USE OF 1,3-SELECTIVE LIPASES FOR PITCH CONTROL IN PULP AND PAPER PROCESSES

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ABSTRACT
Formulations for pitch control, and methods of making and using thereof, are described herein. The formulations contain one or more 1,3-selective lipases. 1,3-selective lipases catalyze the hydrolysis of the terminal ester groups in triglycerides leaving the internal ester group intact. The enzyme formulations can contain one or more additives, such as dispersants, metal ions, absorbents, adsorbents, cationic polymers, and combinations thereof. The enzyme formulation is typically applied as a solution to the pulp stock. The enzyme formulations can be applied at any of one or more various points during the pulping and paper manufacturing processes. The use of selective lipase(s) decreases the total concentration of fatty acids in the system, and catalyzes the formation of monoglycerides, which are more effective at dispersing fatty acids than glycerol, the product of non-selective lipases, thereby improving pulp and paper machine runnability and pulp and paper quality.
Figure 2

Enzyme Treatment

Relative Deposition (vs. Control)

- Paddle
- Bowl
Figure 3B
Figure 3C
Figure 4
Figure 5

Graph showing the relationship between Enzyme Dosage (ppm) and Total Glycerol Content (% o.d. fiber) for EnzOx PC and EnzOx SEL.
Figure 6
USE OF 1,3-SELECTIVE LIPASES FOR PITCH CONTROL IN PULP AND PAPER PROCESSES

FIELD OF THE INVENTION

[0001] The present invention is generally in the field of treating pulp stocks with enzyme formulations in order to reduce pitch deposition, particularly enzyme formulations containing 1,3-selective lipases.

BACKGROUND OF THE INVENTION

[0002] Wood resin is composed of fatty acids and resin acids, triglycerides, steryl esters, and sterols. Wood resins, as well as other extractives such as lignans, pectins, and phenols, are the major components of pitch deposits. During pulping, such as mechanical pulping and/or thermomechanical pulping, the encapsulated resin is liberated from ray parenchyma cells and resin canals. Some of the dispersed resin droplets precipitate onto fiber surfaces impairing fiber to fiber bonding and thereby negatively affect the physical properties of the pulp. Dispersed resin which precipitates later in the pulping and papermaking processes can affect machine runnability and reduce paper quality which can result in increased manufacturing costs.

[0003] Traditionally, pitch deposits in pulping and paper manufacturing have been reduced by debarking and seasoning logs and wood chips and by the use of physicochemical control agents. For example, cationic coagulant chemicals have been used to fix the extractives to the fibers so that the pitch deposits can be removed. However, the use of such fixing agents has its limitations, particularly when used with recycled paper.

[0004] In order to overcome the limitations of physicochemical treatments, biological treatments, particularly the use of enzymes, have been investigated for pitch control. For example, U.S. Pat. No. 5,176,796 to Irie et al.; U.S. Pat. No. 5,256,252 to Sarkar et al.; and U.S. Pat. No. 5,667,634 to Fujita et al. describe the use of acylglycerol lipases to hydrolyze triglycerides in pitch to glycerol and fatty acids to reduce pitch problems caused by triglycerides. This technology has been applied commercially in a number of mills and achieved some success, including reducing pitch deposition on paper machines, increasing the coefficient of friction (COF) and improving paper strength (e.g., Chen et al., 2001, EAPP Journal, Vol. 84, No. 4, pp 44-47; Wang and Jiang, 2003, Proceedings of 2003 International Mechanical Pulping Conference, p 40-47, and Wang et al., 2008, PaperCon '08 Proceedings).

[0005] Lipolytic enzymes break down triglycerides to glycerol and fatty acids, as shown in the following reaction:

\[
\begin{align*}
\text{CH}_2\text{O}^-\text{C}^-\text{R}_1 + 3\text{H}_2\text{O} & \rightarrow \text{R}_1\text{COOH} + \text{R}_2\text{COOH} + \text{CH}_2\text{OH} \\
\end{align*}
\]

[0006] For non-selective lipases, for each mole of triglyceride reacted, three moles of fatty acids are generated during the reaction. On a weight basis, about 90% of triglyceride is converted to fatty acids. For example, if a mill pulp stock contains 1% triglyceride, then full conversion of the triglycerides by non-selective lipases will generate about 0.9% fatty acids, the remaining 0.1% being glycerol. In most processes, the fatty acids created by the enzymatic hydrolysis of triglycerides are managed by fixation onto fibers with cationic coagulants and retention aids, such as resin sizing.

[0007] The above treatments, however, can result in increased concentrations of fatty acids, which may affect pulp and paper machine runnability and pulp and paper quality. For example, large concentrations of fatty acids can react with aluminum, calcium, and other metal ions in the pulping process to form fatty acid soap deposits, known as “butter beans” or “sunflower seeds”, which can create deposition problems more serious than triglycerides and adversely affect pulp and paper machine runnability and pulp and paper quality. Fatty soap deposits are known to create small holes in the finished paper in mills that have used non-selective lipase treatments. When the fatty acids (generated from the enzymatic conversion of triglycerides) are not precipitated by alum or fixed by cationic coagulants, they agglomerate into small particles and create fatty acid spots (that are translucent or semi-translucent) on the finished paper, adversely affecting paper quality.

[0008] There exists a need for improved pitch control methods which decrease the amount of fatty acid concentration in pulp and papermaking processes thereby improving pulp and paper machine runnability as well as pulp and paper quality.

[0009] It is therefore an object of the invention to provide methods for improving pitch control in pulp and paper making.

[0010] It is further an object of the invention to provide pitch control methods which decrease fatty acid concentration and/or agglomeration compared to prior art methods resulting in improved pulp and paper machine runnability and improved pulp and paper quality.

SUMMARY OF THE INVENTION

[0011] Formulations for pitch control, and methods of making and using thereof, are described herein. The formulations contain one or more 1,3-selective lipases. 1,3-selective lipases catalyze the hydrolysis of the terminal ester groups in triglycerides leaving the internal ester group (i.e., the ester group at carbon 2) intact. The selective lipases can be isolated from a variety of microorganisms including, but not limited to, Rhizopus oryzae, Rhizopus delemar, Rhizopus arrhizus, Rhizopus niveus, Aspergillus niger, Pseudomonas alkaligenes, Pseudomonas fragi, Pseudomonas cepacia, Mucor miehei, Humicola lanuginosa, Penicillium roqueforti, Chromobacterium viscosum, Candida cylindracea, and Candida rugosa. In one embodiment, the selective lipase(s) are naturally present in the microorganism. In another embodiment,
one or more organisms, such as microorganisms, are genetically engineered to express or overexpress the 1,3-selective lipase(s).

[0012] The amount of enzyme in the formulation is from about 0.00005% to 1.0%, preferably from 0.001% to 0.5% by weight of dry pulp. In one embodiment, the dosage of the lipase(s) is about 0.001 lbs to about 15 lbs per ton of oven dried pulp (o.d. pulp), preferably from about 0.02 to about 10 lbs/ton o.d. pulp, more preferably from about 0.02 to about 5 lbs/ton o.d. pulp, most preferably from about 0.1 to about 3 lbs/ton o.d. pulp. The enzyme formulations can contain one or more additives, such as dispersants, surfactants, metal ions, cationic polymers, and combinations thereof, which serve to stabilize the enzyme and/or modify enzyme activity.

[0013] The final formulations can be produced in the form of a liquid, gel, or solid. The enzymes can also be immobilized in a solid or gel substrate to increase the stability of the enzyme and/or to increase the number of cycles of use. In one embodiment, the enzyme formulation is applied as a solution to the pulp stock.

[0014] The enzyme treatment is effective at a wide range of temperatures, for example between about 10°C to about 95°C, more preferably from about 30°C to about 75°C. The pH of the pulp stock is from about 3.0 to about 11.0, more preferably from about 4.5 to 7.5. The pH of the stock can be adjusted using a pH modifying agent. Exemplary pH modifying agents include, but are not limited to, alum, sodium aluminates, sulfuric acid, or sodium hydroxide. The pulp can be treated for a period of time from about 0.1 to 36 hours, more preferably from about 0.5 to about 12 hours. The consistency of the pulp stock to be treated is typically between about 0.1% and 35%, more preferably between 0.5% and 10%

[0015] The enzyme formulations can be applied at one or more various points during the pulping and paper manufacturing processes. Suitable locations include, but are not limited to, the latency chest, reject refiner chest, disk filter or decker feed or accept, pulp loop whitewater system; the low density (“LD”) chest, which is a storage chest for pulp; the medium density or consistency chest (MC), which is another storage chest for pulp; the high density (“HD”) chest, which is another storage chest for pulp; the decker, which thickens the pulp; the blend chest; the machine chest; the headbox, which is the location just before the paper machine where the stock is prepared for the paper making process; the paper machine (“PM”) itself where the paper is actually made; the white water system; and combinations thereof.

[0016] The enzyme-based treatments can be used to reduce pitch deposition in mechanical pulps such as thermomechanical pulps and groundwood pulps; chemical pulps such as chemo-thermomechanical pulps and Kraft pulps, and pulps produced from recycled paper. Examples of recycled paper include, but are not limited to, old corrugated containers (OCC), old newspaper (ONP), mixed office waste (MOW), old magazine (OMG), and combinations thereof.

[0017] 1,3-selective lipase(s) catalyze the hydrolysis of the terminal ester groups, leaving the internal ester group intact, resulting in a 35% decrease in the concentration of fatty acids when reacted with triglycerides compared to reaction of triglycerides with non-selective lipases. As discussed above, high fatty acid concentrations can adversely affect pulp and paper machine runnability as well as pulp and paper quality. High fatty acid concentrations are also difficult to disperse and fix to surfaces, such as alum, making it more difficult to remove them from pulp and paper making processes.

[0018] A further advantage of the use of 1,3-selective lipases is the production of monoglycerides. Monoglycerides are strong dispersants and emulsifiers for fatty acids and soaps, reducing the amount of fatty acid soap deposition on pulp and paper making machinery. Therefore, the use of selective lipase(s) not only decreases the total concentration of fatty acids in the system, but forms monoglycerides, which are more effective at dispersing fatty acids than glycerol, the product of non-selective lipases.

[0019] The Examples show that non-selective lipase products, such as EnzOx® PC, produce a much higher amount of pitch deposition than formulations containing 1,3-selective lipases. Extensive studies were conducted to analyze the chemical composition of the deposits produced in the lab tests and at various paper mills that had applied the non-selective enzyme treatments. It was found that the deposits contain mostly aluminum and calcium soaps of fatty acids, produced from reactions between aluminum and calcium ions and fatty acids generated from the hydrolysis of triglycerides by non-selective lipolytic enzymes. In comparison, in the formulation containing 1,3-selective lipase(s) produced much less deposits, even lower than the control (i.e., without an enzyme treatment). The use of selective lipase(s) decreases the total concentration of fatty acids in the system due to the selective hydrolysis of triglycerides and converts triglycerides to monoglycerides which effectively disperses pitch, and thus prevents the deposition of fatty acids and their metal soaps.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIG. 1 is a graph showing the relative pitch deposition (percent paddle deposition) as a function of enzyme formulation from a blend of thermomechanical pulp and old newspaper stock from a newsprint mill. The control is no enzyme treatment. EnzOx® PC is a commercial pitch control product containing non-selective lipases. Formulations A-E are enzyme formulations containing one or more 1,3-selective lipases obtained from different microorganisms.

[0021] FIG. 2 is a graph showing the relative pitch deposition (percent paddle deposition (dark bars) and percent bow deposition (striped bars)) as a function of enzyme formulation from a blend of thermomechanical pulp and old newspaper stock from a newsprint mill. The control is no enzyme treatment. EnzOx® PC is a commercial pitch control product containing non-selective lipases. EnzOx® SEL is a commercial pitch control formulation containing one or more 1,3-selective lipases.

[0022] FIGS. 3A-3C are graphs comparing the paper strength made from pulps treated with no enzyme, non-selective lipase(s), and 1,3-selective lipase(s). FIG. 3A compares the tear index (mN*m²/g) as a function of enzyme formulation. FIG. 3B compares the tensile index (mN/g) as a function of enzyme formulation. FIG. 3C compares the burst index (kPa*m²/g) as a function of enzyme formulation. The control is no enzyme treatment.

[0023] FIG. 4 is a graph comparing the release of fatty acids (free fatty acid content, % oven dried (o.d.) fiber) from a thermomechanical pulp stock when treated with non-selective lipase(s) (EnzOx® PC) and selective lipase(s) (EnzOx® SEL) as a function of enzyme dosage (ppm).

[0024] FIG. 5 is a graph comparing the release of glycerol (total glycerol content, % oven-dried (o.d.) fiber) from a thermomechanical pulp stock treated with non-selective
lipase(s) (EnzOx® PC, SEL) and selective lipase(s) (EnzOx® SEL) as a function of enzyme dosage (ppm).

Fig. 6 is a graph comparing the release of glycerol (total glycerol content, % o.d. fiber) from a thermomechanical pulp stock treated with non-selective lipase(s) (EnzOx® PC SEL) and selective lipase(s) (EnzOx® SEL) as a function of alum dosage (lbs/ton of oven dried fibers).

DETAILED DESCRIPTION OF THE INVENTION

I. Definitions

"1,3-selective lipase(s)" and "1,3-specific lipase(s)" are used interchangeably and refer to a lipase or mixture of lipases that specifically hydrolyze the ester bonds at the C1 and/or C3 positions of triglycerides and diglycerides, yielding one or more two moles of fatty acids and one mole of monoglyceride.

"Pitch deposits" as used herein, refers to a composition composed of low molecular weight olephilic materials (primarily triglycerides, resin acids, fatty acids, waxes, resin esters, fatty alcohols, sterols, and terpenes), as well as pectins, lignans, and phenolic compounds, which are released from wood fibers during chemical and mechanical pulping processes. Some of these resinous substances precipitate as aluminum, calcium and magnesium salts, causing problems with the wet end components of paper machines and affecting paper quality.

"Mechanical pulp" refers to pulp produced by reducing pulpwood logs and chips into fiber components by the use of mechanical energy. Examples include, but are not limited to, stone groundwood pulp, pressurized groundwood pulp and thermomechanical pulp.

"Stone groundwood pulp" or "SGW" as used herein, refers to pulp which is produced by grinding wood into relatively short fibers with stone grinding. This pulp is used mainly in newspaper and wood-containing papers, such as lightweight coated (LWC) and super-calendered (SC) papers.

"Pressurized groundwood pulp" or "PGW" refers to pulp produced by a stone grinder where the whole grinder casing is pressurized and increased shower water temperature is used.

"Thermomechanical pulp" or "TMP" as used herein, refers to pulp that is produced in a thermo-mechanical process where wood chips or sawdust are softened by steam before entering a pressurized refiner. TMP generally has the same end-uses as stone groundwood pulp.

"Semi-chemical pulp" as used herein, refers to pulp produced by a combination of some chemicals (less than those used in Kraft pulping) and unpressurized mechanical processes. A variety of this pulp with pretreated chips at a temperature over 100°C, followed by refining at atmospheric pressure is called "semi-chemical mechanical pulp" or "SCMP". This pulp has properties suitable for tissue manufacture.

"Chemo-Thermomechanical Pulp" or "CTMP" as used herein, refers to mechanical pulp produced by treating wood chips with chemicals (usually sodium sulfite) and steam before mechanical defiberization.

"Recycled pulp" or "recycled fibers" refers to fiber component of a paper or paperboard furnish that is derived from recycled paper and paperboard or waste paper.

II. Methods for the Enzymatic Treatment of Pulp Stocks

Methods of treating a pulp stock with an enzyme formulation containing one or more 1,3-selective lipases, to reduce pitch deposition, control pitch related problems, modify the physical and/or chemical properties of tri-, di-, and mono-glycerides, fatty acids, resin acids, esters of fatty acids and resin acids, and metal soaps of fatty acids and resin acids, or change the concentration of triglycerides, fatty acids, resin acids, and esters of fatty acids and resin acids, are described herein. The enzyme formulations can be used to treat pulp stocks produced by mechanical pulping techniques such as thermomechanical pulping ("TMP"), groundwood pulping ("GW/P"), and stone groundwood pulping ("SGW"), chemical pulping techniques such as chemo-thermomechanical pulping and Kraft pulping; and stocks produced from recycled fibers.

A. Enzymes

1. 1,3-Selective Lipases

The enzyme formulations described herein contain one or more 1,3-specific lipases. 1,3-selective lipases catalyze the selective hydrolysis of one mole of triglycerides to form one mole of monoglyceride and two moles of fatty acids when reacted with triglycerides. The hydrolysis of triglycerides using 1,3-selective lipases is illustrated below:
[0040] 1,3-specific lipase(s) catalyze the hydrolysis of the terminal ester groups, leaving the internal ester group intact. Hydrolysis of triglycerides (the most abundant component on pitch in mechanical pulping processes) with 1,3-selective lipases results in a 33% decrease (a 50% decrease for diglycerides) in the concentration of fatty acids, compared to hydrolysis of triglycerides with non-selective lipases. As discussed above, high fatty acid concentrations can adversely affect pulp and paper machine runnability as well as pulp and paper quality. For example, fatty acid deposition can result in holes in the finished paper, adversely affecting paper quality. High levels of fatty acids are also difficult to disperse and fix to fiber surfaces using cationic fixatives (such as alum) making it more difficult to remove them from the pulp and paper making processes. Moreover, the product of hydrolysis of triglycerides with selective lipases, monoglyceride, is an excellent dispersant of fatty acids and fatty acid soaps and reduces the agglomeration of fatty soaps and thus the amount of fatty soap deposition in the system.

[0041] 1,3-selective lipases can be isolated from a variety of different organisms, primarily microorganisms. Suitable microorganisms include, but are not limited to, *Rhizopus oryzae*, *Rhizopus delenar*, *Rhizopus arrhizus*, *Rhizopus niveus*, *Aspergillus niger*, *Pseudomonas alcaligenes*, *Pseudomonas fragi*, *Pseudomonas cepacia*, *Mucor miehei*, *Humicola lanuginosa*, *Penicillium roqueforti*, *Chromobacterium viscosum*, *Candida cylindracea*, and *Candida rugosa*. These organisms can also contain non-selective lipases. One of ordinary skill in the art can determine whether a particular enzyme is selective or non-selective upon isolation from the microorganism using techniques known in the art.

[0042] The 1,3-selective lipase enzymes can be produced naturally by the microorganism. Alternatively, the selective lipases can be produced by a microorganism through genetic engineering technologies. An organism, such as a microorganism, can be genetically engineered to express or overexpress one or more 1,3-selective lipases. In one embodiment, the enzyme can be encoded and expressing the 1,3-selective lipases are inserted into another organism, such as a microorganism, which will produce the enzyme or enzymes more efficiently. For example, a 1,3-selective lipase gene from *Rhizopus delenar* can be inserted into *E. coli* to produce the selective enzyme(s) more efficiently (Joergner and Haas, 1993, *Lipids*, Vol. 26, no. 2 p 81-88). The enzymes can be isolated from the microorganism and purified using techniques known in the art. In one embodiment, the enzyme is Palatase® (Novozymes AB, Denmark) and/or Newlase F (Ammo Enzymes Inc., Japan).

[0043] The amount of enzyme is from about 0.0001 lbs to about 15 lbs per ton of oven dried pulp (o.d. pulp), preferably from about 0.02 to about 10 lbs/ton o.d. pulp, more preferably from about 0.02 to about 5 lbs/ton (o.d. pulp), most preferably from about 0.1 to about 3 lbs/ton o.d. pulp. The dose of the enzyme ranges from 1 to 2000 ppm based on O.D. fibers. The final concentration of the enzyme formulation is in the range of 0.005% to 0.5%, preferably 0.01% to 0.2% based on O.D. fibers.

[0044] The final formulations can be produced in the form of a liquid, gel, or solid. The enzymes can also be immobilized in a solid or gel substrate to increase the stability of the enzyme and/or to increase the number of cycles of use. In one embodiment, the enzyme is applied to the pulp as a solution or suspension.

[0045] 2. Other Enzymes

[0046] In addition to the 1,3-selective lipases, the formulations can contain one or more additional enzymes. Other enzymes including, but not limited to, amylases, pectinases, cellulases, hemicellulases, phospholipases, polysaccharidases, laccase, and lipoxygenases, can be added to the formulation to increase the performance of the 1,3-selective lipases. Cellulase, xylan and pectin materials from certain plants have been shown to inhibit lipase activities (Dunaif and Schneeman, 1981, *American Journal of Clinical Nutrition*, Vol. 34, pp 1034-1035; Edashige et al., 2005, *Journal of Nutrition Science and Vitaminology*, Vol. 54, pp 409-415). Pectinase and xylanase has also been shown to increase the performance of lipases.

[0047] B. Dispersants

[0048] The formulation may include one or more dispersants, such as surfactants and/or polymers. Suitable dispersants include, but are not limited to, primary and branched alkoxyates, fatty acid alkoxyates, phosphate esters and their salts, alkylphenol alkoxyates, block copolymers of ethylene and propylene oxide, alkane sulfonates, olefin sulfonates, fatty amine alkoxyates, glycercide alkoxyates, glycerol ester alkoxyates, sorbitan ester alkoxyates, polyethylene glycol esters, polyalkylene glycols, polyacrylic acids, sodium polycrylicate, acrylic acid copolymers, acrylate copolymers, acrylic crosslinked copolymers, and their derivatives; maleic acid and acrylic acid or acrylate copolymers, maleic acid/olefin copolymers, and their derivatives; polyvinyl alcohol/polyvinyl acetate copolymers, polyvinyl pyrrolidone and copolymers thereof, and combinations thereof.

[0049] Commercially available polymers include, but are not limited to, Surfonic® N-95, a nonyl phenol ethoxylated surfactant available from Huntsman; Phuronic® F-108, a block copolymer polyoxyalkylene derivative of propylene glycol available from BASF; Igepal, and Tanol 731, a sodium salt of maleic anhydride and disobutylene available from Rohm and Haas; Sokalan CP series and Acusol Series products available from BASF; polyvinyl alcohol/polyvinyl acetate copolymers; Cerov™ 540 available from Celanese Chemicals and Luavtech K series polymers, such as Luavtech K30 and Luavtech K80 available from BASF.

[0050] Examples of copolymers containing vinyl pyrrolidone include, but are not limited to, poly(vinylalcohol-co-vinylpyrrolidone), poly(vinylacetate-co-vinylpyrrolidone), vinylpyrrolidone-vinylimidazolone copolymers, vinylpyrrolidone-vinylcaprolactam copolymers, alkylated PVP, vinylpyrrolidone-polystyrone latex copolymers, vinylpyrrolidone-alkylaminomethacrylate copolymers, vinylpyrrolidone-allylamidopropyl trimethyl ammonium copolymers, vinylpyrrolidone-alpha-olefin copolymers, vinylpyrrolidone-methylvinylimidazolium chloride copolymers, and vinylpyrrolidone-acrylic acid/huyl methacrylate terpolymers.

[0051] The concentration of the dispersant(s) is from about 1% to about 90% by weight of the formulation, more preferably from about 1% to about 20% by weight of the formulation. The application dosage is from about 0.005 lbs/ton to about 20 lbs/ton of solid based on the oven-dried weight of stock fibers, preferably from about 0.025 to about 1.0 lbs/ton. They may be added alone or together with the selective lipase(s) at the same addition locations or separately at different locations.
C. Cationic Enzyme Stabilizers and Fatty Acid Fixatives

The addition of metal ions and/or cationic polymers to the pulp prior to enzyme treatment can stabilize the enzyme formulation and/or increase the rate of the enzymatic reactions at higher temperature and broader pH ranges. This enhances the effectiveness of the enzyme formulation in removing extractives such as long chain triglycerides whose conversion is favored thermodynamically at higher temperatures. The cations and/or cationic polymers can be added at the same time and at the same location as the selective lipase(s) or at different times and/or different locations.

Suitable metal ions include, but are not limited to, aluminum, calcium, magnesium, iron, copper, zinc, titanium, and zirconium. The aluminum ions can be provided by any aluminum salt that is soluble or partially soluble under the conditions of the mill processes. In a preferred embodiment, the aluminum ion is provided by Papermaker’s alum. Preferably, aluminum sulfate or aluminum chloride is used to provide the aluminum salt. Calcium chloride, magnesium chloride, zinc sulfate, copper sulfate, iron sulfate or chloride, titanium chloride, and zirconium sulfate can also be used.

Water soluble polymers, such as cationic water soluble polymers, can be used to stabilize the enzyme formulation and increase the enzyme’s catalytic activity. Examples of such polymers include, but are not limited to, epichlorohydrin/dimethylamine polymers (EPI-DMA) and cross-linked solutions thereof, polydimethyl dimethyl ammonium chloride (DADMAC), polyethyleneimine (PEI), hydrophobically modified polyethyleneimine, polyamines, resin amines, polyacrylamide, DADMAC/acrylamide copolymers, and ionene polymers. Examples of ionene polymers include those set forth in U.S. Pat. Nos. 5,681,862, 5,575,993, and 5,256,252. The polymers can be used in any amount and preferably in dosage ranges from about 0.1 to about 10 lbs per ton based on O.D. fibers, more preferably from about 0.5 to about 5 lbs/ton based on O.D. fibers.

Metal ions or cationic polymers are added to the stock at a range from 0.025% to 3.0% by weight, and more preferably 0.5-1.2% by weight based on O.D. fibers. The enzyme solutions can be added to the stock at the same time as the metal ions and/or cationic polymers or after addition of the metal ions and/or cationic polymers. Alternatively, the compositions containing the 1,3-selective lipase(s) can be formulated with metal ions and/or cationic polymers before the enzyme is added to pulp stocks.

III. Methods of Treatment

The methods described herein may be used with any pitch-containing pulp, particularly with pulps with a considerable content of triglycerides and other esters. Exemplary pulps include mechanical pulps, such as thermomechanical pulps and groundwood pulps; chemical pulps such as chemothermomechanical pulps and kraft pulps; and pulps produced from recycled paper.

The addition points of enzyme formulations can be at any one of or various locations during the pulping and paper manufacturing processes. Suitable locations include, but are not limited to, latency chest, reject refiner chest, disk filter or Decker feed or accept, whitewater system, pulp stock storage chests (either low density (“LD”), medium consistency (MC), or high consistency (HC)), blend chest, machine chest, headbox, saveall chest, paper machine whitewater system, and combinations thereof. In one embodiment, the enzyme formulations are generally added to the pulp chests, preferably together with metal ions or cationic polymers at a place where sufficient mixing and retention/reactions times are available. However, metal ions and/or cationic polymers can also be added to the mill whitewater systems prior to, or after, the enzyme addition.

The enzyme formulation is typically applied as a solution to the pulp stock. The enzyme treatment is effective at a temperature of between about 10° C. to about 95° C., more preferably from about 30° C. to about 75° C. The pH of the pulp stock is from about 3.0 to about 11.0, more preferably from about 4.0 to 7.5. The pH of the stock can be adjusted using a pH modifying agent, such as alum or aluminates.

The consistency of the pulp stock to be treated is typically between about 0.1% and about 35%, more preferably between about 0.5% and about 10%. The pulp can be treated for a period of time from about 0.1 to about 36 hours, more preferably from about 0.5 to about 12 hours.

The addition of metal ions and/or cationic polymers to the pulp prior to enzyme treatment can stabilize the enzyme formulation and/or increase the rate of the enzymatic reactions at higher temperature and broader pH ranges. This enhances the effectiveness of the enzyme formulation in removing extractives such as long chain triglycerides whose conversion is favored thermodynamically at high temperatures. The cations and/or cationic polymers can be added at the same time and at the same location as the selective lipase(s) or at different times and/or different locations.

The effectiveness of the enzyme treatment can be determined by measuring the triglyceride (TG) content in a wood pulp sample at various locations in the pulping and papermaking processes using the triglyceride assay method described in U.S. Pat. No. 7,067,244 by Jiang et al.

IV. Kits

The one or more 1,3-selective enzymes can be packaged in a kit. In one embodiment, the one or more selective enzymes are provided in a container. The enzymes can be formulated as a solution, suspension, semi-solid (gel) or solid. The enzyme formulations may contain one or more additives, such as solvents, dispersants, surfactants, metal ions, polycationic materials, and combinations thereof. Alternatively, the one or more additives can be packaged separately, in one or more additional containers, and can be added to the enzyme formulations prior to use. In another embodiment, the additives are packaged separately and are added to the pulp separately from the enzymes. The kit may further contain instructions for preparing and using the enzyme formulations as well as equipment or devices for preparing or administering the formulations, such as syringes, cannulas, spatulas, and the like.

EXAMPLES

Mechanical Pulp Stock Preparation

Several mechanical pulp (TMP) samples were collected from different mills located in the southeast United States. The fiber consistency of the pulp was generally between 8% and 13% based on o.d. (oven dry) fiber. The pulp samples were stored at 48° C. prior to testing.

Test Methods for Quantification of Pitch Deposition

A Stand Mixer with coated flat beaters, such as the Commercial 5 series from KitchenAid®, was used to determine the effect of enzyme formulations on the amount of
pitch deposits on the beaters. The stainless steel mixing bowls were used to hold fiber stocks having a consistency from about 3% to about 20%, preferably from about 8% to 10% and the mixing temperature was controlled with a water jacket. The mixture temperature was maintained at a temperature from about 25°C to about 95°C, preferably from about 50°C to about 70°C. In the examples below, the temperature was maintained at 60°C.

100-200 g oven dried fibers were weighed out and added to the mixing bowl. The pulp stocks were mixed at a mixing speed between “1” and “4”, preferably “2”. The stocks were mixed for a period of time ranging from about 5 minutes to about 10 hours, preferably from about 20 minutes to about 3 hours. The pH of the stock was adjusted, as needed, to about 5. The enzyme formulation was added to the mixing bowl and mixed for 1 hour. The pulp stock was allowed to cool to room temperature and then mixed for an additional 30 minutes. The amount of pitch deposit on the beaters from the control (i.e., with no enzyme formulation treatment) was visually determined and compared to that of the enzyme treatments by percentage based on the amount of deposition on either the paddle surfaces or on the inside surface of the bowls. Alternatively, the beaters could be weighed to determine the difference in the pitch deposition.

Test Method for Measuring Handsheet Strength

The stock was prepared according to TAPPI T262 before enzymatic treatment. Specifically, the TMP pulp samples were first disintegrated for 20 minutes in a Lorenzont & Wetter disintegrator. The pulp stock of 50 g (o.d.) was conditioned in a Kitchen Aid mixer with and without an enzyme formulation at 3.5% for 60 minutes at 55°C. The enzymatic treatments were conducted at pH 5.2 (using sodium acetate as buffer). The enzyme dosage is expressed in ppm based on oven-dried (o.d.) fibers. The stock was then diluted to 0.3% with cold tap water after treatment for the preparation of handsheets.

The above conditioned or treated pulp stock was used to prepare handsheets according to TAPPI T240 standard procedure. For each condition, 12 handsheets of base weight at 60.0 g/m² were made according to TAPPI T205. The handsheets were conditioned according to TAPPI T402 and then tested for strength according to TAPPI T414, T494 and T403. The tensile, burst and tear strength indexes were measured.

Methods for Measuring Enzyme Reactivity and Selectivity

The pulp was diluted to 1% consistency (based on o.d. fiber) to a total volume of 100 ml using distilled water. The pulp was preheated to a pre-determined temperature (45-90°C) in 150 ml Belco glass flasks. An immersion stir plate was used to ensure that the reaction flasks were well mixed while the reaction was taking place. Prior to addition of the enzyme(s), the reaction flasks were allowed to equilibrate to the temperature of the water bath for 30 minutes. Once the reaction flasks equilibrated, the enzyme formulations were added to the reaction flask and the reaction was allowed to proceed with constant agitation. After a certain period of incubation, samples were taken and immediately cooled in ice water to stop the enzyme reaction. The various chemical contents were determined.

In tests which require an aluminum-free stock, the pulp sample was washed with a diluted sulfuric acid to remove residual aluminum ions from the stock. The stock was then rinsed with deionized water and the pH was adjusted to about 5.2.

Enzyme Formulations

EnzOx® PC and EnzOx® SEL are two lines of pitch control products marketed by Enzymatic Deinking Technologies, LLC, Norcross, Ga. 30093. EnzOx® PC contains non-selective lipases, including Resinase A2X, marketed by Novozymes A/B, Denmark. The percentage of Resinase A2X varies from 1 to 99%, preferably from 10 to 85%. EnzOx® SEL contains one or more 1,3-selective lipases, including Palatase® Novozymes AB, Denmark) and Newlase F (Amino Enzymes Inc., Japan). The percentage of Palatase® and Newlase F varies from 1 to 99%, preferably from 10 to 85% by weight.

Example 1

Comparative Deposition of Selective Lipases from Different Microorganisms

Representative stock samples of TMP secondary refiner accept with a consistency around 50% and recycled newsprint (RNP) with a consistency 3-4% were taken from a southern U.S. newspaper mill and used for the experiments. The pH of the stocks ranged from about 4.5 to 5.5, and alum and sodium aluminate solutions were used to maintain the pH at around 5.2. The experiments were performed using the procedures described above. The control was treated with 6 lbs/ton total alum equivalent and no enzyme was used.

The paddle and bowl deposition resulting from the treatment with 2 lbs/ton of EnzOx® PC, which is a non-selective lipase product, were normalized to 100%. The deposition of the control and other treatments were evaluated relative to EnzOx® PC treatment and deposition. The dosage of the experimental products of selective lipases A, B, C, D and E were based on equivalent protein weight.

FIG. 1 shows the relative pitch deposition of the control and the various enzyme treatments. As shown in FIG. 1, the non-selective lipase product, EnzOx® PC, produced a much higher amount of deposition than the control. Extensive studies were conducted to analyze the chemical composition of the deposits produced in the lab tests and at various paper mills that had applied the non-selective enzyme treatments. It was found that the deposits are mainly aluminum and calcium scabs of fatty acids, produced from reactions between aluminum and calcium ions and fatty acids generated from the hydrolysis of triglycerides by the enzymes. In comparison, the selective lipases (Formulations A, B, C, D and E) produced much less amounts of deposits, even lower than the control (i.e., without an enzyme treatment). The results clearly demonstrate that the formulations described herein are more advantageous than non-selective lipase formulations.

Example 2

Comparative Results of Various Treatments on Paper Properties

The effects of the non-selective lipase treatment and the selective lipase treatment on paper strength properties were evaluated. The testing methods and pulp stock preparation are described above. A 0.5 M acetate buffer was added to the stocks to maintain the pH in the range of 5.0-5.5. The stock was treated with 25 lbs/ton total alum equivalent. After
the stock was mixed for 5 minutes, an enzyme solution (or water for the control) was added to the mixing bowl and mixed for 60 minutes. The amount of pitch deposit on the paddles and bowl surface was visually determined and compared to the control. The control was normalized to 100%, and the various enzyme treatments were evaluated relative to the control.

The results are shown in FIG. 2. EnzOxi® PC, the non-selective lipase treatment, produced about 250%-300% more deposits compared to the Control. In contrast, EnzOxi® SE, the selective lipase treatment, gave about the same amount of deposits as the Control. The deposition results again confirmed that the selective lipase treatment is more effective than non-selective lipase treatment in decreasing pitch deposition. Reducing pitch deposition improves machine runnability and paper quality.

FIG. 3 compares the paper strength properties. It can be seen that compared to the Control, both EnzOxi® PC (the non-selective lipase treatment) and EnzOxi® SE (the selective lipase treatment) significantly increased the tensile (FIG. 3A), tear (FIG. 3B) and burst (FIG. 3C) indices of the paper. The tear, tensile, and burst indices were comparable for the two enzyme treatments.

Example 3

Quantification of Triglyceride Hydrolysis and Fatty Acid Release

In the non-selective lipase treatment, the enzymes hydrolyze triglycerides to glycerol and fatty acids. For each mole of triglyceride, three moles of fatty acids and one mole of glycerol are produced. In contrast, selective lipases hydrolyze triglycerides into monoglycerides, with reduced production of fatty acids and no formation of glycerol. Thus, for each mole of triglyceride, only two moles of fatty acids are generated. Therefore, the selective lipase treatment produces smaller amounts of fatty acids and poses less risk of fatty soap deposition in paper mills.

FIG. 4 compares the total amounts of free fatty acid released by the two different lipase enzyme treatments without the addition of alum. The results demonstrate that the amount of the free fatty acids generated by the non-selective lipase product is much greater than that of the selective lipase product under the same dosage conditions.

FIG. 5 compares the total amounts of glycerol released by the two different enzyme treatments without the addition of alum. FIG. 5 shows that the non-selective lipase treatment yields high amounts of glycerol. In contrast, the selective lipase treatment generated little glycerol content. As discussed above, monoglycerides is a much more effective dispersant of fatty acids/fatty acids soaps than glycerol.

Example 4

Modification of Enzyme Activity by Metal Ions

Metal ions can be used to modify enzyme activity. The effect of alum concentration on the activity of selective and non-selective lipases was investigated. Stocks and enzyme formulations were prepared as described above. FIG. 6 compares the total amounts of glycerol released by the two enzyme treatments in the presence of various amounts of alum. It can be seen that the addition of alum increases the production of glycerol for both the selective and non-selective lipase enzymes. For selective lipases, increasing amounts of alum decreases the selectivity of the enzymes, particularly at high doses.

Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of skill in the art to which the disclosed invention belongs. Publications cited herein and the materials for which they are cited are specifically incorporated by reference.

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims.

We claim:

1. A method for controlling pitch in the production of pulp or paper, the method comprising contacting the pulp with an enzyme composition comprising one or more 1,3-selective lipases.

2. The method claim 1, wherein the one or more 1,3-selective lipases, are isolated from one or more bacteria selected from the group consisting of Rhizopus oryzae, Rhizopus delemar, Rhizopus arrhizus, Rhizopus niveus, Aspergillus niger, Pseudomonas alcaligenes, Pseudomonas fragi, Pseudomonas cepacia, Macroc miehei, Humicola lanuginosa, Penicillium roquefort, Chromobacterium viscosum, Candida cylindracea, and Candida rugosa.

3. The method of claim 1, wherein the one or more 1,3-selective lipases are isolated from an organism that has been genetically engineered to express or overexpress the one or more 1,3-selective lipases.

4. The method of claim 1, wherein the dosage of the lipase (s) is from about 0.02-10 lbs/ton of oven dried pulp.

5. The method of claim 4, wherein the dosage of the lipase (s) is from about 0.02-5 lbs/ton of oven dried pulp.

6. The method of claim 4, wherein the dosage of the lipase (s) is from about 0.1-3 lbs/ton of oven dried pulp.

7. The method of claim 1, wherein the method further comprises contacting the pulp with one or more dispersants, surfactants, absorbents, adsorbents, or combinations thereof.

8. The method of claim 7, wherein the one or more dispersants, surfactants, absorbents, adsorbents, and combinations thereof are contact with the pulp at the same time as the enzyme composition or at a different time than the enzyme composition.

9. The method of claim 7, wherein the dispersant is selected from the group consisting of primary and branched alkoxylates, fatty acid alkoxylates, phosphate esters and their alkoxylates, alkylphenol alkoxylates, block copolymers of ethylene and propylene oxide, alkane sulfonates, olefin sulfonates, fatty amine alkoxylates, glyceroxy alkoxyates, glycerol ester alkoxyates, sorbitan ester alkoxyates, polyethylene glycol esters, polyalkylene glycols, polycrylic acids, sodium polyacrylate, acrylic acid copolymer, acrylate copolymer, acrylic crosslinked copolymer, and their derivatives; maleic acid and acrylic acid or acrylate copolymer, maleic acid/olefin copolymer, and their derivatives, polyvinyl alcohol/polyvinyl acetate copolymers, polyvinyl pyrolidone and copolymers thereof, and combinations thereof.

10. The method of claim 9 wherein the concentration of the dispersant is from about 0.001 to about 10 kilograms/ton of pulp.
11. The method of claim 10 wherein the concentration of the dispersant is from about 0.004 to about 3 kilograms/ton of pulp.

12. The method of claim 9 where the polyvinyl pyrrolidone and copolymers thereof have a molecular weight between 7,000 to 2,500,000 daltons, more preferably between 400,000 and 2,000,000.

13. The method of claim 9 wherein the polyvinyl alcohol/polyvinyl acetate copolymers have a molecular weight between 5,000 and 500,000 daltons, more preferably between 50,000 and 150,000, and a hydrolysis degree between 50% and 100%, more preferably between 70% and 95%.

14. The method of claim 1, wherein the enzyme formulation further comprises one or more polycationic substances which modify the activity of the one or more 1,3-selective lipases.

15. The method of claim 14, wherein the one or more polycationic substances are selected from the group consisting of aluminum sulfate, sodium aluminate, poly(aluminum chloride), polyethyleneimine (PEI), poly-DADMAC, polyvinylpyrrolidone (PVP).

16. The method of claim 1, wherein the pulp stock is produced by a process selected from the group consisting of mechanical pulping, semichemical pulping, chemi-thermo-mechanical pulping, bleached Kraft pulping and recovered fiber pulping.

17. The method of claim 16 wherein the pulp is a mechanical pulp selected from the group consisting of groundwork pulp, pressed groundwork pulp and thermomechanical pulp.

18. The method of claim 1, wherein the pulp is derived from virgin fibers, recycled fibers, and combinations thereof.

19. The method of claim 18, wherein the recycled fibers are selected from the group consisting of old corrugated containers (OCC), old newsprint (ONP), mixed office waster (MOW), old magazines (OMG), and combinations thereof.

20. The method of claim 1, wherein the pulp is contacted with the enzymes at a location in the pulping process selected from the group consisting of the latency chest, reject reclaimer chest, disk filter or decker feed or acceptor, TMP whitewater system, the low density (“LD”) chest, the medium density or consistency chest (MC), the high density (“HD”) chest, the decker, the blend chest, the machine chest, the headbox, the paper machine (“PM”), the white water system, and combinations thereof.

21. The method of claim 1, wherein the formulation is maintained in the pulp stock at a temperature of about 10°C to about 95°C.

22. The method of claim 21 wherein the formulation is maintained in the pulp stock at a temperature of about 30°C to about 75°C.

23. The method of claim 1, wherein the pulp is contacted with the enzyme formulation at a pH from about 3 to about 11.

24. The method of claim 23, wherein the pulp is contacted with the enzyme formulation at a pH from about 4 to about 7.5.

25. An enzyme composition used in the method of claim 1, the composition comprising one or more 1,3-selective lipases.

26. The composition of claim 25, wherein the one or more 1,3-selective lipases, are isolated from one or more bacteria selected from the group consisting of Rhizopus oryzae, Rhizopus delemar, Rhizopus arrhizus, Rhizopus niveus, Aspergillus niger, Pseudomonas alcaligenes, Pseudomonas fragi, Pseudomonas cepacia, Mucor miehei, Humicola lanuginosa, Penicillium roqueforti, Chromobacterium viscosum, Candida cylindracea, and Candida lipolytica.

27. The composition of claim 26, wherein the one or more 1,3-selective lipases are isolated from an organism that has been genetically engineered to express or overexpress the one or more 1,3-selective lipases.

28. The composition of claim 25, wherein the composition further comprises one or more dispersants, surfactants, absorbents, adsorbents, or combinations thereof.

29. The composition of claim 28, wherein the dispersant is selected from the group consisting of primary and branched alkylxoyl fatty acid alkoxylates, phosphate esters and their alkoxylates, alkylphenol alkoxylates, block copolymers of ethylene and propylene oxide, alkanesulfonates, olefin sulfonates, fatty amine alkoxylates, glyceride alkoxylates, glycerol ester alkoxylates, sorbitan ester alkoxylates, polyethylene glycol esters, polyoxyethylene glycols, polyacrylic acids, sodium polycrylate, acrylic acid copolymer, acrylate copolymer, acrylic crosslinked copolymer, and their derivatives; maleic acid and acrylic acid or acrylate copolymer, maleic acid/olefin copolymer, and their derivatives, polyvinyl alcohol/polyvinyl acetate copolymers, polyvinyl pyrrolidone and copolymers thereof, and combinations thereof.

30. The composition of claim 25, wherein the enzyme composition further comprises one or more polycationic substances which modify the activity of the one or more 1,3-selective lipases.

31. The composition of claim 30, wherein the one or more polycationic substances are selected from the group consisting of aluminum sulfate, sodium aluminate, poly(aluminum chloride), polyethyleneimine (PEI), poly-DADMAC, polyvinylpyrrolidone (PVP).

32. A kit containing the composition of claim 23 and at least one container.

33. The kit of claim 32, further comprising instructions for administering the enzyme composition.

34. The kit of claim 32, further containing one or more additives selected from the group consisting of dispersants, surfactants, absorbents, adsorbents, or combinations thereof.

35. The kit of claim 34, wherein the one or more additives are in the same container as the enzyme composition.

36. The kit of claim 34, wherein the one or more additives are in one or more different containers than the enzyme composition.

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