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(54) **Chemical pulping process**

(57) The present invention claims the use of an oxy-alkylene-modified organopolysiloxane, in combination with an alkylated sulfonated diphenyloxide surfactant,

as chemical pulping additives. These pulping additives surprisingly improve the physical properties of wood pulp and products produced therefrom.

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Description

[0001] The present invention relates to additives useful for pulping wood chips. More particularly, the invention relates to the use of at least one oxyalkylene-modified organopolysiloxane and at least one alkylated sulfonated diphenyloxide surfactant as additives for digestive treatments of wood chips in aqueous cooking liquors.

[0002] Chemical pulping is the chemical processing of wood chips and the like to remove significant amounts of lignin therefrom. These can often be further subjected to bleaching and purification operations in a bleach plant, including further delignification of the pulp.

[0003] Lignin is the major noncarbohydrate constituent of wood and, prior to chemical pulping, usually comprises about one-quarter of the raw material, functioning as a binder for the cellulosic fibers. The lignin is dissolved by cooking liquor in the manufacture of wood pulp. The character of the pulp produced is dependent on the extent of lignin removal from the wood chips and hence on the residual lignin content of the final pulp.

[0004] Significant quantities of lignin are removed during chemical pulping to form the fibrous pulp. However, substantial quantities of lignin often remain after conventional chemical pulping processes are complete, generally 2 to 6 weight percent of the pulp. Chemically, lignin is a complex structure which varies depending on the species of wood and is characterized by the presence of repeating phenol propane units.

[0005] It is known that in the conventional methods for manufacturing wood pulp that the wood can be treated with a variety of chemicals such as alkaline earth metal salts, weak acids or sulfuric acid in an aqueous solution. These methods have several disadvantages, in particular the need to continue cooking the wood chips for 6 to 12 hours for the lignin digestion to be complete. In order to accelerate the delignification of the chips, it is necessary to operate at a temperature of 150°C. to 180°C. and under pressure of several atmospheres.

[0006] It is also known that in conventional methods of chemical pulping, wood can be treated with chemicals such as anthraquinone and anthraquinone derivatives in an aqueous solution.

[0007] It has also been disclosed that surface active agents can be used in the production of wood pulp by the sulfate pulp process. For example, Parker et al. in U.S. Patent No. 3,909,345, teach that surface active agents having the general formula $R\{(C_2H_4O)_n(C_3H_6O)_m\}_yH$ wherein R is the nucleus of a reactive hydrogen compound selected from various glycols, diols, amines, piperazines, amides and acids, can be used as additives to sulfate cooking liquor for the purpose of obtaining higher yields of pulp from a given wood chip charge and that these agents permit a greater effectiveness of the cooking process relative to chips which prior to that invention were considered rejects and not pulvable.

[0008] Blackstone et al. in U.S. Patent No. 4,906,331 disclose that compounds having the general formula $HO(C_2H_4O)_a(C_3H_6O)_b(C_2H_4O)_cH$ where a, b and c have a value of at least one, increase the yield of chemical pulping processes and decrease the level of rejects. Chen et al. in U.S. Patent No. 4,952,277 disclose a process for making paper or linerboard, the process comprising cooking wood chips in a Kraft liquor to form a Kraft pulp, the liquor excluding anthraquinone and including a surface active agent having the general formula $C_nH_{2n+1}-C_6H_4-O(C_2H_4O)_xH$ where n is an integer from 8 to 12 and x is a positive integer from 1 to 100, the surface active agent being present in the cooking liquor in an amount effective to increase the yield of pulp. Ling et al. in U.S. Patent No. 5,250,152 teach a method for enhancing the penetration of cooking liquor into wood chips to form a Kraft pulp which comprises adding to the cooking liquor specific surfactants such as ethoxylated dialkylphenols and ethoxylated alcohols.

[0009] Pease in U.S. Patent No. 5,464,502 teaches a method for removing lignin and spent cooking chemicals from pulp which comprises adding, within the washing operation, from 0.1 to 1000 parts per million parts of pulp of an anionic sulfonate surfactant wherein the removal of lignin and spent cooking chemicals occurs at a temperature of from 30°-100°C.

[0010] It has also been disclosed that in chemical pulping processes which produce wood pulp that the wood can be treated with various silicones or siloxanes prior to addition to a digester unit or may be added directly to the digester before or after the digester has been filled with wood chips and liquor. For example, Simmons et al., in U.S. Patent No. 3,147,179, disclose that various silicones and siloxanes are useful as digestion aids in Kraft, soda or sulfite chemical pulping processes.

[0011] German Patent Application No. DE 4440186 discloses a process for obtaining pulp from fibrous materials in which organosilicon compounds such as oxyalkylene-modified organopolysiloxanes are added to the chemical pulping process, wherein the fibrous materials are reacted with a chemical pulping liquor in the presence of the organosilicon compounds.

[0012] WO 96/41915 discloses an improved pulping process which comprises contacting wood chips with a liquid mixture comprised of white liquor and at least one surfactant selected from the group consisting of a polymethylalkylsiloxane containing ethylene oxide and optionally propylene oxide groups, a co- and terpolymer of silicone and a polyhydric alcohol, an alkoxyated aryl phosphate, an alkoxyated branched alkyl phosphate, an alkoxyated branched alcohol, an alkyl polyglycoside, an alkoxyated alkyl polyglycoside, a mixture of alkali metal salts of alkyl aromatic sulfate, a sulfosuccinate and a silicone and combinations thereof for a residence time effective to extract resinous

components without substantial degradation of cellulose and thereafter heating at least a portion of the resulting mixture and wood chips. However, none of the references cited above disclose or suggest that the particular oxyalkylene-modified organopolysiloxanes of the present invention in combination with at least one alkylated sulfonated diphenyloxide surfactant would be useful as digestion aids in such chemical pulping processes.

[0013] The present invention relates to the use of at least one oxyalkylene-modified organopolysiloxane and at least one alkylated sulfonated diphenyloxide surfactant as additives for digestive treatments of wood chips in aqueous cooking liquors.

[0014] It has been discovered in chemical pulping processes which involve the digestion of wood chips in liquors that the subsequent properties of the wood pulp are improved if small amounts of at least one oxyalkylene-modified organopolysiloxane and at least one alkylated sulfonated diphenyloxide surfactant are added to the liquors employed in the digestive treatments.

[0015] Thus this invention relates to a chemical pulping process comprising the steps of: (I) forming a mixture comprising (A) wood chips, (B) an aqueous cooking liquor, (C) at least one oxyalkylene-modified organopolysiloxane, and (D) at least one alkylated sulfonated diphenyloxide surfactant, (II) heating the mixture of step (I) to a temperature of at least 150°C. for a period of time to substantially delignify the wood chips (A) so as to form a pulp therefrom, (III) maintaining the heated mixture of step (II) at a pressure to prevent boiling of aqueous cooking liquor (B) during step (II), and (IV) recovering the pulp from said mixture. It is an object of the present invention to increase pulp yield, lower the lignin content and improve the strength of the cooked, washed pulp in chemical pulping processes by the addition of at least one oxyalkylene-modified organopolysiloxane and at least one alkylated sulfonated diphenyloxide surfactant to wood chips, cooking liquor or a digester.

[0016] This invention relates to a chemical pulping process comprising the steps of: (I) forming a mixture comprising (A) wood chips, (B) an aqueous cooking liquor, (C) at least one oxyalkylene-modified organopolysiloxane compound having the formula $R^1R^2SiO(R^2SiO)_a(RXSIO)_bSiR^2R^1$ wherein R is a monovalent hydrocarbon group having from 1 to 20 carbon atoms, X is a polyoxyalkylene group selected from the group consisting of $-R^2(OC_2H_4)_cOR^3$, $-R^2(OC_2H_4)_c(OC_3H_6)_dOR^3$, $-R^2(OC_2H_4)_c(OC_4H_8)_eOR^3$, $-R^2(OC_3H_6)_d(OC_4H_8)_eOR^3$ and $-R^2(OC_2H_4)_c(OC_3H_6)_d(OC_4H_8)_eOR^3$, wherein R¹ is R or X, R² is a divalent group selected from hydrocarbon groups having from 1 to 20 carbon atoms and hydrocarbon groups containing oxygen, R³ is selected from a hydrogen atom, an alkyl group, an aryl group or an acyl group, a has an average value from 1 to 500, b has an average value from 1 to 500, and c, d and e independently have an average value from 1 to 150; and (D) at least one alkylated sulfonated diphenyloxide surfactant, (II) heating the mixture of step (I) to a temperature of at least 150°C. for a period of time to substantially delignify the wood chips (A) so as to form a pulp therefrom, (III) maintaining the heated mixture of step (II) at a pressure to prevent boiling of aqueous cooking liquor (B) during step (II), and (IV) recovering the pulp from said mixture.

[0017] The term "chemical pulp" as used herein, refers to the product of manufacture of wood pulp from raw wood primarily by chemical means. Chemical pulps are formed by the removal of lignin from raw wood by chemical action to form a fibrous pulp.

[0018] Wood chips (A) can be in the form of whole tree chips including bark, branches, hardwood chips, softwood chips, sawdust or combinations thereof. The wood chips can be prepared by a de-barking operation in which bark is removed from the logs and the logs are then shredded or cut into chips of suitable small size to facilitate their digestion. Whole tree chips do not need to be de-barked prior to shredding or chipping. The wood chips (A) of this invention may also be "presteamed". Presteamed wood chips are prepared by preheating the wood chips in a steaming vessel to drive out air and open the wood pores of the chips which allows the aqueous cooking liquor (B), described hereinbelow, to more easily penetrate into the wood. This steaming process can be carried out in a continuous cooking operation or in a batchwise fashion for batch digester operations.

[0019] The aqueous cooking liquor, Component (B), can be selected from the group consisting of Kraft cooking liquors, soda cooking liquors and sulfite cooking liquors. The aqueous cooking liquor (B) can also further comprise at least one ingredient selected from the group consisting of black liquor, polysulfide and anthraquinone-containing compounds. Thus a combination of two or more of these optional ingredients can also be used. The anthraquinone-containing compounds are exemplified by anthraquinone, anthraquinone-2-carboxylic acid, anthraquinone-1,5-disulfonic acid disodium salt hydrate, anthraquinone-2,6-disulfonic acid disodium salt and anthraquinone-2-sulfonic acid sodium salt monohydrate. It is believed that the addition of an anthraquinone-containing compound to the aqueous cooking liquor significantly contributes to the removal of lignin.

[0020] The Kraft cooking liquors generally comprise sodium hydroxide and sodium sulfide as the active cooking components of the liquor. It is preferred that the aqueous cooking liquor to wood ratio is from 2:1 to 6:1. The percentage of total active alkali in aqueous cooking liquor (B) depends on the species of wood to be pulped and on the desired degree of delignification of the wood. For example, if a "board" grade of pulp with moderate delignification is desired or a "bleaching" grade of pulp with as much delignification as possible without severe degradation to the cellulosic components is desired, the concentration generally varies from 12-25% total active alkali, and preferably from 10-30% as Na₂O based on the oven dry weight of the wood chips. The Na₂O represents both the amount of NaOH and Na₂S

to be used. The Na_2S used will furnish 15-25% of the total Na_2O while the remainder is furnished by NaOH . In actual plant practice, some of the aqueous cooking liquor may be circulated so that the total Na_2O content may include salts such as sodium carbonate, sodium hydrosulfate, sodium sulfate and sodium thiosulfate. This is due to the addition of some black liquor to the freshly prepared aqueous cooking liquor prior to its addition to the wood chips. The black liquor may comprise 10 to 50 percent of the aqueous cooking liquor added to a fresh charge of wood chips. The sulfide content of the aqueous cooking liquor (B) is expressed as sulfidity, i.e. the percentage ratio of Na_2S expressed as Na_2O , to the total active alkali is preferably from 10-40%.

[0021] As used herein to describe Component (C), the oxyalkylene-modified organopolysiloxane, it is understood that the various siloxane units and the oxyethylene, oxypropylene and oxybutylene units may be distributed randomly throughout their respective chains or in respective blocks of such units or in a combination of random or block distributions.

[0022] Those skilled in the art will appreciate that the term "oxyalkylene-modified organopolysiloxane compound," standing alone, encompasses a number of compounds, including those based upon cyclic, branched and resinous siloxane compounds. While cyclic, branched and resinous oxyalkylene-modified siloxanes can be used in combination with alkylated sulfonated diphenyloxide surfactants they are comparatively expensive and thus, are not as cost effective as the particular oxyalkylene-modified organopolysiloxane compounds used in accordance with the present invention.

[0023] In the above formula for Component (C), R is a monovalent hydrocarbon group having from 1 to 20 carbon atoms exemplified by alkyl groups such as methyl, ethyl, propyl, butyl, hexyl, octyl and decyl, cycloaliphatic groups such as cyclohexyl, aryl groups such as phenyl, tolyl and xylyl and aralkyl groups such as benzyl and phenylethyl. It is preferred that R is selected from methyl or phenyl. The several R radicals can be identical or different, as desired.

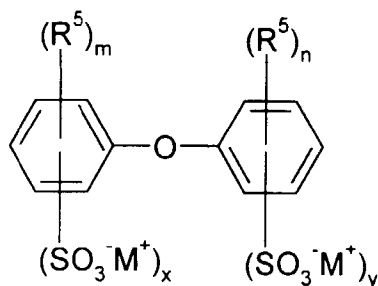
[0024] The group R^2 is a divalent hydrocarbon group having from 1 to 20 carbon atoms which is exemplified by alkylene groups exemplified by methylene, ethylene, propylene, butylene, pentylene, trimethylene, 2-methyltrimethylene, pentamethylene, hexamethylene, 3-ethyl-hexamethylene, octamethylene, $-\text{CH}_2(\text{CH}_3)\text{CH}-$, $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$, $-(\text{CH}_2)_{18}-$ and cycloalkylene radicals such as cyclohexylene, arylene radicals such as phenylene, combinations of divalent hydrocarbon radicals such as benzylene ($-\text{C}_6\text{H}_4\text{CH}_2-$), or R^2 is a divalent hydrocarbon group containing oxygen such as $-\text{CH}_2\text{OCH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2-$, $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$, $-\text{COOCH}_2\text{CH}_2\text{OOC}-$, $-\text{CH}_2\text{CH}_2\text{OCH}(\text{CH}_3)\text{CH}_2-$ and $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$. Preferred alkylene groups have from 2 to 8 carbon atoms.

[0025] The group R^3 can be a hydrogen atom, an alkyl group, an aryl group or an acyl group. The alkyl groups are exemplified by methyl, ethyl, propyl, butyl, hexyl, octyl and decyl. The aryl groups are exemplified by phenyl, tolyl and xylyl. The acyl group can have from 1 to 20 carbon atoms and include groups such as acetyl, propionyl, butyryl, isobutyryl, lauroyl, myristoyl and stearoyl 3-carboxypentadecanoyl. Preferably, the acyl group is a group having the formula $-\text{C}(\text{O})\text{R}^4$ wherein R^4 denotes a monovalent hydrocarbon group. The monovalent hydrocarbon groups of R^4 are as delineated above for R. It is preferred that R^4 is a lower alkyl group such as methyl, ethyl or butyl.

[0026] In the above formula for Component (C), preferably a has an average value from 20 to 500, b has an average value from 1 to 500, and c, d and e independently have an average value from 1 to 50. It is especially preferred that a has an average value from 100 to 300, b has an average value from 5 to 50 and c, d and e independently have an average value from 1 to 36. It is highly preferred that a has an average value from 150 to 200.

[0027] Preferably Component (C) is an oxyalkylene-modified organopolysiloxane compound having the formula $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_a(\text{MeXSIO})_b\text{SiMe}_3$, wherein X is selected from the group consisting of $-(\text{CH}_2)_n(\text{OC}_2\text{H}_4)_c\text{OH}$, $-(\text{CH}_2)_n(\text{OC}_2\text{H}_4)_c(\text{OC}_3\text{H}_6)_d\text{OH}$, $(\text{CH}_2)_n(\text{OC}_2\text{H}_4)_c\text{OCH}_3$, $-(\text{CH}_2)_n(\text{OC}_2\text{H}_4)_c(\text{OC}_3\text{H}_6)_d\text{OCH}_3$, $(\text{CH}_2)_n(\text{OC}_2\text{H}_4)_c\text{OC}(\text{O})\text{CH}_3$ and $-(\text{CH}_2)_n(\text{OC}_2\text{H}_4)_c(\text{OC}_3\text{H}_6)_d\text{OC}(\text{O})\text{CH}_3$ wherein Me denotes methyl, a has an average value from 100 to 300, b has an average value from 1 to 50, n has a value of 2 to 10, c has an average value of 1 to 36 and d has an average value of 1 to 36. In a preferred embodiment of this invention, a has an average value from 150 to 200. Component (C) can also comprise a mixture of the above delineated oxyalkylene-modified organopolysiloxanes.

[0028] Component (D) of the present invention is at least one surfactant from alkylated sulfonated diphenyloxides. Suitable alkylated sulfonated diphenyloxide surfactants are exemplified by a compound having the following formula or a mixture comprising compounds having the following formula:



wherein each R^5 is independently selected from the group consisting of saturated alkyl radicals, substituted saturated alkyl radical, unsaturated alkyl radicals and substituted unsaturated alkyl radicals, each m and n is independently 0, 1 or 2, each M is independently selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, ammonium and substituted ammonium and each x and y are individually 0, 1 or 2. Each R^5 group can be independently an alkyl group having from 3 to 24 carbon atoms, preferably 10 to 20 carbon atoms and most preferably 12 to 16 carbon atoms, with 16 carbon atoms being especially preferred. The alkyl groups can be linear, branched or cyclic, with linear or branched radicals being preferred. The ammonium ion radicals are of the formula $(R')_3NH$ wherein each R' is independently hydrogen, a C_1 - C_4 alkyl or a C_1 - C_4 hydroxyalkyl radical. Illustrative C_1 - C_4 alkyl or hydroxyalkyl radicals include methyl, ethyl, propyl, isopropyl, butyl, hydroxymethyl and hydroxyethyl. Typical ammonium ion radicals include ammonium (NH_4), methylammonium (CH_3NH_3), ethylammonium ($C_2H_5NH_3$), dimethylammonium ($(CH_3)_2NH_2$), methylethylammonium ($CH_3NH_2C_2H_5$), trimethylammonium ($(CH_3)_3NH$), dimethylbutylammonium ($(CH_3)_2NHC_4H_9$), hydroxyethylammonium ($HOCH_2CH_2NH_3$) and methylhydroxyethylammonium ($CH_3NH_2CH_2CH_2OH$). Preferably, each M is selected from the group consisting of hydrogen, sodium, potassium or ammonium.

[0029] Alkylated diphenyl oxide sulfonates and their methods of preparation are well-known and reference is made thereto for the purposes of this invention. Representative methods of preparation of sulfonates are disclosed in U.S. Patent Nos. 3,264,242, 3,634,272 and 3,945,437. Commercial methods of preparation of the alkylated diphenyl oxide sulfonates generally do not produce species which are exclusively monoalkylated, monosulfonated, dialkylated or disulfonated. The commercially available species are predominantly (greater than 90 percent) disulfonated and are a mixture of mono- and dialkylated with the percentage of dialkylation being 15 to 25 and the percentage of monoalkylation being 75 to 85 percent. Most typically, the commercially available species are 80 percent monoalkylated and 20 percent dialkylated.

[0030] Commercially available materials suitable as Component (D) are exemplified by sodium hexyl diphenyloxide disulfonate, at a concentration of 45%, a liquid anionic surfactant (available as Dowfax™ C6L from The Dow Chemical Company, Midland, Mi.), sodium decyl diphenyloxide disulfonate, at a concentration of 45%, a liquid anionic surfactant (available as Dowfax™ C1OL from The Dow Chemical Company, Midland, Mi.), sodium dodecyl diphenyloxide disulfonate, at a concentration of 45%, a liquid anionic surfactant having an HLB of 16.7 (available as Dowfax™ 2A1 or Dowfax™ 2EP from The Dow Chemical Company, Midland, Mi.), sodium dodecyl diphenyloxide disulfonate, at a concentration of 92%, a powdered anionic surfactant having an HLB of 16.7 (available as Dowfax™ 2A1-D from The Dow Chemical Company, Midland, Mi.), sodium n-decyl diphenyloxide disulfonate, at a concentration of 45%, a liquid anionic surfactant having an HLB of 17.8 (available as Dowfax™ 3B2 from The Dow Chemical Company, Midland, Mi.), sodium n-decyl diphenyloxide disulfonate, at a concentration of 92%, a powdered anionic surfactant having an HLB of 17.8 (available as Dowfax™ 3B2-D from The Dow Chemical Company, Midland, Mi.), Dowfax™2000, at a concentration of 36%, a proprietary liquid anionic surfactant (available from The Dow Chemical Company, Midland, Mi.), sodium n-hexadecyl diphenyloxide disulfonate, at a concentration of 35%, a liquid anionic surfactant having an HLB of 14.4 (available as Dowfax™ 8390 Solution Surfactant from The Dow Chemical Company, Midland, Mi.), and sodium n-hexadecyl diphenyloxide disulfonate, at a concentration of 92%, a powdered anionic surfactant having an HLB of 14.4 (available as Dowfax™ 8390-D from The Dow Chemical Company, Midland, Mi.).

[0031] The wood chips (A), aqueous cooking liquor (B), oxyalkylene-modified organopolysiloxane compound (C) and alkylated sulfonated diphenyloxide surfactant (D) may be added to a digester in any order. For example, the oxyalkylene-modified organopolysiloxane compound (C) and alkylated sulfonated diphenyloxide surfactant (D) of this invention may be added directly to the digester before or after the digester is charged with chips and liquor or may be added to the liquor or chips prior to addition of the liquor or chips to the digester. Preferably, the oxyalkylene-modified organopolysiloxane (C) and alkylated sulfonated diphenyloxide surfactant (D) are added to cooking liquor (B) before it is circulated through the wood chips (A) in a digester.

[0032] The term "digester" as used herein, refers to a cylindrical metal vessel, used chiefly in the preparation of wood pulp for papermaking, in which lignin is separated from cellulose by chemical means. Standard commercial digesters are 12 feet in diameter and 45 feet high with a wall thickness of 2 inches. These types of digesters hold 20 cords of wood. Elevated pressure and temperature are applied to the mixture to separate, by dissolution, as completely as possible, the lignin content of the cellulosic fibers of the wood. Usually, steam to heat and pressurize the digester is supplied through a pipe to the digester (i.e., direct steam injection). The heat can also be supplied by circulating steam and a heat exchanger. The oxyalkylene-modified organopolysiloxane (C) and alkylated sulfonated diphenyloxide surfactant (D) can be used in Kraft pulping using either a continuous or a batch digester, continuous digestion Kraft pulping with extended delignification using staged alkali addition and countercurrent final cooking, batch digestion Kraft pulping with extended delignification using rapid liquor displacement and cold blowing techniques or Kraft-anthraquinone pulping to achieve enhanced delignification using either a continuous or batch digestion stage.

[0033] Usually the concentration of oxyalkylene-modified organopolysiloxane compound (C) and alkylated sulfonated surfactant (D) ranges from 50 to 1,000 weight parts per million (based on dry weight of wood chips), more preferably from 50 to 500 parts per million, and most preferably from 50 to 300 parts per million.

[0034] In the preferred embodiment of the invention, the amount of oxyalkylene-modified organopolysiloxane compound (C) ranges from 10 parts to 90 parts by weight and the amount of alkylated sulfonated diphenyloxide surfactant, Component (D) ranges from 90 parts to 10 parts by weight per 100 parts of the combined weights of (C) and (D). In the process of the invention, it is even more preferred that the amount of Component (C) ranges from 25 parts to 75 parts by weight and Component (D) ranges from 75 parts to 25 parts by weight per 100 parts of the combined weights of (C) and (D).

[0035] Those skilled in the art will appreciate that commercially available alkylated sulfonated diphenyloxide surfactants are often diluted with fairly substantial quantities of water (up to 50%, by weight.) The preferred ranges for the use of Components (C) and (D) as set forth above are based upon "solids" content, exclusive of such water content.

[0036] In manufacturing operations, it is preferable to add the oxyalkylene-modified organopolysiloxane compound (C) and alkylated sulfonated diphenyloxide surfactant (D) as an aqueous solution so as to facilitate the admixture of the additives with the liquor during digestion. The mixture of Step (I) is generally formed at temperatures of below 80°C.

[0037] Step (II) in the chemical pulping process of this invention comprises heating the mixture of step (I) to a temperature of at least 150°C for a period of time to substantially delignify the wood chips (A) so as to form a pulp therefrom. Preferably, the mixture of Step (I) is heated to temperatures of from 150 to 180°C. This temperature is then maintained for a period of time to substantially delignify the wood chips (A) so as to form a pulp therefrom, generally from 0.5 hours to 6 hours, preferably from 0.5 hours to 3 hours.

[0038] Step (III) in the chemical pulping process of this invention comprises maintaining the heated mixture of step (II) at a pressure to prevent boiling of aqueous cooking liquor (B) during step (II). Generally steam is allowed to enter the digester until a maximum pressure of from 100 to 150 psi is reached. This pressure is then maintained from 0.5 hours to 6 hours, preferably from 0.5 hours to 3 hours.

[0039] Step (IV) in the chemical pulping process of this invention comprises recovering the pulp from said mixture. The pulp can be recovered by any method known to those skilled in the art. Typically, the pulp is recovered by a method comprising discharging the cooked chips from a digester under pressure, the mechanical force of which breaks up the wood chips into individual fibers, producing pulp which contains fiber and exhausted liquor which is black in color, washing the black liquor from the pulp and then screening the pulp to remove uncooked chips and other large fragments.

[0040] It should be pointed out that organopolysiloxanes are also employed for suppressing foam in the washing stages of some Kraft mills. As such, and because of normal black liquor recycle procedures, trace amounts of organopolysiloxanes may have been known to inadvertently enter a digester with the recycled black liquor. The trace amounts of organopolysiloxane have produced no recognizable benefits to the Kraft pulps and accordingly the small amounts of organopolysiloxane compounds employed in accordance with the present invention are distinguishable from the trace amounts which inadvertently enter a digester through the normal use of certain organosilicon compounds for foam control in the pulp washing phases of the processes.

[0041] The combination of oxyalkylene-modified organopolysiloxane compound (C) and alkylated sulfonated diphenyloxide surfactant (D) improve the physical characteristics of pulp treated therewith, especially the tensile and tear strength of the produced pulp.

[0042] The Kappa number associated with a delignified pulp represents a measure of residual lignin content. Kappa number are generally measured in accordance with TAPPI Classical Method T 236 cm-85. Those skilled in the art will appreciate that the degree of delignification which is desirable for a given chemical pulping process is directly related to the desired end product. For instance, if the desired end product is unbleached Kraft liner, the target Kappa number generally ranges from 65 to 115, indicating a fairly high level of residual lignin. Whereas in bleached Kraft pulp, suitable for use in fine paper, such as writing paper, the desired Kappa number target may be from 25 to 35, indicating a much higher degree of delignification. Thus, in accordance with the present invention, the heating step (II) is limited such that the mixture is heated to a temperature in excess of 150°C. for a period of time to substantially delignify the (A) wood chips so as to form a pulp therefrom. As used herein, the term "substantially delignify" means that the delignification has taken place to the desired extent, depending upon the desired end product.

Examples

[0043] The performance of the chemical pulping process of this invention was compared to the performance of Kraft cooks completed with and without anthraquinone. The test cooks were carried out under typical Kraft pulp cooking conditions utilizing a laboratory scale digester equipped with temperature and pressure monitoring devices. Duplicate digester runs were completed in each case to measure the efficacy of the method of the invention.

[0044] The wood chips utilized in this study were conventional Southern Pine softwood chips obtained from a commercial pulping operation. The moisture content of the chips was measured and the wood chips were loaded into the laboratory digester on a dry weight basis. Thereafter, an aqueous cooking liquor in the form of a white liquor with an effective alkali content of 16.5% by weight (expressed as Na₂O) and a sulfidity of 29.9% by weight (expressed as Na₂O), in accordance with that hereinabove described, was added to the digester. The weight ratio of the cooking

liquor to wood chips was 3.7:1.

[0045] In the first run series (RUN1), no additions of oxyalkylene-modified organopolysiloxanes, alkylated disulfonated diphenyloxide surfactant or anthraquinone or its derivatives were made to the white liquor. In the second run series, RUN2, anthraquinone (at 600 ppm) was added to the white liquor prior to addition to the laboratory digester. In the third and fourth run series, RUN3 and RUN4, a mixture of 45 weight parts of oxyalkylene-modified organopolysiloxane, 45 weight parts of alkylated disulfonated diphenyloxide surfactant and 10 weight parts of water were added to the white liquor at a level of 500 ppm prior to addition to the digester.

[0046] The oxyalkylene-modified organopolysiloxane used in RUN3 was a random rake copolymer having the general formula $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_a(\text{MeXSIO})_b\text{SiMe}_3$ wherein Me denotes methyl and is used hereafter with the same meaning, a is 157, b is 21, X is a polyoxyalkylene group having the formula $-\text{C}_3\text{H}_6-(\text{OC}_2\text{H}_4)_c-(\text{OC}_3\text{H}_6)_d-\text{OH}$ wherein c is 18 and d is 18.

[0047] The oxyalkylene-modified organopolysiloxane used in RUN4 was a random rake copolymer have the general formula $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_a(\text{MeXSIO})_b\text{SiMe}_3$ wherein a is 25, b is 6, X is a polyoxyalkylene group having the formula $-\text{C}_3\text{H}_6-(\text{OC}_2\text{H}_4)_c-(\text{OC}_3\text{H}_6)_d-\text{OH}$ wherein c is 10 and d is 4.

[0048] The alkylated disulfonated diphenyloxide surfactant was Dowfax™ 8390 Solution Surfactant (sodium n-hexadecyl diphenyloxide disulfonate, at a concentration of 35%, a liquid anionic surfactant having an HLB of 14.4, from The Dow Chemical Company, Midland, Mi.).

[0049] All digester cooks reported in the examples were completed at a cooking temperature of 171°C. The time to obtain the specified cooking temperature was 60 minutes and once obtained, the cooking temperature was held constant for 80 minutes such that the H-factor for each of the laboratory cooks was 1450. The pressure during each digester cook reached a maximum of 110 psi. The cooking conditions were to substantially delignify the wood chips and form a pulp therefrom. After the cooking was complete, the digester was vented to reduce the pressure to atmospheric conditions. The pulp was washed, dewatered and screened on a standard eight cut laboratory flat screen. The screened pulp yield, percentage pulp rejects and total pulp yield were determined. The residual effective alkali and residual active alkali of the spent liquor was measured. These results are reported in Table 1.

[0050] The screened pulp from each run series was combined to form a composite pulp. Thereafter aliquots of each composite pulp sample were subjected to mechanical treatment (beating) in accordance with TAPPI classical test method T 248 cm-85, until Canadian Standard Freeness values of 725, 675, 575, 425, 300 and 250 mls were obtained. Five standard 60 g/m² handsheets were cast from each pulp aliquot at each Freeness value in accordance with TAPPI official test method T 205 om-88. The handsheets were then conditioned and tested for tensile strength and tearing resistance in accordance with TAPPI official test method T 220 om-88. The strength indices reported in Tables 2-5 were calculated from the conditioned weight of the handsheet and represent the numerical average obtained from the five handsheets.

Table 1

	RUN1	RUN2	RUN3	RUN4
Residual Effective Alkali (g/l as NaOH)	13.64	11.78	11.78	13.33
Residual Active Alkali (g/l as NaOH)	17.05	17.36	16.12	17.67
Total Yield (%)	44.02	44.01	43.68	43.40
Screened Yield (%)	43.45	43.45	43.05	42.65
KAPPA Number	30.4	25.60	28.95	27.80

Table 2

	RUN1					
PFI Revolutions	0	2000	4000	8000	1000	12000
Canadian Standard Freeness (mls)	736	674	587	444	353	246
Tear Index (mN•m ² /g)	23.7	18.8	16.7	14.9	13.5	13.1
Tensile Index (N•m/g)	39.8	71.4	79.9	83.6	87.5	90.3

Table 3

	RUN2					
PFI Revolutions	0	2000	4000	8000	1000	12000
Canadian Standard Freeness (mls)	734	674	596	487	320	256
Tear Index (mN•m ² /g)	24.9	17.6	14.7	14.0	12.6	12.5
Tensile Index (N•m/g)	38.6	73.7	85.4	81.5	91.4	86.1

Table 4

	RUN3					
PFI Revolutions	0	2000	4000	8000	1000	12000
Canadian Standard Freeness (mls)	734	684	580	430	290	205
Tear Index (mN•m ² /g)	27.2	19.1	16.9	14.4	14.4	13.8
Tensile Index (N•m/g)	41.7	66.8	79.2	80.8	93.0	94.9

Table 5

	RUN4					
PFI Revolutions	0	2000	4000	8000	1000	12000
Canadian Standard Freeness (mls)	722	683	602	388	304	232
Tear Index (mN•m ² /g)	23.7	17.1	15.6	13.2	12.6	12.4
Tensile Index (N•m/g)	41.2	66.6	70.3	85.7	95.6	94.2

[0051] The remainder of the composite pulp from RUN1, RUN2, RUN3 and RUN4 were treated in a series of pulp bleaching processes to obtain a minimum target TAPPI brightness (also known as GE brightness) of 86. TAPPI brightness is determined by irradiating standard handsheets with 457nm light at an incident angle of 45 degrees and measuring the percentage of reflectance at 0 degrees. The procedure for calibration and measuring TAPPI brightness is described in TAPPI Official Test Method T 452 om-92. The bleaching sequence consisted of an Oxygen treatment stage followed by a Chlorine Dioxide stage further followed by an Extraction Stage with oxygen and peroxide applied and finally an additional Chlorine Dioxide Stage. The industry designation for this bleaching sequence being: OD₁E_{op}D₂. The CED viscosity of each final bleached pulp was also measured per TAPPI classical test method T 254 cm-85. GE Brightness and CED Viscosity results are reported in Table 6.

Table 6

	RUN1	RUN2	RUN3	RUN4
GE Brightness	87.4	88.1	88.3	87.8
CED Viscosity (cps)	18.5	17.2	19.0	18.6

[0052] Thereafter, aliquots of bleached pulp from each run series were subjected to mechanical treatment (beating) in accordance with TAPPI classical test method T 248 cm-85 until Canadian Standard Freeness values of 725, 675, 550, 425, 300 and 250 mls, respectively, were obtained. Five standard 60 g/m² handsheets were cast from aliquots of pulp at each Freeness value in accordance with TAPPI official test method T 205 om-88. The handsheets were then conditioned and tested for tensile strength and tearing resistance in accordance with TAPPI official test method T 220 om-88. The bleached strength indices reported in Tables 7 - 10 were calculated from the conditioned weight of the handsheet and represent the numerical average obtained from the five handsheets.

Table 7

	RUN1					
PFI Revolutions	0	2000	4000	6000	8000	10000
Canadian Standard Freeness (mls)	724	626	497	430	319	231

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Table 7 (continued)

	RUN1					
PFI Revolutions	0	2000	4000	6000	8000	10000
Tear Index (mN•m ² /g)	25.7	16.7	14.0	13.5	12.3	13.1
Tensile Index (N•m/g)	33.3	81.0	86.8	93.6	96.1	99.0

Table 8

	RUN2					
PFI Revolutions	0	2000	4000	6000	8000	10000
Canadian Standard Freeness (mls)	732	618	529	403	374	200
Tear Index (mN•m ² /g)	21.9	15.8	14.3	12.9	12.8	12.5
Tensile Index (N•m/g)	24.5	74.4	81.4	90.8	87.9	94.9

Table 9

	RUN3					
PFI Revolutions	0	2000	4000	6000	8000	12000
Canadian Standard Freeness (mls)	722	627	538	408	348	272
Tear Index (mN•m ² /g)	27.2	19.1	16.9	14.4	14.4	13.8
Tensile Index (N•m/g)	26.1	80.4	86.7	88.1	88.4	97.1

Table 10

	RUN4					
PFI Revolutions	0	2000	4000	6000	8000	10000
Canadian Standard Freeness (mls)	722	632	544	455	368	279
Tear Index (mN•m ² /g)	21.4	16.2	13.6	12.5	13.2	13.3
Tensile Index (N•m/g)	26.1	76.4	82.8	87.3	90.5	93.2

[0053] Referring now to Table 1, it can be seen that the chemical pulping process of this invention (RUN 3 and RUN 4) produces pulp having a lower KAPPA number when compared to pulp produced by a prior art chemical pulping process (RUN1).

[0054] Referring to Tables 2-5, it can be seen that the chemical pulping process of this invention (RUN3 and RUN4) produces pulp having improved fiber strength when compared to the pulp produced by prior art chemical pulping processes (RUN1 and RUN2). Specifically, the tear indices of the pulp measured and reported in Table 4 (RUN3) produced by the chemical pulping process of this invention, is measurably higher than the tear indices of the pulp reported in Table 2 (RUN1) and Table 3 (RUN2), produced by prior art chemical pulping processes, at all levels of Canadian Standard Freeness. In addition, the tensile indices of the pulp measured and reported in Table 5 (RUN4), produced by the chemical pulping process of this invention, are measurably higher than the tensile indices of the pulp reported in Table 2 (RUN1) and Table 3 (RUN2), produced by prior art chemical pulping processes, at a Canadian Standard Freeness of 300 to 500.

[0055] Referring to Tables 7-10, where the fiber strength characteristics of the produced pulp were measured after the pulp had been bleached, it can be seen that the chemical pulping process of this invention Table 9 (RUN3) produces pulp having improved tear indices when compared to pulp produced by prior art chemical pulping processes Table 7 (RUN1) and Table 8 (RUN2). Further, particularly beneficial results are noted in the relationship between tensile index and tear index provided in Table 9 (RUN 3), the chemical pulping process of this invention, when compared to the tensile index-tear index relationship of the prior art chemical pulping processes in Table 7 (RUN 1) and Table 8 (RUN 2). At any specified tensile index, the tear index obtained on pulp from the chemical pulping process of this invention Table 9 (RUN 3) is measurably greater than the tear index obtained at the same tensile index on pulp from either of the prior art chemical pulping processes Table 7 (RUN 1) and Table 8 (RUN 2).

Claims

1. A chemical pulping process comprises the steps of:

(I) forming a mixture comprising

(A) wood chips;

(B) an aqueous cooking liquor;

(C) an least one oxyalkylene-modified organopolysiloxane compound having the formula $R^1R_2SiO(R^2SiO)_a(RXSIO)_bSiR_2R^1$ wherein R is a monovalent hydrocarbon-group having from 1 to 20 carbon atoms, K is a polyoxyalkylene group selected from of $-R^2(OC_2H_4)_cOR^3$, $-R^2(OC_2H_4)_c(OC_3H_6)_dOR^3$, $-R^2(OC_2H_4)_c(OC_4H_8)_eOR^3$, $-R^2(OC_3H_6)_d(OC_4H_8)_eOR^3$ and $-R^2(OC_2H_4)_c(OC_3H_6)_d(OC_4H_8)_eOR^3$ wherein R^1 independently has the same meanings as R or X, R^2 is a divalent group selected from hydrocarbon groups having from 1 to 20 carbon atoms and hydrocarbon groups containing oxygen, R^3 is selected from a hydrogen atom, an alkyl group, an aryl group or an acyl group, a has an average value from 1 to 500, b has an average value from 1 to 500 and c, d and e independently have an average value from 1 to 150; and

(D) at least one surfactant selected from alkylated sulfonated diphenyloxides;

(II) heating the mixture of step (I) to a temperature of at least 150°C. for a period of time to substantially delignify the wood chips (A) so as to form a pulp therefrom;

(III) maintaining the heated mixture of step (II) at a pressure to prevent boiling of aqueous cooking liquor (B) during step (II); and

(IV) recovering the pulp from said mixture.

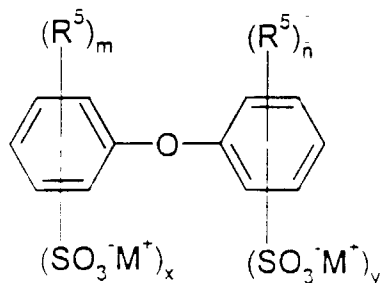
2. A process according to claim 1 wherein the wood chips (A) are presteamed wood chips.

3. A process according to claim 1 or 2, wherein (B) is selected from Kraft cooking liquors, soda cooking liquors and sulfite cooking liquors.

4. A process according to claim 3 wherein (B) further comprises at least one ingredient selected from black liquor, polysulfide and anthraquinone-containing compounds.

5. A process according to any of claims 1 to 4, wherein (C) is an oxyalkylene-modified organopolysiloxane compound having the formula $Me_3SiO(Me_2SiO)_a(MeXSIO)_bSiMe_3$ wherein Me denotes methyl, X is selected from $-(CH_2)_n(OC_2H_4)_cOH$, $-(CH_2)_n(OC_2H_4)_c(OC_3H_6)_dOH$, $-(CH_2)_n(OC_2H_4)_cOCH_3$, $-(CH_2)_n(OC_2H_4)_c(OC_3H_6)_dOCH_3$, $-(CH_2)_n(OC_2H_4)_cOC(O)CH_3$ and $-(CH_2)_n(OC_2H_4)_c(OC_3H_6)_dOC(O)CH_3$, a as an average value from 100 to 300, b has an average value from 1 to 50, n has a value of 2 to 10, c has an average value of 1 to 36 and d has an average value of 1 to 36.

6. A process according to any of claims 1 to 5, wherein (D) is a compound having the formula or a mixture comprising compounds having the formula:



wherein each R^5 is independently selected from saturated alkyl radicals, substituted saturated alkyl radical, unsaturated alkyl radicals and substituted unsaturated alkyl radicals, each m and n is independently 0, 1 or 2, each M is independently selected from hydrogen, an alkali metal, an alkaline earth metal, ammonium and substituted ammonium and each x and y are independently 0, 1 or 2.

7. A process according to any of claims 1 to 5, wherein (D) is selected from sodium hexyl diphenyloxide disulfonate, sodium decyl diphenyloxide disulfonate, sodium dodecyl diphenyloxide disulfonate, sodium n-decyl diphenyloxide disulfonate, sodium n-hexadecyl diphenyloxide disulfonate,
- 5 8. A process according to any of claims 1 to 7, wherein Step (II) comprises heating the mixture of Step (I) at a temperature of 150 to 180°C. for 0.5 hour to 6 hours.
9. A process according to any of claims 1 to 8, wherein the pressure in Step (III) is from 100 to 150 psi.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 3531

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The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 3 August 1999	Examiner Nestby, K
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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