

US 20090020243A1

### (19) United States

# (12) Patent Application Publication Xu et al.

(10) Pub. No.: US 2009/0020243 A1

(43) **Pub. Date: Jan. 22, 2009** 

## (54) USE OF CYCLODEXTRINS FOR REDUCING DEPOSITS DURING PAPER PRODUCTION

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(21) Appl. No.: 12/212,382

(22) Filed: Sep. 17, 2008

#### Related U.S. Application Data

- (63) Continuation of application No. 11/282,520, filed on Nov. 19, 2005, now abandoned.
- (60) Provisional application No. 60/630,318, filed on Nov. 23, 2004.

#### **Publication Classification**

(51) **Int. Cl.** *D21C 5/02* (2006.01)

(52) U.S. Cl. ...... 162/5

(57) ABSTRACT

The present invention relates to a method for preventing or reducing deposits in pulp and paper making processes by including a cyclodextrin during or after pulp formation in an amount effective for preventing or reducing the deposits. Optionally the cyclodextrin comprising the deposit is subsequently separated from the pulp.

## USE OF CYCLODEXTRINS FOR REDUCING DEPOSITS DURING PAPER PRODUCTION

### CROSS REFERENCE TO RELATED APPLICATIONS

**[0001]** This application is a continuation of U.S. patent application Ser. No. 11/282,520 filed Nov. 19, 2005 which claims the benefit under 35 U.S.C. 119 of U.S. provisional application No. 60/630,318 filed Nov. 23, 2004, the contents of which are fully incorporated herein by reference.

#### FIELD OF THE INVENTION

[0002] The present invention relates to a method for reducing deposits during paper production.

#### BACKGROUND OF THE INVENTION

[0003] Wastepaper has long served as a source of raw fiber material for papermaking. It has been standard practice in the art to reclaim wastepaper to allow the reclaimed paper fibers to be used as part or all of the stock of subsequent production of a variety of paper and paperboard products. Today, greater utilization of reclaimed fibers has provided incentive for taking steps to upgrade the reclaimed products.

[0004] These steps include treatment to effectively remove ink from waste fibers in order to permit their use in the manufacture of e.g. newsprint and high quality papers. Removal of ink during the pulp formation process will prevent the ink from re-depositing on fibers in the pulp. Increasing amounts of e.g. old newspapers (ONP) and waste magazines (WM) are becoming available with increased participation of end consumers in recycling. Other steps in order to reduce deposits during formation of pulp made from waste paper includes removal of other water insoluble materials which tend to agglomerate and deposit on various parts of the paper manufacturing equipment. Such deposits include stickies (waste paper contaminants of an adhesive character) or hydrophobic fatty acids and esters.

[0005] In the course of conventional paper reclamation, deinking procedures include steps for converting the wastepaper to pulp and contacting the pulp with an alkaline aqueous deinking medium containing a chemical deinking agent. The mechanical action and the alkalinity of the aqueous medium cause the partial removal of ink from the pulp fiber. The deinking agent completes this removal and produces an aqueous suspension and/or dispersion of the ink particles. The resulting mixture is subsequently treated to separate the suspended/dispersed ink from the pulp. This separation may be by flotation and/or washing techniques known in the art. [0006] Conventional deinking chemicals comprise a complex mixture of chemicals, e.g. sodium hydroxide, sodium silicate, chelating agents, hydrogen peroxide, surfactants, dispersants, collector chemicals and agglomeration chemicals. Typical deinking processes are described in L. D. Fergusen "Deinking Chemistry: part 1" July 1992 TAPPI Journal pp. 75-83; L. D. Fergusen "Deinking Chemistry: part 2" August 1992 TAPPI Journal pp. 49-58; and J. L. Spielbauer "Deinking System Overview" Voith Inc. Appleton, pp. 1-9. [0007] The hydrophobic fatty acids and esters are very problematic during the paper making process. They can cause severe deposits on the process equipment. Even after Resinase<sup>TM</sup> (lipase) treatment, the newly formed long chain fatty acids are still too hydrophobic to dissolve in the process

water. Other types of deposits are caused by polymers. For

example, in the paper industry polymers comprising vinyl acetate are used as a binder and coating material. During recycling these polymers tend to agglomerate together with fibers and other substances to form so-called "stickies", which reduce the quality of the paper product and results in a significant downtime of the machine.

[0008] WO 00/34450, WO 01/92502 and U.S. Pat. No. 5,176,796 report the use of certain lipases and esterase in the manufacture of paper, viz. for pitch control. According to the above US patent, pitch is a natural constituent of wood, and triglyceride is a major component thereof. WO 01/98579 discloses the use of lipase and/or esterase for control of the problem with stickies during recycling of paper.

[0009] A need therefore exists for a method for reducing the deposit problems associated with papermaking from pulp produced from waste paper, especially a method by which both of the above described deposit problems are solved at the same time.

#### SUMMARY OF THE INVENTION

[0010] A solution to the above problem is provided by the method of the invention relating to a method of preventing or reducing deposits in a pulping process by including a cyclodextrin during or after pulp formation.

[0011] The present invention therefore relates to a method of preventing or reducing deposits in a pulping process by treating a pulp with a cyclodextrin in an amount effective for preventing or reducing the deposits.

#### DETAILED DESCRIPTION OF THE INVENTION

[0012] The most important feature of cyclodextrin is their ability to form solid inclusion complexes (host-guest complexes). The lipophilic cavity of cyclodextrin molecules provides a micro-environment into which an appropriately sized non-polar moiety can enter to form an inclusion complex. Inclusion in cyclodextrins exerts a profound effect on physiochemical properties of guest molecules as they are temporarily locked or caged within the host cavity, which give rise to some unique beneficial modifications of the guest molecules. The properties include solubility enhancement of highly insoluble guests, stabilization of labile guests against the degradation, masking off flavors, and controlled release of drugs and flavors.

[0013] During newspaper deinking, Flexo ink in particular, the soluble ink tends to re-deposit back to the pulp fiber. Cyclodextrin can be used to trap those small ink particles and improve the deinking efficiency, which should result in high brightness and less dirt count.

[0014] Cyclodextrin may also effectively entrap hydrophobic lipid materials (fatty acids and esters) and enhance their solubility in water. Cyclodextrin can also work with Resinase and other enzymes to improve the efficiency. Along the same line, Cyclodextrin may also work on the sticky material during recycling.

[0015] As used herein "stickies" designate waste paper contaminants of an adhesive character causing sticking of paper-machine parts during reprocessing. As examples of such contaminants, ink, tar, and latex are mentioned.

[0016] Further examples of stickies are tacky agglomerates of fibres, adhesives, coatings, binders and other materials, which form in a recycled papermaking process. Accordingly, stickies are mainly of concern for paper manufacturing processes in which recycled paper is used.

[0017] Stickies are water insoluble and tend to agglomerate and deposit on various parts of the paper manufacturing equipment, thereby causing paper quality problems, breaks of the paper web, and costly downtime periods for cleaning the equipment. For example, stickies may deposit on the paper forming felts thereby rendering the drainage of water from the forming paper web less efficient, which again may give rise to problems as described above.

[0018] Stickies have been distinguished in various ways, e.g. by size, or by specific gravity:

[0019] Primary stickies are so small as to usually not cause any problems, whereas secondary stickies or macro stickies are larger and tend to deposit. Macro stickies are generally of such size as to be retained on fine screens. Example of fine screens are those having slots of about 50-200, 60-190, or 70-180, or 80-170, or 80-160, or of about 80-150 micrometer.

[0020] High density and low density stickies may under certain conditions be removable by various types of mechanical equipment, but problems remain in particular with the so-called neutral range density stickies, i.e. stickies of a specific gravity of about 0.9 to about 1.1, or about 0.95 to about 1.05, or about 0.98 to about 1.02.

**[0021]** The chemical composition of stickies from various parts of the world may vary, mainly depending on the characteristics of the local paper manufacturing processes. Likewise, for the same reason, the composition of stickies may vary from factory to factory.

[0022] The following components are examples of components, one or more of which are typically found in stickies: natural wood pitch, such as fatty acids, resin acids and fatty acids; synthetic coating binders, printing inks and adhesives, such as Acrylic Resins, Poly Vinyl Acetate (PVAc), Styren Butadien Resin (SBR), Poly Ethylene (PE) and Poly Propylene (PP), polyester, hydroxyl polyester, urethane acrylate, epoxy acrylate, acrylic acid ester, block copolymers and H/C resins.

[0023] As described above the deposits according to the invention can in general be in the form of ink deposits, deposits of hydrophobic lipid materials (fatty acids and esters), or stickies. The ink deposits may contain non-contact laser inks, xerographic toners, letterpress ink generally used in printing newsprint, magazine print, offset printing ink, ultraviolet or electron beam cured ink.

[0024] Depending on the nature of the deposit the cyclodextrin comprising the deposit should be removed or separated from the pulp. When applying the cyclodextrin for removing ink particles from pulp the cyclodextrin should e.g. be separated from the pulp after treatment.

[0025] Separation of cyclodextrin comprising the deposits from the pulp can be performed in any suitable way such as washing, flotation and press.

[0026] The present invention describes a method of treatment of wood pulps or pulp from printed paper with cyclodextrin alone, or cyclodextrin and a conventional enzyme (e.g.; a lipase), or lipase and in situ generated cyclodextrin from starch and glycosyltransferase (CGTase) to reduce pitch or deposit troubles during pulp and paper making processes. This invention can also be applied to the deinking process of waste paper to reduce the residual ink particles in paper by preventing redeposits onto pulp fibers.

[0027] The deinking agent, the cyclodextrin, would usually be supplied to the waste paper initially, i.e. when the pulping stage commences. Alternatively, the deinking agent may be

supplied to wastepaper which is already in the form of a pulp, that is, to wastepaper which has first been substantially reduced to individual fibers. In the former case, the pulping step where the deinking agent is present is also sometimes termed "re-pulping". The cyclodextrin can in another embodiment be generated enzymatically in situ by a glycosyl transferase.

[0028] Pulping can be conducted using any of the various conventional processes and equipment designed for this purpose. Most conveniently, the wastepaper process feedstock is treated in a device known as a "hydrapulper", which produces a slurry of the fibers in water.

[0029] In one aspect of the invention the cyclodextrin is used as a deinking agent in combination with conventional enzymes used in deinking processes.

[0030] Accordingly, the method of the invention may be carried out with a cyclodextrin and a combination of enzymes in order to make the enzymatic process effective against a broader range of contaminants, such as proteinaceous impurities, starch-containing impurities, triglyceride containing impurities as well as contaminants containing hemi-celluloses and pectins. The enzymes can be selected from amongst proteases, amylases, pullulanases, lipases, hemicellulases, endoglucanases, cutinases, and pectinases. These enzymes may be wild-type enzymes, or mutants or variants thereof having the relevant enzyme activity, i.e. catalyzing at least one of the reactions indicated at the following web-site for the relevant enzyme class: http://www.expasy.ch/enzymel.

[0031] The lipase enzyme to be used in the present invention is one that can hydrolyze ester bonds. Such enzymes include, for example, lipases, such as triacylglycerol lipase (EC 3.1.1.3), lipoprotein lipase (EC 3.1.1.34), monoglyceride lipase (EC 3.1.1.23), lysophospholipase, ferulic acid esterase and esterase (EC 3.1.1.1, EC 3.1.1.2). The numbers in parentheses are the systematic numbers assigned by the Enzyme Commission of the International Union of Biochemistry in accordance with the type of the enzymatic reactivity of the enzyme.

**[0032]** The lipase may be a microbial lipase, e.g. from bacteria or fungi such as *Humicola* or *Pseudomonas*, particularly lipase from *H. lanuginosa* (this lipase being referred to as Resinase A 2x $\mathbb{R}$ )).

[0033] Preferred microbial lipases to be used in the methods of the present invention may be of bacterial, yeast or fungal origin, and suitable examples include a lipase derived or obtainable from a strain of *Humicola* spp., *Rhizomucor* spp., *Candida* spp., *Aspergillus* spp., *Rhizopus* spp. or *Pseudomonas* spp., especially from a strain of *H. lanuginosa*, *Rh. miehei*, *C. antarctica*, *Aspergillus niger* or *Pseudomonas* cepacia. Specific examples of such lipases are lipase A and lipase B of *C. antarctica*, described in WO 88/02775, the *Rh. meihei* lipase described in EP 238 023, the *H. lanuginosa* lipase described in EP 305 216, and the *P. cepacia* lipase described in EP 214 761 and WO 89/01032.

[0034] The lipase may be a native enzyme found in nature, or it may be a variant thereof obtained by altering the amino acid sequence. Examples of such variants are those described in WO 92/05249, WO 94/25577, WO 95/22615, WO 97/04079 and WO 97/07202, WO 98/08939, WO 99/42566, EP 943 678, and WO 00/60063.

[0035] Specific examples of suitable, commercially available, lipases are, e.g., Resinase A 2×, Novozyme 735, and Novozyme 525 (all available from Novozymes A/S, Denmark).

[0036] It is known from WO 95/14807 that, in the case of starch coated paper, the deinking effect can be improved by including a treatment with a starch-degrading enzyme and, consequently, in a further embodiment of the invention, the pulping is carried out in the presence of a starch degrading enzyme.

[0037] The starch-degrading enzyme is preferably an amylase, e.g. an α-amylase, a glucoamylase or a debranching enzyme. A single enzyme or a combination may be used, e.g. α-amylase together with glucoamylase and/or a debranching enzyme. Examples of preferred α-amylases are those derived from strains of *Bacillus*, e.g. *B. amyloliquefaciens* (*B. subtilis*), *B. licheniformis* or *B. stearothermophilus* and from strains of *Aspergillus*, e.g. *A. oryzae*. Examples of commercial products are BANTM, TermamylTM, Aquazyme UltraTM and FungamylTM (products of Novozymes A/S).

[0038] Preferred glucoamylases are the glucoamylases derived from a strain of *Aspergillus niger*, e.g. the commercial product AMG (product of Novozymes A/S).

**[0039]** The debranching enzyme is preferably a pullulanase, particularly one derived from a strain of *Bacillus* acidopullulyticus, e.g. the commercial product Promozyme<sup>TM</sup> (product of Novozymes A/S).

**[0040]** In addition, it is well known that cellulases may aid the deinking process. Furthermore, it is well known that cellulases may improve the drainability of the paper pulp. Consequently, in a still further embodiment of the invention the pulping is carried out in the presence of a cellulase.

[0041] Such cellulases are typically be derived from bacteria and fungi, such as Aspergillus niger, Trichoderma virde, Thielatia terrestris, Humicola sp. and Bacillus sp. The cellulase may be a mono component or multi component cellulase, although mono component cellulases are preferred. A class of cellulases that are especially useful are cellulases lacking a cellulose binding-domain (CBD). Cellulose-binding domains have been described by P. Tomme et al. in J. N. Saddler & M. H. Penner (eds.), "Enzymatic Degradation of Insoluble Carbohydrates" (ACS Symposium Series, No. 618), 1996. A number of cellulases are known to contain a catalytic domain without a CBD; such a cellulase may be used as such in the invention. It is also known that other cellulases contain a catalytic domain and a CBD; such a cellulase may be truncated to obtain a catalytic core domain without the CBD, and this core may be used in the invention.

**[0042]** Cellulases may be classified into families on the basis of aminoacid sequence similarities according to the classification system described in Henrissat, B. et al.: Biochem. J., (1991), 280, p. 309-16, and Henrissat, B. et al.: Biochem. J., (1993), 293, p. 781-788. Some preferred cellulases are those belonging to Family 5, 7, 12 and 45.

[0043] A preferred Family 5 cellulase without CBD is an alkaline cellulase derived from a strain of *Bacillus*. One such Family 5 cellulase is the endo-glucanase from *Bacillus* strain KSM-64 (FERM BP-2886). The cellulase and its amino acid sequence are described in JP-A 4-190793 (Kao) and Sumitomo et al., Biosci. Biotech. Biochem., 56 (6), 872-877 (1992).

[0044] Another Family 5 cellulase from *Bacillus* is the endo-glucanase from strain KSM-635 (FERM BP-1485). The cellulase and its amino acid sequence are described in JP-A 1-281090 (Kao), U.S. Pat. No. 4,945,053 and Y. Ozaki et al., Journal of General Microbiology, 1990, vol. 136, page 1973-1979. A third Family 5 cellulase from *Bacillus* is the endo-glucanase from strain 1139. The cellulase and its amino

acid sequence are described in Fukumori F. et al., J. Gen. Microbiol., 132:2329-2335 (1986) and JP-A 62-232386 (Riken). Yet another preferred Family 5 cellulase without CBD is an endo-beta-1,4-glucanase derived from a strain of *Aspergillus*, preferably *A. aculeatus*, most preferably the strain CBS 101.43, described in WO 93/20193 (Novo Nordisk).

[0045] The Family 7 cellulase may be derived from a strain of Humicola, preferably H. insolens. An example is endoglucanase EG I derived from H. insolens strain DSM 1800, described in WO 91/17244 (Novo Nordisk). The mature cellulase has a sequence of the 415 amino acids shown at positions 21-435 in FIG. 14 of said document and has a specific activity of 200 ECU/mg (based on pure enzyme protein). This cellulase may further be truncated at the C-terminal by up to 18 amino acids to contain at least 397 amino acids. As examples, the cellulase may be truncated to 402, 406, 408 or 412 amino acids. Another example is a variant thereof denoted endo-glucanase EG I\* described in WO 95/24471 (Novo Nordisk) and having a sequence of 402 amino acids shown in FIG. 3 therein. Alternatively, the Family 7 cellulase may be derived from a strain of *Myceliophthora*, preferably M. thermophila, most preferably the strain CBS 117.65. An example is an endo-glucanase described in WO 95/24471 (Novo Nordisk) comprising the amino acids 21-420 and optionally also the amino acids 1-20 and/or 421-456 of the sequence shown in FIG. 6 therein. As another alternative, the Family 7 cellulase may be derived from a strain of *Fusarium*, preferably F. oxysporum. An example is an endo-glucanase derived from F. oxysporum described in WO 91/17244 (Novo Nordisk) and Sheppard, P. O. et al., Gene. 150:163-167, 1994. The correct amino acid sequence is given in the latter reference. This cellulase has a specific activity of 350 ECU/mg.

[0046] A preferred Family 12 cellulase without CBD is CMC 1 derived from Humicola insolens DSM 1800, described in WO 93/11249 (Novo Nordisk). Another preferred Family 12 cellulase without CBD is EG III cellulase from Trichoderma, particularly Trichoderma viride or Trichoderma reesei, described in WO 92/06184 (Genencor). Alternatively, the Family 12 cellulase may be derived from a strain of Myceliophthora, preferably M. thermophila, most preferably the strain CBS 117.65. Such a cellulase (termed C173) can be produced by cloning DNA from CBS 117.65, and subsequently transforming Aspergillus oryzae, a noncellulolytic host organism, and expressing the cellulase by cultivation of the transformed host, and separating the only cellulolytic active ingredient from the culture broth. C173 has optimum activity at pH 4-6.5, a specific activity of 226 ECU per mg protein and a molecular weight of 26 kDa (for the mature protein).

[0047] A preferred Family 45 cellulase without CBD is the EG V-core derived from *Humicola insolens*, described in Boisset, C., Borsali, R., Schulein, M., and Henrissat, B., FEBS Letters. 376:4952, 1995. It has the amino acid sequence shown in positions 1-213 of SEQ ID NO: 1 of WO 91/17243 (Novo Nordisk). Another preferred Family 45 cellulase without CBD is FI-CMCase from *Aspergillus* aculeatus described by Ooi et al., Nucleic Acids Research, Vol. 18, No. 19, p. 5884 (1990).

[0048] Examples of commercially available cellulases include Novozym 613, Novozym 476, and Novozym 342 (all available from Novozymes A/S, Denmark).

[0049] In a particular embodiment the cyclodextrin can be generated in situ by the enzymatic action of a glycosyl trans-

ferase converting starch to cyclodextrin. Particularly the glycosyl transferase is CGTase. Additional cyclodextrin may or may not be added. In case a glycosyltransferase is added incubation time should be long enough to allow formation of sufficient amounts of the cyclodextrin. In one embodiment the treatment should be in the range from 15 to 120 minutes.

[0050] Cyclomaltodextrin glucanotransferase (E.C. 2.4.1. 19), also designated cyclodextrin glucanotransferase or cyclodextrin glycosyltransferase, in the following termed CGTase, catalyses the conversion of starch and similar substrates into cyclomaltodextrins via an intramolecular transglycosylation reaction, thereby forming cyclomaltodextrins, in the following termed cyclodextrins (or CD), of various sizes. Commercially most important are cyclodextrins of 6, 7 and 8 glucose units, which are termed alpha-, beta-, and gammacyclodextrins, respectively. Commercially less important are cyclodextrins of 9, 10, and 11 glucose units, which are termed delta-, epsilon-, and zeta-cyclodextrins, respectively. Most CGTases have both starchdegrading activity and transglycosylation activity. Although some CGTases produce mainly alpha-cyclodextrins and some CGTases produce mainly betacyclodextrins, CGTases usually form a mixture of alpha-, beta- and gamma-cyclodextrins. Selective precipitation steps with organic solvents may be used for the isolation of separate alpha-, beta- and gamma-cyclodextrins. To avoid expensive and environmentally harmful procedures, the availability of CGTases capable of producing an increased ratio of one particular type of cyclodextrin, in particular with respect to alpha-, beta- or gamma-cyclodextrin, is desirable.

[0051] Useful CGTases for the purpose of the present invention are described in the following. CGTases which primarily form alpha-cyclodextrin, also called alpha-CG-Tase, such as, for example, the CGTase from Bacillus macerans (U.K. Patent No. 2,169,902), from Klebsiella pneumoniae (EPA 220,714) and from Bacillus stearothermophilus (U.K. Pat. No. 2,169,902). CGTases which primarily form beta-cyclodextrin, or beta-CGTase, such as, for example, the CGTase from Bacillus circulans (U.S. Pat. No. 4,477,568), from Bacillus megaterium (U.S. Pat. No. 3,812,011), from Bacillus ohbensis (Japan Patent No. 74,124,285), from Micrococcus sp. (EPA No. 017,242) and from alkalophilic Bacillus sp. (J. Gen. Microbiol. 1988, 134, 97-105; Appl. Microbiol. Biotechnol. 1987, 26, 149-153). Two articles (Agric. Biol. Chem., 1986, 50, (8), 2161-2162 and Denpun Kagaku 1986, 33, 137) describe a gamma-CGTase from Bacillus subtilis No. 313. This CGTase is distinguished by the formation of gamma-cyclodextrin and linear oligosaccharide. Since CGTases generate only cyclic products from starch, this "CGTase" is a transitional form between an alphaamylase (generates linear oligosaccharide from starch) and a CGTase. This "gamma-CGTase" is unsuitable for preparing gamma-cyclodextrin because only low yields can be achieved (see EPA 327,099, page 2, lines 40-43).

**[0052]** A preferred CGTase is derived from a strain of *Bacillus*, e.g. the commercial product Toruzyme<sup>TM</sup> (product of Novozymes A/S).

[0053] Since enzyme activity usually is affected by temperature it is important to maintain an appropriate pulp slurry temperature while the deinking agent is contacted with the pulp slurry in the case when an enzyme is also applied. The temperature has to be consistent with the activity temperature profile of the enzyme, and preferably the process is run at a temperature where the employed enzyme, e.g. a lipase or a CGTase, has maximum activity. Since a number of commer-

cially available lipases have a substantial activity in the temperature range of from 25 to  $75^{\circ}$  C. it is contemplated that the process can be run using temperatures, which do not deviate substantially from the temperatures normally used in such processes. Typically, pulping with the deinking agent is carried out at a temperature from 25 to  $75^{\circ}$  C., preferably from 30 to  $70^{\circ}$  C., such as from 35 to  $65^{\circ}$  C., e.g. from 40 to  $60^{\circ}$  C., more preferably from 45 to  $60^{\circ}$  C., such as from 45 to  $55^{\circ}$  C., e.g. about  $50^{\circ}$  C.

**[0054]** For in situ generation of CDs with CGTases, the treatment temperature of the pulp should be in between 25-100° C., preferably from 30 to 90° C., such as from 35 to 85° C., more preferably from 45 to 75° C., e.g. about 70° C.

[0055] The efficiency of the deinking agent can be significantly influenced by the pH of the pulp slurry while contacting the deinking agent with the pulp slurry, since fluctuations in the pH can result in deactivation of the optionally added enzyme. The pH of the pulp slurry should be in the range of from 4 to 9. In a preferred embodiment of the invention, the pulping with the deinking agent is carried out at a pH between 4.5 and 8.5, in particular between 5 and 8.5, such as between 5.5 and 8.5, more preferably between 6 and 8.5, such as from 6.5 to 8.5, e.g., between 7.5 and 8.5. The pulp slurry pH has to be consistent with the activity pH range of the enzyme or combination of enzymes, and in a preferred embodiment the process is run at a pH where the employed enzymes has optimal activity. The pH of the pulp may be adjusted by means of buffering agents, such as sodium citrate, sodium carbonate, sodium phosphate and the like. It is particularly preferred, however, that hydroxides, in particular alkali metal-hydroxides, such as sodium hydroxide, is not added at any stage, i.e. prior to, during or after pulping.

[0056] With regard to the in situ generation of CDs with CGtases, the treatment pH of the pulp should be in between 4-9, preferably from pH 5 to 8, more preferably from 5.5-7, e.g. about pH 6.

[0057] The waste paper to be deinked according to the invention may be any reclaimed fiber, such as old newspapers (ONP), waste magazines (WM), mixed and sorted office waste, computer print outs, white ledger waste paper, etc.

[0058] In a preferred embodiment of the invention the wastepaper comprises ONP, WM or a combination thereof.

[0059] In one embodiment of the invention the amount of ONP constitutes at least 10% by weight of the total amount of wastepaper, preferably at least 20% by weight, e.g. at least 30% by weight, e.g. at least 40% by weight, more preferably at least 50% by weight, such as at least 60% by weight, e.g. at least 70% by weight, most preferably at least 80% by weight, such as at least 90% by weight, e.g. at least 95% by weight of the total amount of wastepaper. In a further embodiment of the invention the wastepaper consists essentially of ONP.

[0060] In another embodiment of the invention the amount of WM constitutes at least 10% by weight of the total amount of wastepaper, preferably at least 20% by weight, e.g. at least 30% by weight, e.g. at least 40% by weight, more preferably at least 50% by weight, such as at least 60% by weight, e.g. at least 70% by weight, most preferably at least 80% by weight, such as at least 90% by weight, e.g. at least 95% by weight of the total amount of wastepaper. In a further embodiment of the invention the wastepaper consists essentially of WM.

[0061] In a still further embodiment of the invention the wastepaper comprises 1-60% by weight of WM and 40-99%

by weight of ONP, preferably 10-50% by weight of WM and 50-90% by weight of ONP, such as 20-50% by weight of WM and 50-80% by weight of ONP, e.g. 30-50% by weight of WM and 50-70% by weight of ONP.

[0062] In addition to water, pulp and deinking agent, the pulp may further contain substances conventionally employed in deinking process, e.g. brightening agents, solvents, antifoam agents and water softeners, in particular brightening agents.

[0063] Although not particularly preferred the pulp may also contain additional surfactants, such as non-ionic and cationic surfactants. Examples of non-ionic surfactants are, e.g., alkoxylated fatty acids, such as Di 6000 from High Point Chemical Corp.; alkyl phenyl ethers of polyethylene glycol, such as the Tergitol® series from Union Carbide; alkylphenolethylene oxide condensation products, such as the Igepal® series from Rhone Poulenc; and aryl alkyl polyether alcohols, such as Rohm and Haas' Triton® X 400 series, e.g. Trition® X 100. Examples of cationic surfactants include imidazole compounds, such as Amasoft® 16-7 and Sapamine® P from Ciba-Geigy and quaternary ammonium compounds, such as Quaker® 2001 from Quaker Chemicals and Cyanatex® from American Cynamid.

[0064] The overall deinking process generally comprises pulping or maceration of the wastepaper and ink removal by a flotation system, a water washing system or a combined flotation/washing system. A screening or coarse cleaning

[0065] Separation of ink particles or hydrophobic lipid materials entrapped in cyclodextrin complexes may be performed by well known techniques in the art such as by washing and/or flotation.

[0066] The invention will be further illustrated in the accompanying examples below.

#### **EXAMPLES**

#### Example 1

Removal of Fatty Acids from Solution by  $\alpha$ -Cyclodextrin

[0067] Removal of fatty acids from solutions by addition of  $\alpha\text{-cyclodextrin}$  was tested by preparing a 0.1% linoleic acid suspension and a 1.0%  $\alpha\text{-cyclodextrin}$  solution as follows: 1. 250  $\mu l$  linoleic acid was transferred to a 250 ml volumetric fleels

- 2. Deionized water was slowly added while agitating on a whirly mixer.
- 3. Linoleic acid solution stays suspended as long as agitation is continued

[0068] A 1.0%  $\alpha$ -cyclodextrin solution was prepared by dissolving 2 g of  $\alpha$ -cyclodextrin in 200 ml deionized water. [0069] The 0.1% linoleic acid suspensio was mixed with the 1.0% cyclodextrin solution at different ratios of fatty acid to cyclodextrin and the increase in turbidity was determined. The results are given in the Table 1 below.

TABLE 1

Tu	arbidity (NTU, Nephelometric Turbidity Units) measurements of mixtures of fatty acid (FA) and cyclodextrin (CD).								
Test tube	Fatty acid 0.1%	Volume (ml)	Cyclodextrin,	Volume (ml)	Water (ml)	Ratio FA:CD	Turbidity (NTU)		
1	Linoleic acid	0	_	0	30	_	0		
2	Linoleic acid	20	α	1	9	2:1	64		
3	Linoleic acid	20	α	10	0	1:5	168		
3b	Linoleic acid	20	_	0	10	_	72		
4	Linoleic acid	10	α	10	10	1:10	252		
5	Linoleic acid	10	α	20	0	1:20	378		
5b	Linoleic acid	10	_	0	20	_	40		
6	Linoleic acid	6	α	24	0	1:40	414		
6b	Linoleic acid	6	_	0	24	_	24		
7	Linoleic acid	4	α	20	6	1:50	342		
7b	Linoleic acid	4	_	0	26	_	20		

stage can be utilized to remove contaminants such as glass, stone, metal and staples. A centrifugal cleaning stage (or stages) can be utilized to remove light weight materials such as plastic. Typical deinking processes are described in L. D. Fergusen "Deinking Chemistry: part 1" July 1992 TAPPI Journal pp. 75-83; L. D. Fergusen "Deinking Chemistry: part 2" August 1992 TAPPI Journal pp. 49-58; and J. L. Spielbauer "Deinking System Overview" Voith Inc. Appleton, pp. 1-9.

[0070] The results show that it is possible to remove fatty acids, exemplified by linoleic acid, from solution by entrapment in cyclodextrin. It is observed that an optimal ratio of fatty acid to cyclodextrin of 1:40 exists. Optimal ratios of cyclodextrin to fatty acid may depend on the particular fatty acid to be removed and can be easily determined by simple experimentation.

Example 2
Use of Cyclodextrin for Wash Deinking of ONP

[0071] Deinking of old newspaper (ONP) by adding cyclodextrin during pulp formation and subsequent washing was tested using the following protocol:

[0072] Add 50 g of shredded old newspaper, 1500 ml of water and 4 kg/ton of Tomah wash deinking surfactant to a pulper. Set the temperature at 45° C. Add cyclodextrin (2 kg/t) and mix for 10 minutes. Transfer slurry into a bucket with 1.5 l of water at the same temperature as the slurry and stir the slurry for 30 min. Make No Wash (NW), Wash (W), and Hyper Wash (HW) pads after 5 minutes and 30 minutes of stirring.

[0073] For a No Wash pad (NV), weigh out 180 g. of slurry, fill up to 300 ml with water, stir, and pour into filter with a Whatman 40 ashless filter paper. For Wash pad (W), weigh out 180 g of slurry, and wash with 1 L of DI water in a Britt jar. Hyper Wash (HW) pads were made in the same manner as the wash pad (W) except using 5 L of DI water during washing. [0074] The pads are evaluated for brightness on a MacBeth Color Eye analyser using Tappi test methods T452. The results of the brightness readings are given in table 2 below.

TABLE 2

Brightness	Control	Alpha CD	Beta CD
5 min NW	41.5	41.3	41.4
5 min W	43.9	45.2	44.8
5 min HW	44.9	45.8	45.7
30 min NW	39.6	41.7	41.3
30 min NW	43.5	44.7	44.2
30 min HW	44.7	45.6	45.3

[0075] It is clear that both alpha-cyclodextrin and beta-cyclodextrin significantly improved the pulp brightness during wash deinking.

#### Example 3

Use of Cyclodextrin for Deinking of ONP by Flotation

[0076] Deinking of old newspaper (ONP) by adding cyclodextrin during pulp formation and subsequent removal by flotation was tested using the following protocol:

[0077] Set pulper temperature to  $50^{\circ}$  C. Add 2 L water, 250 g ONP, 2 kg/ton of Huntsman flotation deinking surfactant and 2.5 kg/ton of cyclodextrin to the pulper. Mix for 10 min and transfer the slurry into a bucket with 3 L of water and stir it for 30 min at  $50^{\circ}$  C.

[0078] Add pulp slurry and 10 L water to a flotation cell (Delta 25 from Voith). Float for 5 min. By the end of the flotation make No Wash pads (NW) and determine brightness as mentioned above. The test results of the brightness evaluation are given in table 3 below.

TABLE 3

Brightness	Control	Alpha CD	Beta CD
NW Pads	46.07	47.03	48.23
Std Dev.	0.06	0.25	0.12

[0079] It is evident that the addition of cyclodextrin to the flotation deinking process improved the pulp brightness. It appears that  $\beta$ -cyclodextrin is more effective than  $\alpha$ -cyclodextrin for brightness improvement.

- 1. A method of preventing or reducing deposits in a pulp and paper making process by treating a pulp with a cyclodextrin in an amount effective for preventing or reducing the deposits.
- 2. The method according to claim 1, wherein the cyclodextrin forms a solid inclusion complex with the deposit and wherein said complex is subsequently separated from the pulp.
- 3. The method according to claim 1, wherein a source of raw fiber material for pulp formation is provided from printed paper.
- **4**. The method according to claim **3**, wherein the printed paper comprises old newspapers (ONP) and/or waste magazines (WM).
- 5. The method according to claim 1, wherein the deposits comprise fatty acid or ester deposits on process equipment.
- **6**. The method according to claim **1**, wherein the deposits comprise stickies.
- 7. The method according to claim 3, wherein the deposits comprise ink deposits on pulp fibers.
- 8. The method according to claim 7, wherein the ink deposits comprise non-contact laser inks, xerographic toners, letterpress ink generally used in printing newsprint, magazine print, offset printing ink, ultraviolet or electron beam cured ink.
- 9. The method according to claim 1, wherein the cyclodextrin comprises alpha-, beta- and/or gamma-cyclodextrin.
- 10. The method according to claim 9, wherein the cyclodextrin is alpha- or beta-cyclodextrin.
- 11. The method according to claim 1, wherein the cyclodextrin is provided partly or completely by enzymatic conversion of starch in situ.
- 12. The method according to claim 11, wherein the enzyme comprises a glycosyltransferase.
- 13. The method according to claim 12, wherein the glycosyltransferase comprises a CGTase.
- 14. The method according to claim 1, wherein cyclodextrin treatment is combined with enzymatic treatment and wherein the enzyme is chosen from the group consisting of proteases, amylases, pullulanases, lipases, hemicellulases, endoglucanases, cutinases, and pectnases.

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