hydrolyzing enzyme can be introduced after the flotation stage and before the paper machine headbox. In some paper making processes, there is no flotation step, such as with the recycling of OCC. Thus, the at least one zeolite and at least one detackifier and/or ester hydrolyzing enzyme can be added at or after the pulper and/or at or before the headbox, and/or can be added in the paper machine white water.

[0052] The manner in which the at least one zeolite and optionally at least one detackifier and/or ester hydrolyzing enzyme are introduced or brought into contact with the fiber containing the organic contaminants can be in any fashion, such as by injection points, pouring into the area to be treated, and/or using repulpable bags of dry or liquid enzymes. The introduction of the treatment chemicals can be immediate, slow release, timed release, intermittent, and/or continuous.

[0053] In the methods of the present invention, the treatment chemicals can be introduced at multiple points or at just one point of the paper making operation. In addition, more than one type of at least one zeolite, detackifier (if used), and/or ester hydrolyzing enzyme (if used) can be used, mixtures can be used, or any other variations as long as at least one at least one zeolite with or without at least one detackifier and/or ester hydrolyzing enzyme are introduced in some fashion in order to control organic contaminants present in fibers having organic contaminants. The treatment chemicals (or mixture) can be pre-formed prior to introducing to the papermaking operation, or the individual components can be added separately or can be pre-combined and added to a feed line, or can be added in any order or combination. The addition can be by batch, continuously, semi-continuously, or any combination thereof. The treatment chemicals may or may not be diluted with fresh water or process water.

[0054] In the methods of the present invention, the controlling of the organic contaminants

present in fibers having organic contaminants can be incorporated into any paper making operation, including tissue paper. Typically, the remaining aspects of the paper making operation as is known to those skilled in the art can be used in order to form paper products. Thus, the conventional additive materials used with paper making pulps during stock preparation can be used as well in the present invention. Continuous or non-continuous paper making machines can then convert aqueous suspensions of fibers and other ingredients into dry sheets of paper using such conventionally known operations which involve Fourdrinier machines, twin wire machines or cylinder machines or other paper making devices. Subsequent treatments of the sheets of paper to achieve the desired characteristics such as machine calendering and/or coating of the papersheets and the like can also be used in the present invention. Regarding the tissue paper, a method of manufacturing crepe paper can be used, including soft, absorbent tissue paper webs, and particularly to modes of creping of such webs to attain adequate softness and adhesive characteristics while minimizing operational difficulties. According to the present invention, a thin paper web is formed from a slurry of water and treated fiber using a conventional web forming technique. The web is then dewatered and preferably is at least partially dried. The web is then conveyed, for example, carried on a fabric, to a large preferably steam-heated rotary drum dryer, referred to herein and elsewhere as a Yankee dryer. The web commonly enters the dryer at a circumferential dryer position that is preferably at least about halfway around, and more preferably at least about 75% around, the cylindrical dryer with respect to the zone of web de-contact from the drum. The de-contact zone is equipped with a creping blade against which the web abuts so as to be pushed backwardly upon itself and attain the well-known tissue crepe paper structure. Other tissue drying systems such as Through Air Drying (TAD) may be used. Creping systems, methods,

and adhesives are described in the following U.S. Patent Nos. which are incorporated herein in their entireties by reference: 3,640,841; 4,304,625; 4,440,898; 4,788,243; 4,994,146; 5,025,046; 5,187,219; 5,326,434; 5,246,544; 5,370,773; 5,487,813; 5,490,903; 5,633,309; 5,660,687; 5,846,380; 4,300,981; 4,063,995; 4,501,640; 4,528,316; 4,886,579; 5,179,150; 5,234,547; 5,374,334; 5,382,323; 5,468,796; 5,902,862; 5,942,085; 5,944,954; 3,879,257; 4,684,439; 3,926,716; 4,883,564; and 5,437,766.

[0055] Although not desiring to be bound by theory, it is believed that the combined at least one zeolite with or without detackifier and/or ester hydrolyzing enzyme used in methods of the present invention reduce and/or inhibit stickies problems by at least one or more of the following mechanisms or effects, including aiding in separating them from the wastepaper; removing them from the fiber and the de-inking process; preventing agglomeration of residual stickies in the pulp; preventing deposition on the fabric, felt and dryer; and/or retaining microscopic stickies in the sheet at a size too small to cause manufacturing or converting problems.

[0056] Processing of Virgin Fibers. A method is also provided for contacting fibers, particularly virgin fibers, with at least one zeolite optionally with at least one detackifier and/or one or more ester hydrolyzing enzymes, and optionally lipoxxygenase, which has been found to improve control of pitch. Ester hydrolyzing enzymes, such as lipase, can be used to reduce the concentration of fatty esters in pulp and paper mill systems. Fatty esters are quite prone to deposit in pulp and paper mills and it is expected that by reducing the fatty ester content, that reduced deposition will be seen. However, this has not proven to be the case. Fatty acids which are the reaction product of the action of the enzyme with fatty esters often deposit, which will cause the mill to have operational and quality problems. The combination of at least one

zeolite with or without at least one detackifier and/or ester hydrolyzing, and optionally lipoxigenase enzymes, can unexpectedly provide improved pitch control. These combinations reduce the amount of pitch in the paper mill furnish and also detackifies the remaining pitch so the deposition of the remaining pitch is inhibited. The utility of the treatment process is not believed dependent upon whether the pulp is derived from softwood, hardwood or blends thereof. For purposes of this application, virgin fiber refers to cellulosic fiber other than recycled fiber, and can include bleached or unbleached Kraft, sulfite pulp or other chemical pulps, and groundwood (GW) or other mechanical pulps such as, for example, thermomechanical pulp (TMP), or chemical-mechanical pulps, for example, chemical thermomechanical pulp (CTMP), Alkaline Peroxide Mechanical Pulp (APMP).

[0057] Lipoxigenases. Lipoxigenases are iron-containing enzymes that catalyze the dioxygenation of polyunsaturated fatty acids to form fatty acid hydroperoxides. Lipoxigenases are found in plants and animals. Preferred amounts of the lipoxigenase are from about 0.004 lbs. to about 4 lbs. per ton of dry fiber treated, and more preferably from about 0.01 to about 2 lbs. per ton of dry fiber treated, and most preferably from about 0.05 to about 0.5 lbs. per ton of dry fiber treated. The water-soluble cellulose and ester hydrolyzing enzymes may be used in this composition that further includes lipoxigenase in respective range amounts that are similar to those described above for the composition preferably used in treating recycled fiber. More than one lipoxigenase can be used, such as two, three, or four or more. The lipoxigenase can be pre-combined with the water-soluble cellulose derivative and/or the ester hydrolyzing enzyme, or can be added separately to a feed stream or to the pulp stream or elsewhere.

[0058] The at least one zeolite optionally with at least one detackifier and/or ester hydrolyzing enzymes, and optional lipoxigenase enzymes, are effective in controlling pitch

deposition in paper making systems, such as Kraft, acid sulfite, groundwood and other mechanical pulp paper making systems. For example, pitch deposition in the brown stock washer, screen room and decker systems in Kraft pulp making processes can be controlled. The term "paper making system" is meant to include all pulp processes. Generally, it is thought that these polymers can be utilized to prevent pitch deposition on all wetted surfaces from the pulp mill to the reel of the paper machine under a variety of pH's and conditions. More specifically, the present invention effectively decreases the deposition of metal soap and other resinous pitch components not only on metal surfaces, but also on plastic and synthetic surfaces such as machine wires, felts, foils, uhle boxes and headbox components. The treatment chemicals of the present invention can be added to the pulp at any stage of the paper making system. The treatment chemicals can be added in dry particulate form or as an aqueous suspension. The effective amount of these compositions to be added depends on the severity of the pitch problem which often depends on a number of variables, including the pH of the system.

[0059] For purposes of the present invention, controlling pitch present in fibers having pitch is understood as one or more of the following: reducing the size of pitch particles, reducing the number or amount of measurable particles present, and/or reducing the tackiness of the pitch. Preferably, when controlling pitch using the methods of the present invention, all of these reductions occur. Preferably, the reduction of the size of pitch particles is by at least about 5%, more preferably by from about 10% to about 75% as compared to when no treatment chemicals are present. Similarly, the reduction in the number or amount of pitch present in the fiber is reduced by at least about 5%, and more preferably by from about 10% to about 75% (e.g., by weight) when compared to no treatment chemicals are present. Also, the reduction of tackiness of the pitch is preferably reduced by at least about 5%, and more preferably by from

about 10% to about 75% when compared to fibers which have not been treated with treatment of the present invention.

[0060] The present invention is also effective in treating water at a clarifier stage in a papermaking process. More particularly, the control of organic contaminants from fibers in a papermaking system involves treating the water in a clarifier or clarifier stage or immediately prior to the clarifier or clarifier stage. The treatment can be the same as above, namely, with at least one zeolite with or without at least one detackifier and/or at least one ester hydrolyzing enzyme, for a sufficient time and in a sufficient amount to control the organic contaminants present in the water. The examples of treatment amount of each treatment chemical, and all of the other options with regard to the previous methods apply equally here.

[0061] For purposes of the present invention, the term "treatment chemicals" includes a) at least one zeolite and optionally b) at least one detackifier and/or at least one ester hydrolyzing enzyme, and, optionally, c) any other conventional component.

[0062] The present invention further relates to paper or paperboard or tissue paper or creped paper made from the processes of the present invention. The present invention further relates to a wet web paper or tissue (e.g., the paper or tissue existing prior to the dryer stage), which comprises pressed pulp fibers, at least at least one zeolite. The amounts present in the pressed pulp fibers can be as follows for each component:

At least one zeolite: 0.2 to 40#/ton (dry fiber)

Detackifier: 0 to 5#/ton (dry fiber)

Ester hydrolyzing enzyme: 0 to 3 #/ton (dry fiber).

[0063] As an option, the enzyme, if used, can be introduced once pulp is present in the pulper. The enzyme, if used, can be introduced prior to the at least one zeolite and/or at least

one detackifier (if used). As an option, all of the treatment chemicals combined can be added at a single time as part of a liquid suspension. Optionally, each treatment chemical can be introduced separately as a dry component or as a liquid suspension. The treatment chemicals can be fed batchwise, semi-batchwise, semi-continuously, or continuously.

[0064] The present invention includes the following aspects/embodiments/features in any order and/or in any combination:

1. The present invention relates to a method for controlling deposition of organic contaminants from fibers in paper making systems, comprising contacting said fibers with a) at least one zeolite and optionally b) at least one detackifier, or at least one ester hydrolyzing enzyme or both, for a sufficient time and in a sufficient amount to control the organic contaminants present in the fibers.
2. The method of any preceding or following embodiment/feature/aspect, wherein b) is present and is said at least one ester hydrolyzing enzyme.
3. The method of any preceding or following embodiment/feature/aspect, wherein b) is present and is at least one detackifier.
4. The method of any preceding or following embodiment/feature/aspect, wherein b) is present and is at least one ester hydrolyzing enzyme and at least one detackifier.
5. The method of any preceding or following embodiment/feature/aspect, wherein said at least one zeolite and detackifier are present together as a liquid suspension and added to a pulp slurry containing said fibers.
6. The method of any preceding or following embodiment/feature/aspect, wherein said at least one zeolite, detackifier, and ester hydrolyzing enzyme are present together in a liquid suspension and added to a pulp slurry containing said fibers.

7. The method of any preceding or following embodiment/feature/aspect, wherein said at least one zeolite and ester hydrolyzing enzyme are present together in a liquid suspension and added to a pulp slurry containing said fibers.
8. The method of any preceding or following embodiment/feature/aspect, wherein said at least one zeolite and optionally b) are added to a pulp slurry containing said fibers prior to a forming stage.
9. The method of any preceding or following embodiment/feature/aspect, wherein said organic contaminants comprise synthetic polymers from adhesives, glues, hot-melts, coatings, coating binders, de-inking chemicals, ink residues, wood resins, rosin, contact adhesive binders, unpulped wet strength resins, pitch, or combinations thereof.
10. The method of any preceding or following embodiment/feature/aspect, wherein said fibers comprise recycled fibers.
11. The method of any preceding or following embodiment/feature/aspect, wherein said organic contaminants comprise stickies.
12. The method of any preceding or following embodiment/feature/aspect, wherein the ester hydrolyzing enzyme comprises lipase.
13. The method of any preceding or following embodiment/feature/aspect, wherein at least one detackifier comprises at least one water-soluble cellulose derivative.
14. The method of any preceding or following embodiment/feature/aspect, wherein said water-soluble cellulose derivative comprises methyl cellulose, hydroxyl methyl cellulose, hydroxyethyl methyl cellulose, hydropropyl methyl cellulose, cetyl hydroxyethylcellulose or hydroxybutyl methyl cellulose, singly or in any combination thereof.

15. The method of any preceding or following embodiment/feature/aspect, wherein said fibers containing organic contaminants comprise fibers from old corrugated containers, old newsprint or old newspapers, mixed office waste, or any combinations thereof.
16. The method of any preceding or following embodiment/feature/aspect, wherein the organic contaminants are at least controlled by reducing the amount of organic contaminants present in the fiber.
17. The method of any preceding or following embodiment/feature/aspect, wherein the organic contaminants are at least controlled by reducing the size of the organic contaminants present in the fibers.
18. The method of any preceding or following embodiment/feature/aspect, wherein the organic contaminants are at least controlled by reducing the tackiness of the organic contaminants present in the fibers.
19. The method of any preceding or following embodiment/feature/aspect, wherein said at least one zeolite, and optionally at least one detackifier and/or at least one ester hydrolyzing enzyme are introduced prior to a pulping stage.
20. The method of any preceding or following embodiment/feature/aspect, wherein said at least one zeolite, and optionally at least one detackifier and/or at least one ester hydrolyzing enzyme are introduced during a pulping stage.
21. The method of any preceding or following embodiment/feature/aspect, wherein said at least one zeolite, and optionally at least one detackifier and/or at least one ester hydrolyzing enzyme are introduced during or right before a stock preparation stage.

22. The method of any preceding or following embodiment/feature/aspect, wherein said at least one zeolite, and optionally at least one detackifier and/or at least one ester hydrolyzing enzyme are introduced after a flotation or a de-inking stage.
23. The method of any preceding or following embodiment/feature/aspect, wherein said at least one zeolite and optionally b) are in contact with the fibers for a time of from about 1 minute to about 8 hours.
24. The method of any preceding or following embodiment/feature/aspect, further comprising forming said fibers into paper or paperboard products.
25. The method of any preceding or following embodiment/feature/aspect, wherein said at least one zeolite and optionally b) are introduced prior to the paper machine headbox.
26. The method of any preceding or following embodiment/feature/aspect, wherein said at least one zeolite and optionally b) are introduced in the paper machine white water.
27. The method of any preceding or following embodiment/feature/aspect, wherein said fibers comprise virgin fibers, said organic contaminants comprise pitch and/or wood extractives.
28. The method of any preceding or following embodiment/feature/aspect, wherein said liquid suspension further comprises lipoxxygenase.
29. The method of any preceding or following embodiment/feature/aspect, wherein the ester hydrolyzing enzyme comprises esterase, lipase, or cutinase, singly or in any combination thereof.
30. The method of any preceding or following embodiment/feature/aspect, wherein said water-soluble cellulose derivative is a methyl ether cellulose derivative.

31. A method for controlling organic contaminants from fibers in paper making systems, comprising treating water in a clarifier or immediately prior to said clarifier with a) at least one zeolite and optionally b) at least one detackifier, or at least one ester hydrolyzing enzyme, or both, for a sufficient time and in a sufficient amount to control the organic contaminants present in said water.

32. The method of any preceding or following embodiment/feature/aspect, wherein b) is present and is said at least one ester hydrolyzing enzyme.

33. The method of any preceding or following embodiment/feature/aspect, wherein b) is present and is said at least one detackifier, and wherein said at least one zeolite and detackifier are present together as a liquid suspension and added to said water.

34. The method of any preceding or following embodiment/feature/aspect, wherein b) is present and is said at least one detackifier and at least one ester hydrolyzing enzyme, and wherein said at least one zeolite, detackifier and ester hydrolyzing enzyme are present together in a liquid suspension and added to said water.

35. The method of any preceding or following embodiment/feature/aspect, wherein said water further comprises pulp fibers.

36. The method of any preceding or following embodiment/feature/aspect, wherein said a) and b) are added separately to said fibers.

[0065] The present invention can include any combination of these various features or embodiments above and/or below as set forth in sentences and/or paragraphs. Any combination of disclosed features herein is considered part of the present invention and no limitation is intended with respect to combinable features.

[0066] The present invention will be further clarified by the following examples, which are

intended to be purely exemplary of the present invention, in which parts are proportions by weight unless otherwise specified.

EXAMPLES

[0067] In the following tested samples, ethylene-vinyl acetate (EVA) as a model of tack stickies was used as it is one of major components in recycle pulp contaminates. In the Examples, several variations of the present invention were tested and compared with comparative treatments or controls.

Example 1

[0068] **Testing procedure for detackification testing:** Take 500 ml of tap water in 1000 ml beaker and place beaker on a hot plate with temperature control and magnetic agitation. Use Ethylene-vinyl acetate (EVA) as a model of tack stickies. Warm up water to designed temperature and add EVA into water at designed concentration. Start agitation at designed speed for certain period of time. Dilute the test samples and add in stickies solution under agitation, continue to agitate the mixture for designed time and remove samples from the hot plate. Place a black filter paper on a funnel filter. Carefully filter the mixture of solution through the filter paper. Remove the filter paper and dry it on a hot plate. Use a coated paper to cover on the filter paper and place them in a heated carver press at 220° F and 5000 psi for 2 minutes. Remove coated paper from the filter paper and use the filter paper for testing.

[0069] **Stickies counting:** Use a scanner to scan the filter paper and use Use Speck 2 software to analyze the results. The results can be displayed as particle numbers (Count) and areas (PPM).

[0070] **Testing conditions:**

Temperature: 120° F

pH: 7.0

Contaminant Mix Time: 20 minutes

Product Mix Time: 40 minutes.

[0071] **Results:** Tables 1 and 2 summarize the comparisons of various inorganic particles and methylcellulose in detackification performance by using EVA as tacky compound. Zeolite shows better performance on reduction of tacky material deposition than the other mineral particles.

[0072] To better understand the results, the goal in effective organic contaminant control (stickies control) is to reduce or avoid “large” contaminants (stickies) which can foul up a pulp/paper line, and a further goal is to have “small” contaminants (stickies) if any contaminants are going to be present, as these are far less likely to foul up a pulp/paper line. In looking at the Tables, better results are where the count for “large” contaminants is low/lower and the count for “medium” contaminants is low/lower, and the count for “small” contaminants is high/higher. As can be seen in Table 1, B, C, and D, were all effective in raising the “small” count compared to the “Control”. But, C and D were effective in lowering the “large” count compared to the Control and C (Zeolite) was most effective in this ability even compared to D. This was also true for reducing the “medium” count.

[0073] In Table 2, where the amount of simulated stickies (EVA) was doubled compared to Table 1, and the dosage was also doubled, the effects of the present invention (Sample L) were even more apparent in reducing all counts and even the “small” count, which is surprising and impressive.

[0074] In all Tables (for sticky counting):

Small= 0.01 to 0.1 mm²

Medium= greater than 0.1 mm² to 1.0 mm²

Large= greater than 1.0 mm² to 2.0 mm² and higher.

[0075] Detackification testing:

Table 1.

Comparison of performance of mineral particles on detackification

| Group-1 | EVA, 50 ppm, 300 rpm, 20/40 min, Dosage 25 ppm | | | |
|-------------------|--|----------|-------------|--------------|
| | A (Control) | B (Talc) | C (Zeolite) | D (BLX13826) |
| Small (Count) | 253 | 5061 | 1335 | 4824 |
| PPM | 279 | 4772 | 1257 | 3888 |
| Medium (Count) | 121 | 589 | 121 | 246 |
| PPM | 1258 | 5422 | 996 | 2078 |
| Large (Count) | 33 | 42 | 11 | 18 |
| PPM | 3850 | 3584 | 817 | 2319 |

Control = water with EVA without any additive.

Talc = suspended in water – for example a 50 ppm dosage would be made by adding 0.05 g talc/L water.

Zeolite = zeolite suspended in water – for example a 50 ppm dosage would be made by adding 0.05 g zeolite/L water. (avg. particle size of zeolite in all examples was about 4.5 microns).

BLX-13826 is a commercial product of Buckman Laboratories, Inc. (Memphis, TN) and is a Diatomaceous earth (DE)/Methycellulose formulation.

Table 2.

Comparison of performance of mineral particles on detackification

| Group-3 | EVA, 100 ppm, 350 rpm, 20/40 min, Dosage 50 ppm | | | |
|----------------|---|--------|----------|-------------|
| | I (Control) | J (DE) | K (Talc) | L (Zeolite) |
| Small (Count) | 353 | 724 | 523 | 198 |
| PPM | 402 | 1171 | 781 | 254 |
| Medium (Count) | 158 | 1207 | 375 | 102 |
| PPM | 1760 | 14961 | 3920 | 935 |
| Large (Count) | 39 | 170 | 73 | 2 |
| PPM | 3038 | 12815 | 6712 | 112 |

[0076] Table 3 and Fig 1 show performance comparison of zeolite and zeolite combination with dispersant or enzyme. The results indicate the combination of zeolite and enzyme further improve the efficiency of detackification.

[0077] Fig 1 also shows the comparison of a zeolite formulation with some existing commercial non-zeolite containing products in detackification efficiency. The zeolite formulation (Z-1) showed better performance than existing products at the same dosage condition.

[0078] As seen in Table 3, all of the zeolite formulations (M, N and O) were effective in reducing all contaminant counts (small, medium and large), again showing the effectiveness of the present invention.

Table 3.

Comparison of performance of mineral particles on detackification

| Group-4 EVA, 100 ppm, 350 rpm, 20/40 min, Dosage 50 ppm | | | | |
|---|------------------------------|-------------------------------|-------------|-------------|
| | M (Zeolite/ BSP248 90:10) | N (Zeolite/ NS51032 90:10) | O (Zeolite) | P (Control) |
| Small (Count) | 401 | 507 | 391 | 879 |
| PPM | 601 | 772 | 530 | 1074 |
| Medium (Count) | 370 | 324 | 273 | 652 |
| PPM | 3795 | 3077 | 2606 | 7553 |
| Large (Count) | 43 | 26 | 44 | 99 |
| PPM | 4218 | 2798 | 3676 | 11917 |

BSP 248= Busperse 248 product from Buckman Laboratories, Inc and is a pitch control product that contains a dispersant.

NS51032 is a lipase product from Novozyme.

Zeolite = zeolite suspended in water – for example a 50 ppm dosage would be made by adding 0.05 g zeolite/L water.

Control= water and ppm amount of EVA.

In Fig 1: (EVA concentration 100 ppm. Dosage lb/t: OPP745 50 ppm; OPP 525 25 ppm; BLX-13827 100 ppm; Z-1 50 ppm; OPP525/BSP 2281 and Z-1/BSP 2281:37.5 ppm). All dosages based on as-received.

OPP 745 = OPTIMYZE 745 product from Buckman Laboratories, Inc – a lipase/surfactant mixture.

OPP 525= OPTIMYZE 525 product from Buckman Laboratories, Inc – a stabilized lipase product.

BLX-13827= Diatomaceous earth with methylcellulose and lipase enzyme (commercial product of Buckman Laboratories, Inc).

Z-1= Zeolite 12%, Methocel 1%, NS51032 1.5%, Resinase HT 0.5%, Xanthan gum 0.4%, Propylene glycol 2.0%, Water 82.6%.

BSP 2281 = BUSPERSE 2281 product from Buckman Laboratories, Inc is a solvent/surfactant mixture.

Example 2

[0079] Pulmac testing (Using recycled pulp). Testing procedure for pulp stickies testing:

Pulmac Master Screen was used for stickies test for recycled pulp.

Testing conditions: OCC pulp obtained from paper mill.

After screening, use coated paper to cover on black filter paper and place them in a heated carver press at 220° F and 5000 psi for 3 minutes. Remove coated paper after heating press and use the same stickies counting method as mentioned above for stickies analysis.

[0080] Table 4 and Fig 2 show the comparison of zeolite formulation with some existing commercial non-zeolite containing products in stickies reduction in pulp by using Pulmac testing. Zeolite formulation (Z-1) provided better efficiency on stickies reduction.

[0081] As can be seen in Table 4 and Figure 4, the zeolite formulation (Z-1) had almost comparable reduction in "count" but more importantly was able to reduce the size of the stickies better than the enzymes alone or with Diatomaceous earth.

Table 4.

Performance comparison of some products on stickies control by using Pulmac testing.

| % Reduction of stickies | | | | |
|-------------------------|------------|------------|---------------|-----|
| | OPP 735 | OPP 742 | BLX- 13827 | Z-1 |
| Count | 69% | 65% | 58% | 57% |
| PPM | 81% | 85% | 81% | 87% |
| Size | 38% | 56% | 55% | 69% |

Note: All products used the same dosage level as received

BLX-13827 is DE/Methycellulose/Enzyme formulation and Z-1 is

Zeolite/Methycellulose/Enzyme formulation. OPP 735 and OPP 742 are

Buckman enzyme products.

[0082] The zeolite was Z-Ultra from ZEO Inc., and was used in the amount of 2.4 pounds per dry ton of fiber. The methycellulose detackifier was Methocel F50 from Dow Chemical Co., and used in the amount of 0.6 pound per dry ton of fiber. The enzyme(s) was NS51032 and Resinase HT from Novozyme used in the amount of 0.26 pound per dry ton of fiber.

[0083] In Example 2, a machine chest stock resulting from used hot melt glued, single wall corrugated containers was obtained from a mill and had approximately 3 to about 5% by weight consistency of fibers or solids. This stock was then diluted to a 1% by weight consistency the pH was adjusted to 7.4 and then heated to approximately 50 to 60°C. 1,000 milliliter samples of the dilute stock were then placed on a hot plate to maintain the 50 to 60°C temperature and the dilute stock was mixed at a constant rate of approximately 100-150 rpm. Then, one of the Treatments listed above was used, and the resulting different samples were mixed for 1 to 2 hours. The compositions tested are identified as above for purposes of this example.

[0084] The samples were then diluted to 10 liters by introducing water and then these samples were screened through a Pulmac Masterscreen using a 0.004 inch screen. The contaminants collected on the filter pad were dried in an oven. A clean piece of black filter paper and unused calcium carbonate coated paper with the calcium carbonate in contact with the collection pad was placed on top of the collection pad and the pieces were then placed on a Carver Press and pressed for 3 minutes at 220°F (105°C) at a pressure of 5,000 psi. The top filter and the calcium carbonate coated paper was then peeled off and the amount of

contaminants by counts and ppm were measured using an Optimax Flatbed Scanner. This same set-up was used to determine the “Counts” as ppms.

[0085] Applicants specifically incorporate the entire contents of all cited references in this disclosure. Further, when an amount, concentration, or other value or parameter is given as either a range, preferred range, or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

[0086] It will be apparent to those skilled in the art that various modifications and variations can be made to the embodiments of the present invention without departing from the spirit or scope of the present invention. Thus, it is intended that the present invention covers other modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

WHAT IS CLAIMED IS:

1. A method for controlling deposition of organic contaminants from fibers in paper making systems, comprising contacting said fibers with a) at least one zeolite and optionally b) at least one detackifier, or at least one ester hydrolyzing enzyme or both, for a sufficient time and in a sufficient amount to control the organic contaminants present in the fibers.
2. The method of claim 1, wherein b) is present and is said at least one ester hydrolyzing enzyme.
3. The method of claim 1, wherein b) is present and is at least one detackifier.
4. The method of claim 1, wherein b) is present and is at least one ester hydrolyzing enzyme and at least one detackifier.
5. The method of claim 3, wherein said at least one zeolite and detackifier are present together as a liquid suspension and added to a pulp slurry containing said fibers.
6. The method of claim 4, wherein said at least one zeolite, detackifier, and ester hydrolyzing enzyme are present together in a liquid suspension and added to a pulp slurry containing said fibers.

7. The method of claim 2, wherein said at least one zeolite and ester hydrolyzing enzyme are present together in a liquid suspension and added to a pulp slurry containing said fibers.
8. The method of claim 1, wherein said at least one zeolite and optionally b) are added to a pulp slurry containing said fibers prior to a forming stage.
9. The method of claim 1, wherein said organic contaminants comprise synthetic polymers from adhesives, glues, hot-melts, coatings, coating binders, de-inking chemicals, ink residues, wood resins, rosin, contact adhesive binders, unpulped wet strength resins, pitch, or combinations thereof.
10. The method of claim 1, wherein said fibers comprise recycled fibers.
11. The method of claim 1, wherein said organic contaminants comprise stickies.
12. The method of claim 1, wherein the ester hydrolyzing enzyme comprises lipase.
13. The method of claim 1, wherein at least one detackifier comprises at least one water-soluble cellulose derivative.
14. The method of claim 13, wherein said water-soluble cellulose derivative comprises methyl cellulose, hydroxyl methyl cellulose, hydroxyethyl methyl cellulose, hydropropyl

methyl cellulose, cetyl hydroxyethylcellulose or hydroxybutyl methyl cellulose, singly or in any combination thereof.

15. The method of claim 1, wherein said fibers containing organic contaminants comprise fibers from old corrugated containers, old newsprint or old newspapers, mixed office waste, or any combinations thereof.

16. The method of claim 1, wherein the organic contaminants are at least controlled by reducing the amount of organic contaminants present in the fiber.

17. The method of claim 1, wherein the organic contaminants are at least controlled by reducing the size of the organic contaminants present in the fibers.

18. The method of claim 1, wherein the organic contaminants are at least controlled by reducing the tackiness of the organic contaminants present in the fibers.

19. The method of claim 1, wherein said at least one zeolite, and optionally at least one detackifier and/or at least one ester hydrolyzing enzyme are introduced prior to a pulping stage.

20. The method of claim 1, wherein said at least one zeolite, and optionally at least one detackifier and/or at least one ester hydrolyzing enzyme are introduced during a pulping stage.

21. The method of claim 1, wherein said at least one zeolite, and optionally at least one detackifier and/or at least one ester hydrolyzing enzyme are introduced during or right before a stock preparation stage.
22. The method of claim 1, wherein said at least one zeolite, and optionally at least one detackifier and/or at least one ester hydrolyzing enzyme are introduced after a flotation or a de-inking stage.
23. The method of claim 1, wherein said at least one zeolite and optionally b) are in contact with the fibers for a time of from about 1 minute to about 8 hours.
24. The method of claim 1, further comprising forming said fibers into paper or paperboard products.
25. The method of claim 1, wherein said at least one zeolite and optionally b) are introduced prior to the paper machine headbox.
26. The method of claim 1, wherein said at least one zeolite and optionally b) are introduced in the paper machine white water.
27. The method of claim 1, wherein said fibers comprise virgin fibers, said organic contaminants comprise pitch and/or wood extractives

28. The method of claim 6, wherein said liquid suspension further comprises lipoxygenase.
29. The method of claim 1, wherein the ester hydrolyzing enzyme comprises esterase, lipase, or cutinase, singly or in any combination thereof.
30. The method of claim 1, wherein said water-soluble cellulose derivative is a methyl ether cellulose derivative.
31. A method for controlling organic contaminants from fibers in paper making systems, comprising treating water in a clarifier or immediately prior to said clarifier with a) at least one zeolite and optionally b) at least one detackifier, or at least one ester hydrolyzing enzyme, or both, for a sufficient time and in a sufficient amount to control the organic contaminants present in said water.
32. The method of claim 31, wherein b) is present and is said at least one ester hydrolyzing enzyme.
33. The method of claim 31, wherein b) is present and is said at least one detackifier, and wherein said at least one zeolite and detackifier are present together as a liquid suspension and added to said water.

34. The method of claim 31, wherein b) is present and is said at least one detackifier and at least one ester hydrolyzing enzyme, and wherein said at least one zeolite, detackifier and ester hydrolyzing enzyme are present together in a liquid suspension and added to said water.
35. The method of claim 31, wherein said water further comprises pulp fibers.
36. The method of claim 1, wherein said a) and b) are added separately to said fibers.

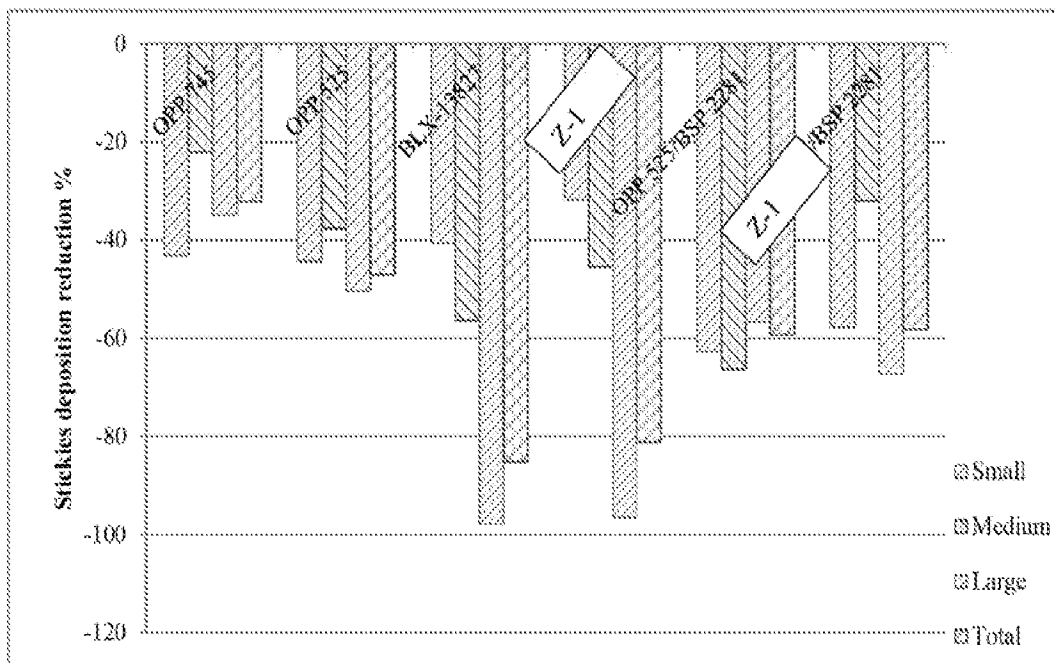


Fig 1.

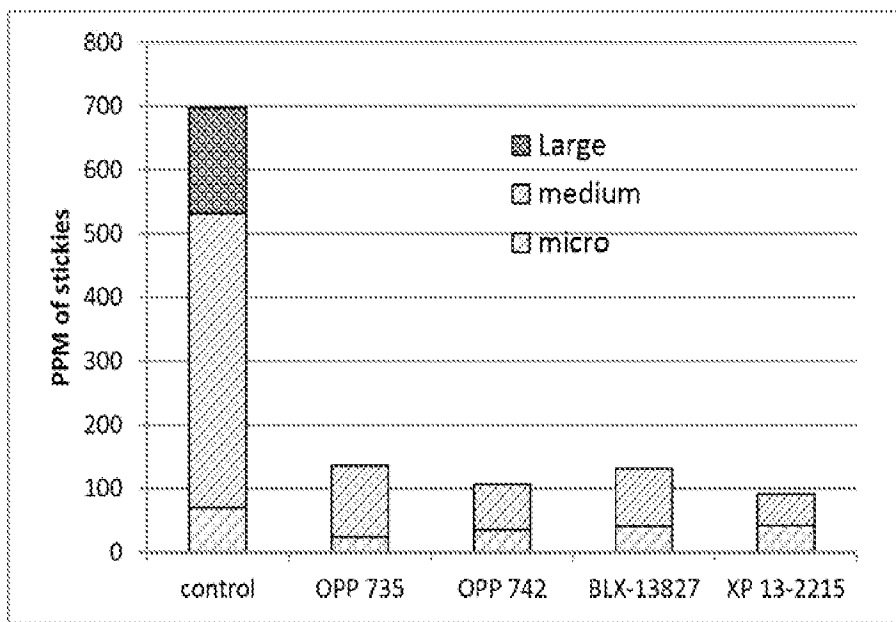


Fig 2.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/049516

A. CLASSIFICATION OF SUBJECT MATTER

INV. D21C9/08 D21H21/02 D21H17/68
ADD. D21C9/083

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)

D21C D21H

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)

EP0-Internal, WPI Data

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Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Karlsson, Lennart

INTERNATIONAL SEARCH REPORT

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