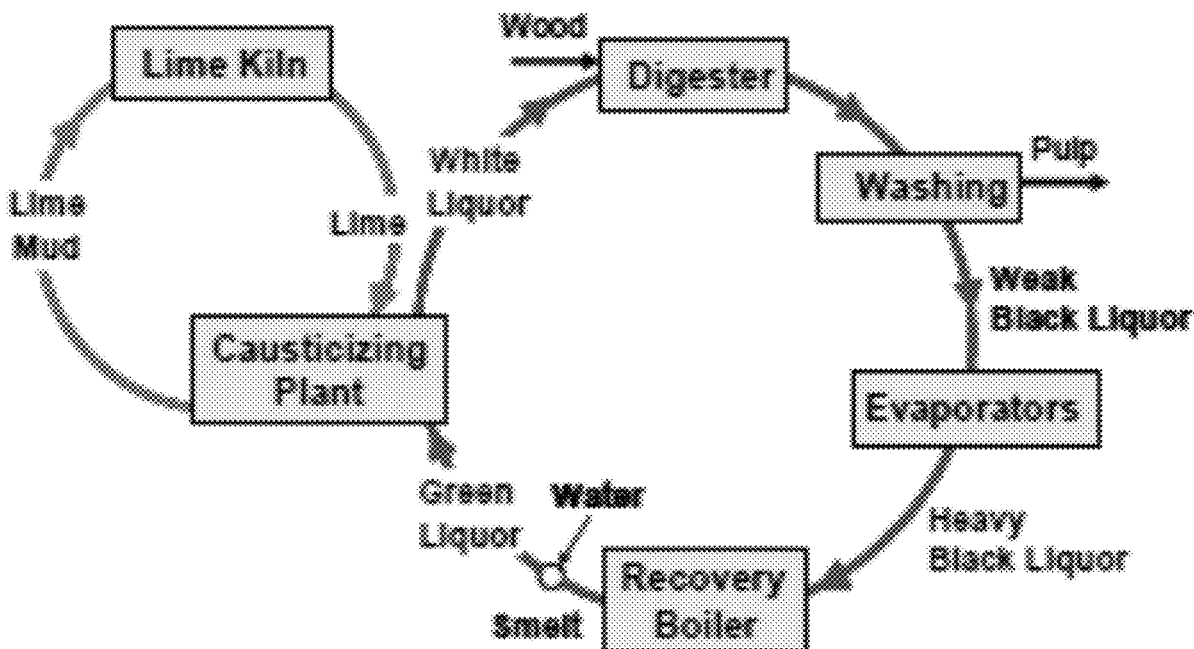




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Nicholson et al.(10) **Pub. No.: US 2021/0002826 A1**(43) **Pub. Date: Jan. 7, 2021**(54) **KRAFT PULP MILL SCALE CONTROL
WITH END GROUP MODIFIED
POLYCARBOXYLATES**(71) Applicant: **SOLENIS TECHNOLOGIES, L.P.**,
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Wilmington, DE (US)(21) Appl. No.: **16/916,127**(22) Filed: **Jun. 30, 2020****Related U.S. Application Data**(60) Provisional application No. 62/869,235, filed on Jul.
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CPC **D21C 11/106** (2013.01); **D21C 11/0092**
(2013.01)(57) **ABSTRACT**

Scale build-up on metal surfaces of a black liquor evaporator is prevented or mitigated by treating the black liquor with a deposit inhibiting concentration of a water-soluble polymer containing a polycarboxylate chain and a 3-mercaptopropionic acid end group.



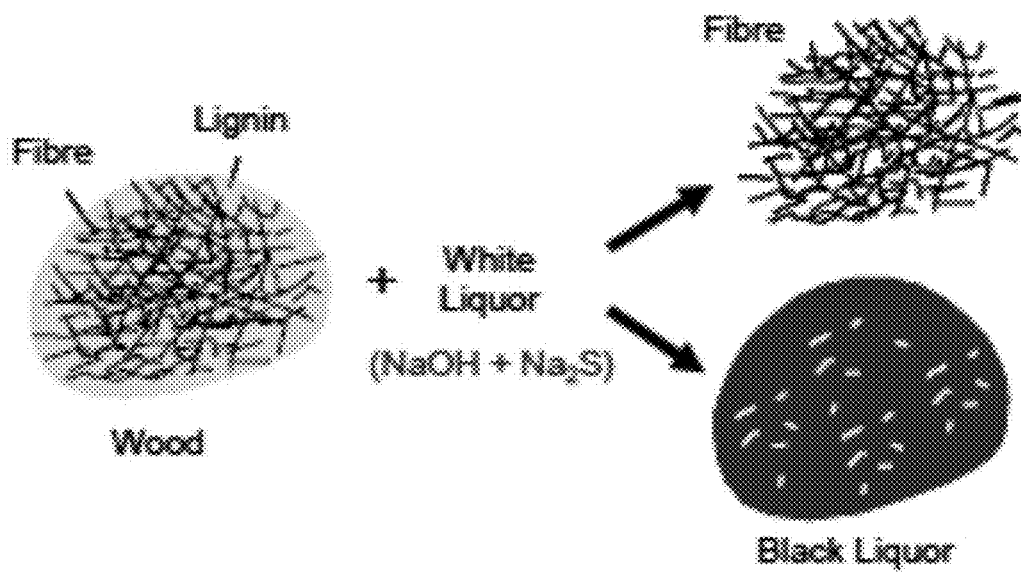


FIG. 1

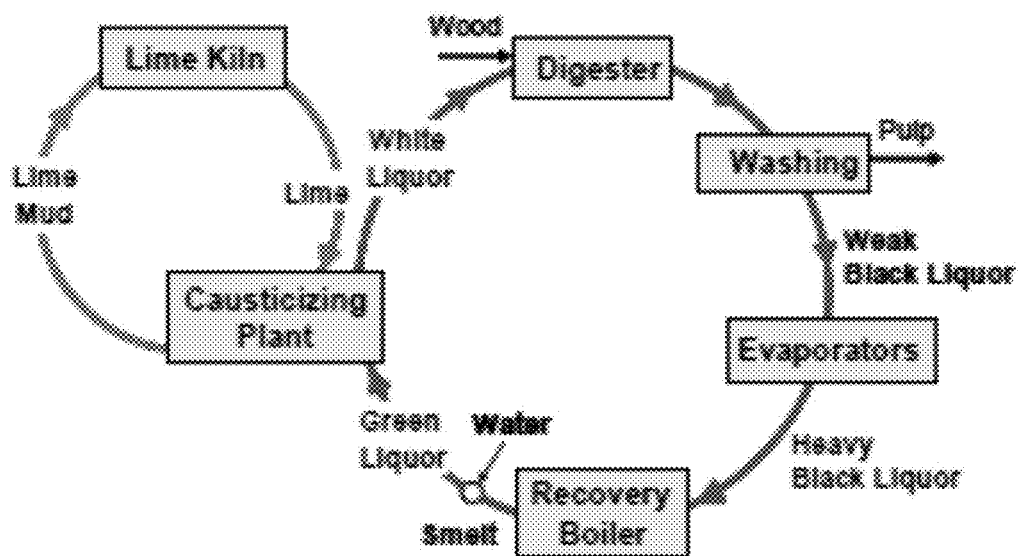
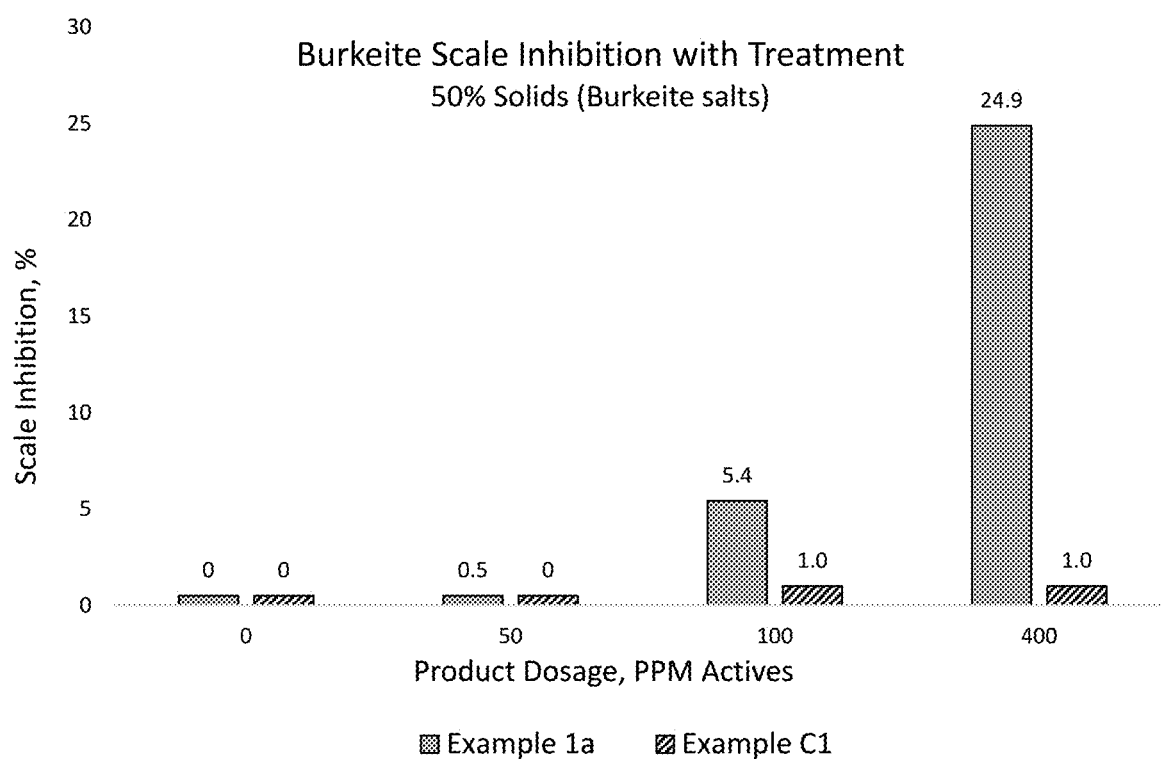
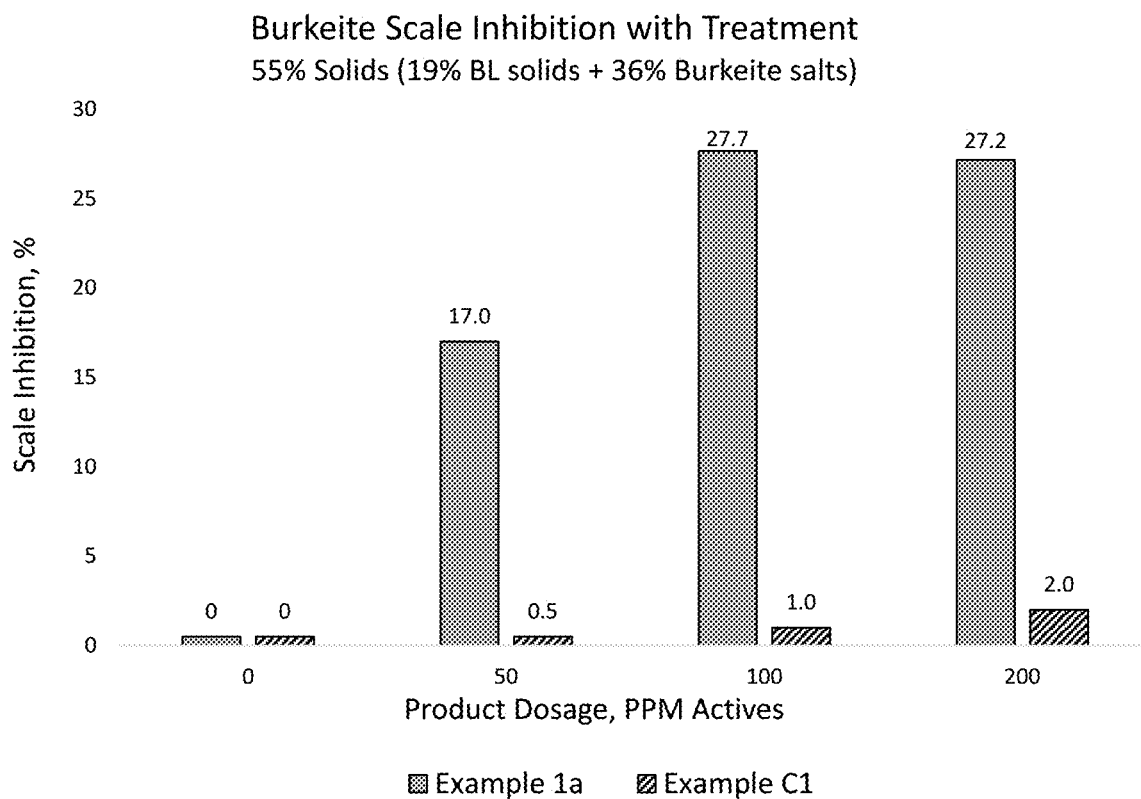


FIG. 2

**Figure 3****Figure 4**

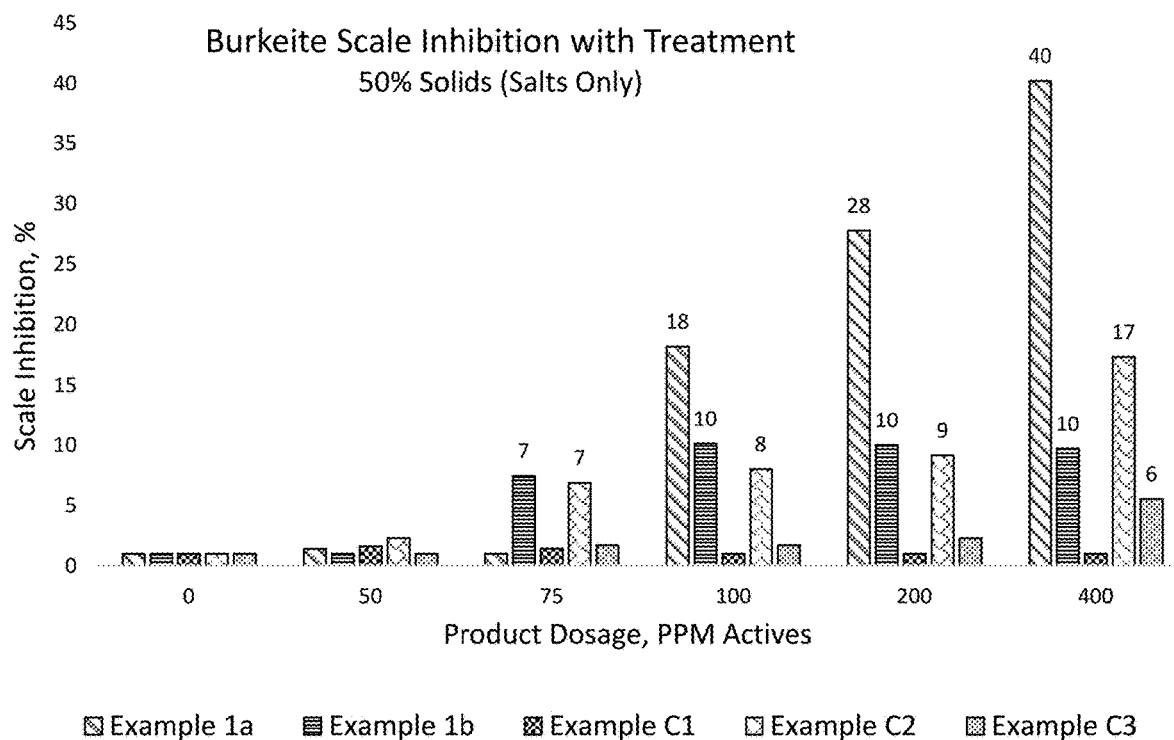


Figure 5

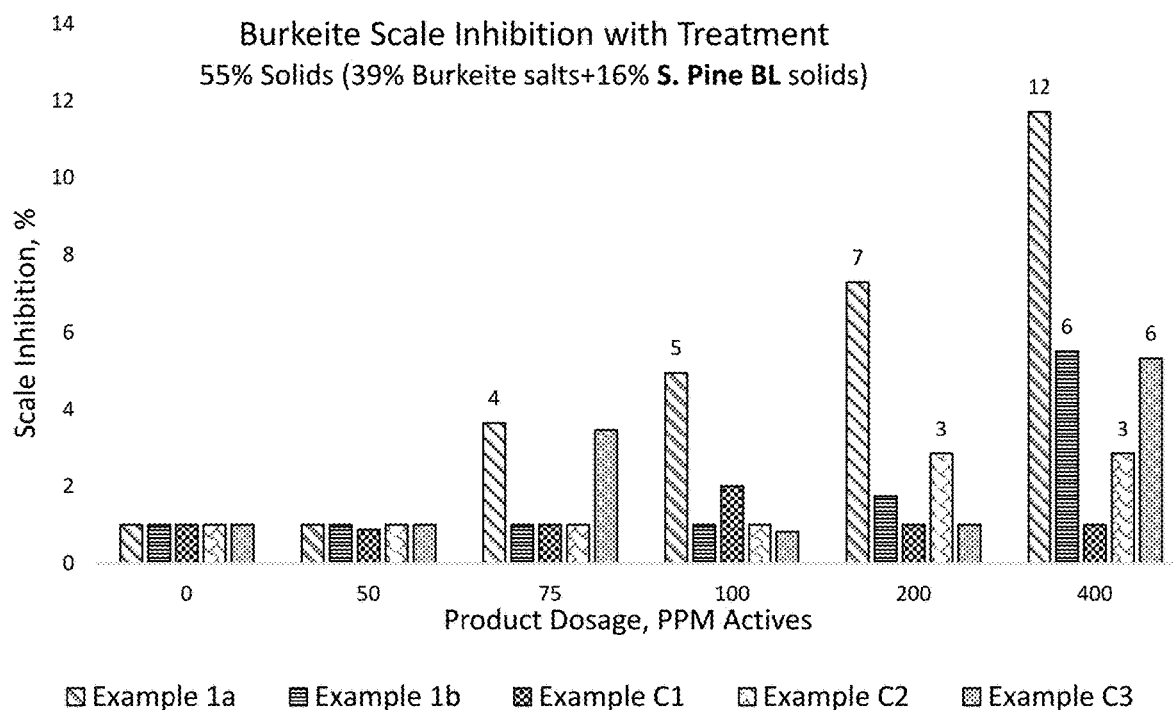


Figure 6

KRAFT PULP MILL SCALE CONTROL WITH END GROUP MODIFIED POLYCARBOXYLATES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. provisional application Ser. No. 62/869,235 filed Jul. 1, 2019, the disclosure of which is incorporated by reference.

TECHNICAL FIELD

[0002] The present disclosure generally relates to scale control in the Kraft process for paper making, and more particularly relates to antiscalants for use in the black liquor concentration process.

BACKGROUND

[0003] The kraft pulping process is one of the major pulping processes in the pulp and paper industry. Spent liquor resulting from the kraft pulping process (black liquor or "BL") contains various organic materials as well as inorganic salts, the deposition of which detracts from an efficient chemical recovery cycle. Inorganic pulping chemicals and energy are recovered by incinerating BL in a recovery boiler. For an efficient combustion in the recovery furnace, BL coming from the pulp digesters with relatively low solids concentration has to be evaporated and concentrated to at least 60% solids, typically in a multistage process (i.e., a multi-effect evaporator).

[0004] Kraft pulp mill evaporator systems can be the bottleneck in chemical recovery limited mills. Sodium salts Na_2SO_4 and Na_2CO_3 are heavily loaded in the liquor as it is concentrated by evaporation up to 50+ % in the evaporator train before transfer to a crystallizer. These salts can crystallize together in varying proportions to give scales of different hardness and solubility (Burkeite is a common example: Na_2SO_4 and Na_2CO_3 in a 2:1 mole ratio). These are water soluble but cause evaporators at the high concentration end to lose efficiency quickly, especially in mass crystallization events that can occur every few days. All evaporator effect cleaning cycles are performed offline in a few hours but require the entire train to be throttled back to handle less liquor to make up for the missing effect. This requires the production of pulp to be decreased, a loss that can be quantified for a value proposition.

[0005] Control of calcium carbonate is a rather developed area outside evaporator applications. On the other hand, burkeite, which precipitates when total solids concentration reaches approximately 50%, represents a specific problem of evaporators and concentrators.

[0006] There thus exists an ongoing need to develop alternative and more efficient methods of monitoring and inhibiting burkeite and other scale deposition in the pulp and paper industry. Such inhibition is of particular importance in pulp mill evaporators and concentrators.

BRIEF SUMMARY

[0007] Polymeric anti-scalants with a flexible end group are provided to be used in the Kraft process to inhibit the formation of Burkeite scale in the evaporators used in the process. In one embodiment a method for inhibiting scale build-up on metal surfaces of a black liquor evaporator

involves treating the black liquor with a deposit inhibiting concentration of the anti-scalant.

[0008] In another embodiment, a composition is provided that comprises black liquor and 50 ppm or more of the anti-scalant polymer. In yet another embodiment, a system for recovering waste material from a kraft pulp process for paper production is provided, comprising an evaporator for concentrating a weak black liquor to a heavy black liquor, wherein the evaporator comprises a scale-inhibiting amount of an anti-scalant polymer described herein.

[0009] In these and other embodiments, the anti-scalant is a water-soluble polymer that contains a polycarboxylate chain and a 3-mercaptopropionic acid end group. In various embodiments, the anti-scalant is a water-soluble polymer having the general structure R1-R2-R3, wherein R2 is a polycarboxylate, R1 and R3 are independently hydrogen or an end group, and at least one of R1 and R3 is the end group $\text{—S—CH}_2\text{CH}_2\text{COOH}$. In certain embodiments, the water-soluble polymer contains a polycarboxylate portion R2 that is a homopolymer or copolymer of acrylic acid. In various embodiments the water-soluble polymer is a homopolymer or copolymer of acrylic acid chain terminated with 3-mercaptopropionic acid. It can be prepared by polymerizing carboxyl functional olefins such as acrylic acid and optional olefins such as ethylene in the presence of a chain terminating effective amount of 3-mercaptopropionic acid. During synthesis, the 3-mercaptopropionic group is incorporated at the end of the growing polycarboxylate chain. Incorporation of the end group stops the growing chain and controls the molecular weight of the anti-scalant polymer being synthesized. In various embodiments, the water-soluble polymer has a weight average molecular weight of 2000 to 12000 daltons. In the methods and systems disclosed herein, an anti-scalant effective amount of the water-soluble polymer is used. In various embodiments, the effective amount is 10 ppm or greater, 20 ppm or greater, 50 ppm or greater, or 100 ppm or greater.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The present invention will hereinafter be described in conjunction with the following drawing figures, wherein like numerals denote like elements, and

[0011] FIG. 1 is a schematic diagram of the kraft pulping process, illustrating the separation of wood chips into cellulose fibers for paper making and black liquor containing the waste products of the process.

[0012] FIG. 2 is a schematic diagram of the kraft recovery process.

[0013] FIGS. 3 to 6 are graphs showing scale inhibition with candidate anti-scalants.

DETAILED DESCRIPTION

[0014] The following detailed description is merely exemplary in nature and is not intended to limit the invention or the application and uses of the invention. Furthermore, there is no intention to be bound by any theory presented in the preceding background or the following detailed description.

[0015] The Kraft Process

[0016] In the production of pulp by the kraft process (also known as the sulfate process), bark and chipped wood are treated with alkaline aqueous liquid to remove organic contaminants, of which lignin is a major constituent. Typically, wood chips are heated in a 10% solution of sodium

hydroxide that contains about 20 mole percent of sodium sulfide. The reaction is carried out at temperatures of about 140 to 180° C. for a suitable time ranging from 1 to 3 hours. [0017] The resulting organic residues are removed from the chips by draining over a screen and washing with a wash water. The wash water is separated from the chips and contains dissolved lignin, emulsified soaps, other organic ingredients, and substantial amounts of inorganic salts alkalis. The wash water after separation from the chips is referred to as black liquor.

[0018] These process steps are illustrated in FIG. 1, which illustrates a non-limiting embodiment of treating wood chips containing cellulose fibers and lignin with a so-called white liquor that contains the noted alkali (sodium hydroxide) and sodium sulfide. The reaction product includes a pulp containing cellulose fibers suitable for making paper and a liquid stream known as the black liquor. The black liquor contains considerable amounts of organic and inorganic solids including alkalis. The kraft process provides a method of recovering these materials for re-use by incinerating the liquor to recover the energy content.

[0019] One embodiment of a recovery process is illustrated in FIG. 2, which shows the steps of concentrating the resulting black liquor in evaporators, recovering the pulping chemicals, and recovering heat from combustion of organics in recovery boilers. In this way the process minimizes the impact of waste material (black liquor) from the pulping process, recycles the pulping chemicals NaOH and Na₂S, and co-generates steam and power from the waste materials.

[0020] As produced, the black liquor will usually contain about 12-20% by weight of solid material. This is called the weak black liquor. Before the weak black liquor can be used as fuel and inorganic components recovered, the material has to be concentrated, usually to a solids content of about 45% by weight or higher. For example, in an embodiment, the black liquor has at least 50% solids by weight. The concentration of the black liquor is usually conducted in multiple-effect evaporators. The concentrated product is called the heavy black liquor. The heavy black liquor varies in composition from mill to mill. But as a rule it contains inorganic carbonates, sulfides, sulfites, sulfates and silica as well as organic sulfur compounds, in addition to the organic components.

[0021] A common problem with use of a black liquor evaporator is the formation of deposits that tend to stick to walls or tubes of the evaporator units. Build-up of the deposits decreases the overall efficiency of evaporation. For example, the deposits decrease heat transfer, requiring increased energy input to accomplish a desired concentration by evaporation. The deposits are predominantly organic residues and soluble salts, and as such they can be removed by boil outs with water. But deposition leads to more frequent boil-outs and an increase in down time.

[0022] To fight the tendency of the process to form deposits in the evaporators, the current teachings disclose the use of an anti-scalant polymer in the black liquor. In various embodiments, use of the anti-scalant extends the time between evaporator effect cleanings by 15% or more, which represents a measurable achievement above the normal time interval.

Anti-Scalant Polymer

[0023] This disclosure provides a polyacrylic with a modified end group as an anti-scalant polymer that can prevent or

lessen the buildup of Burkeite scale in the evaporators described herein. The anti-scalant polymer is typically initiated with a suitable free radical initiator system and terminated with a group S—CH₂CH₂COOH, known as a 3-mercaptopropionic acid (or MPA) group. The MPA group is incorporated into an acrylic polymer by including 3-mercaptopropionic acid (HS—CH₂CH₂COOH) in a suitable weight or molar percentage in a mix of acrylic monomers subjected to copolymerization conditions in the presence of a suitable radical initiator. Under the conditions, the MPA acts as a chain terminator in a statistical way. The molecular weight of the anti-scalant polymer made in this way depends upon the proportion of chain terminating 3-MPA in relation to the chain extending olefins and acrylates making up the polymer synthesis. In various embodiments, the weight average molecular weight ranges from about 2000 to about 12000 grams per mole.

[0024] Equivalently, the extent of incorporation of the MPA end groups can be measured as a percentage, where incorporation of the MPA, measured either by weight or by mole, derives from the weight proportion or molar proportion of MPA in the original mix of olefin and acrylic monomers used to create the acrylic polymer with modified end groups. Suitable mole percent incorporation levels of MPA end group can be determined empirically and are provided in the Examples section below.

[0025] The anti-scalant polymers can thus be referred to as chain terminated polyacrylics having an end group of MPA. These are made by a process of copolymerizing a mixture of 3-MPA and of monomers selected from olefins and carboxyl containing monomers such as acrylates. Anti-scalants made this way are represented chemically with the formula (I)



where R1 and R3 are independently either H or a functional group, and at least one of them is the functional group 3-MPA (—S—CH₂CH₂COOH); and where R2 is a polycarboxylate, and where R4 is hydrogen, methyl, or ethyl. Alternatively, the polymer can be simplified and written as formula (II)



where R6 is a polycarboxylate chain and R5 and R7 are chain initiators or terminators, respectively, at least one of which is —S—CH₂CH₂COOH.

[0026] In formula (I) and formula (II), R2 and R6 independently represent a polycarboxylate. A polycarboxylate is formed by polymerization of acrylic acid or by copolymerization of a plurality of monomers including acrylic acid to make an anti-scalant polymer with an MPA end group. When polymerization is carried out with only acrylic acid, then R2 and R6 are each simply polyacrylic acid moieties, which is one kind of polycarboxylate. More generally, the polycarboxylates R2 and R6 are synthesized from one or more monomers selected from acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, crotonic acid, angelic acid, senecioic acid, salts thereof, and esters thereof. In various embodiments, acrylic acid is used in a major amount of such mixtures, for example as more than 50 mole percent, more than 60 mole percent, more than 75 mole percent and more than 80 mole percent up to 90 mole percent. In an embodiment, the polymer is made with 100 mole percent acrylic acid. In addition to the carboxylate monomers, olefins such as ethylene and propylene can be part of the polycarboxylate R2 and R6, as long as the

resulting polymer maintains water solubility and effectiveness as an inhibitor of Burkeite scale growth or formation.

[0027] The functional groups R1 and R3 may be different, with one being the 3-MPA ($\text{—S—CH}_2\text{CH}_2\text{COOH}$) functional group. The other is H or the residue from the initiator and can be alcohol —OH , sulfate, sulfonate or other functional groups resulting from the use of various initiators known to those skilled in the art, which can include hydrogen peroxide, potassium persulfate, sodium metabisulfite or other effective water soluble initiators.

Use of the Anti-Scalant Polymer

[0028] The current teachings provide for use of an effective amount, or a deposit inhibiting amount, of an anti-scalant polymer having the above noted structure. In various embodiments, using the polymer as described leads to reduction in scaling on metal surfaces of the evaporators that concentrate the black liquor from a kraft pulping process. An aspect of the use of the anti-scalant polymer is the reduction or elimination of Burkeite scale formation in the process. Elimination or reduction of scale formation during the process leads to increased throughput or product with the same energy input, with decrease downtime for descaling in offline cleaning cycles.

[0029] The anti-scalant polymer is used or added into the system at any location that enables it to be present in the evaporators where the weak black liquor is being concentrated to produce a heavy black liquor for input into the recovery process (see generally FIGS. 1 and 2). The anti-scalant polymer can be introduced in the cycle in the digester, in the wash water, or added directly into the weak black liquor as that stream is fed as input to the evaporators. The polymer can be added in a concentrate or at any dilution that provides a deposit-inhibiting level of polymer in the black liquor that is fed to the evaporators.

[0030] A deposit inhibiting amount of anti-scalant can be determined empirically in the kraft process as that level that provides a noticeable effect in decreasing the amount of scale formed during operation of the process, or that provides for an increased amount of time between offline cleaning cycles (or decreased downtime for flush outs) necessitated by build-up of burkeite scale in the evaporators. Lab tests can show a deposit inhibiting amount as that which reduces the weight of scale deposited on laboratory reactor surfaces.

[0031] In various embodiments, use of the anti-scalant polymer at a level of 10 ppm or greater, at a level of 20 ppm or greater, at a level of 50 ppm or greater, or at a level of 100 ppm or greater is observed to reduce scale formation. Advantageously, the scale inhibition is dose responsive, and so deposits are further inhibited when the level of anti-scalant is increased to 200 ppm, 400 ppm, or to 500 ppm. These are levels that have been observed to be effective at reducing scale, as further illustrated in the examples that follow. At these levels of treatment, reductions in scale formation of at least 25% can be achieved, representing a significant increase over the use of a phosphonate chelant or non-MPA terminated acrylate polymer.

EXAMPLES

Example C1—Phosphonate Group

[0032] The chelant or anti-scalant of Example C1 is a phosphonate chelant DETPMPA or diethylene triamine penta(methylene phosphonic acid) sodium salt.

Example C2—Sulfonate Group

[0033] The chelant of Example C2 is a polyacrylate made using sodium metabisulfite as initiator. This leaves a sulfonate end group. The molecular weight is approximately 2.5 times that of Example 1a. It is commercially available from Solenis LLC.

Example C3—Hydroxyl Group

[0034] The chelant of Example C3 is a polyacrylate made using isopropanol as chain transfer agent, leaving an alcohol end group. The molecular weight is approximately equal to that of Example 1a. It is commercially available from Lubrizol Corp.

Example 1a—MPA End Group

[0035] The chelant of Example 1a is a polyacrylate made using 9.5% by weight mercaptopropionic acid as a chain transfer agent.

Example 1b—MPA End Group

[0036] The chelant of Example 1b is a polyacrylate made using 5.4% by weight mercaptopropionic acid as a chain transfer agent. The molecular weight is approximately 20% higher than that of Example 1a.

Example 2

[0037] A 50% wt/vol concentrated solution of $\text{Na}_2\text{SO}_4/\text{Na}_2\text{CO}_3$ in a 2:1 mole ratio (2.68:1 weight ratio) is mixed and heated in rolling Parr autoclaves under conditions described in the table below. The treatment additives from Example C1 and Example 1a are dissolved in the warmed aqueous mixture immediately prior to closing the reactors and placing them in the oven.

[0038] Typical Experimental Conditions:

Temperature, ° C.	120
Time at temp, hr	5
Salts concentration, % wt/vol	50
Molar Ratio $\text{Na}_2\text{SO}_4/\text{Na}_2\text{CO}_3$	2/1
Solution in 125 mL vessel, mL	25
Solution pH	11.2-13

[0039] During the heat up process, the insoluble fraction of the solids dissolves into solution until the reverse solubility point is reached, after which further temperature increase causes precipitation onto the hot metal surfaces to occur. After the designated heating time the vessels are cooled, during which a massive crystallization event deposits scale on the bottom of the vessels. The aqueous phase is poured off, the vessels are dried in an oven at 110° C. overnight, and the scale is determined gravimetrically.

[0040] The inhibition of scale formation is calculated based on the mass of scale deposited on the walls of the reactor containing the formulation (g treated), versus the mass of scale deposited on the walls of a reactor containing no treatment (g untreated) run at the same time together in the same experiment.

$$\% \text{ inhibition of scale} = \frac{[(\text{g untreated} - \text{g treated}) / \text{g untreated}] \times 100}{1}$$

[0041] Results are shown in FIG. 3. Example C1 did not inhibit scale significantly. Using an anti-scalant of Example

1a (having a 3-MPA end group) increased inhibition of scale with increased dosage reaching 25% inhibition at 400 ppm.

Example 3

[0042] A mixture of softwood kraft black liquor and $\text{Na}_2\text{SO}_4/\text{Na}_2\text{CO}_3$ (2:1 mole ratio 2.68:1 weight ratio) giving a total solids content of 55% (19% from BL solids+36% from Burkeite salts) is mixed and heated in rolling Parr autoclaves under conditions described in the table below.

Typical Experimental Conditions with Black Liquor Solids:

Temperature, ° C.	120
Time at temp, hr	5
Solids concentration, % wt/vol	55
Fraction of 55% from BL solids, %	19
Ratio $\text{Na}_2\text{SO}_4/\text{Na}_2\text{CO}_3$	2/1
Solution in 125 mL vessel, mL	25
Solution pH	13

[0043] The rest of the sample treatment and scale measurement is the same as in Example 2.

[0044] Results are in FIG. 4. Example C1 did not significantly inhibit scale. The anti-scalant of Example 1a inhibited scale more effectively, reaching maximum inhibition of 28% at 100 ppm and maintaining it at 27% at a dosage of 200 ppm.

Example 4

[0045] Burkeite scale is generated in rolling stainless steel autoclaves heated in a convection oven. Typical experimental conditions are shown in the table below.

[0046] Typical Experimental Conditions:

Temperature, C.	120
Time at temp, hr	5
Salts concentration, % wt/vol	50
Molar Ratio $\text{Na}_2\text{SO}_4/\text{Na}_2\text{CO}_3$	2/1
Solution in 125 mL vessel, mL	25
Solution pH	11.2-13

[0047] A “salts only” system is prepared using solutions of sodium sulfate and sodium carbonate at 50% solids wt/vol using a molar ratio of sulfate to carbonate of 2:1 (2.68 weight ratio). The salts are weighed directly into each vessel, deionized water is added, and the solution is hand stirred in the vessel with heating on a hot plate to dissolve the salts. Anti-scalant products are then added as 1% solutions with continued stirring. The vessels are capped and placed in a roller oven and raised to 120° C. over 2 hours with constant rolling to simulate the kinetic motion of the scaling solution over the steel surface. The vessels are held at 120° C. for 5 hours with continuous rolling after which they are cooled on ice to 35° C., and then held at that temperature in a constant temperature water bath for 45 minutes. The solution is then completely decanted from the vessel before oven drying the vessels for 18 hours at 110° C. The scale formed on the vessel wall is determined gravimetrically.

[0048] Results are shown in FIG. 5. The flexible end group modified acrylic acid polymers of Example 1a and Example 1b perform better than the phosphonate DETPMPA (Example C1) and the alcohol terminated polyacrylate of Example C3, and also show an advantage in comparison to

Example C2, which contains a sulfonate end group instead of a 3-MPA group of the Examples 1a and 1b.

Example 5

[0049] A “black liquor” system is prepared using the cooking liquor from a southern pine kraft pulp. Typical experimental conditions are shown in the table below.

Typical Experimental Conditions with Black Liquor Solids:

Temperature, C.	120
Time at temp, hr	5
Solids concentration, % wt/vol	55
Fraction of 55% from BL solids, %	16
Ratio $\text{Na}_2\text{SO}_4/\text{Na}_2\text{CO}_3$	2/1
Solution in 125 mL vessel, mL	25
Solution pH	13

The black liquor contained 16% dissolved solids to which sodium sulfate and sodium carbonate were added to raise the solids content to 55% wt/vol, using a ratio of sulfate to carbonate of 2:1 (2.68 weight ratio). The salts were weighed directly into each vessel, black liquor was added, and the solution was hand stirred in the vessel with heating on a hot plate to dissolve the salts. Anti-scalant products were then added as 10% solutions with continued stirring. The vessels were heated to simulate scale forming conditions in the same procedure as the previous example. The procedure for measurement of the scale formed was also the same.

[0050] Results are shown in FIG. 6. The flexible end group modified acrylic acid polymers of Example 1a and Example 1b perform better than the phosphonate DETPMPA (Example C1) and alcohol terminated polyacrylate (Example C3). Example 1a shows an improvement compared to Example 1b, indicating the improved performance in burkeite scale reduction is a function both of the incorporated end group and on the relative content of the end group in the polymer.

[0051] While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.

What is claimed is:

1. A method for inhibiting scale build-up on metal surfaces of a black liquor evaporator, the method comprising treating the black liquor with a deposit inhibiting concentration of a water-soluble polymer comprising a polycarboxylate chain and a 3-mercaptopropionic acid end group.
2. The method according to claim 1, wherein the water-soluble polymer has general structure R1-R2-R3, wherein R2 is a polycarboxylate, R1 and R3 are independently hydrogen or an end group, and at least one of R1 and R3 is the end group $-\text{S}-\text{CH}_2\text{CH}_2\text{COOH}$.

3. The method according to claim 1, wherein the water-soluble polymer comprises a homopolymer or copolymer of acrylic acid.

4. The method according to claim 1, wherein the concentration of the water-soluble polymer in the black liquor is 100 ppm or greater.

5. The method according to claim 1, wherein the water-soluble polymer has a weight average molecular weight of 2000 to 12000 daltons.

6. The method according to claim 1, wherein the water-soluble polymer is a homopolymer or copolymer of acrylic acid chain terminated with 3-mercaptopropionic acid.

7. A composition comprising black liquor and 50 ppm or more of a water-soluble polymer comprising a polycarboxylate chain and a 3-mercaptopropionic acid end group.

8. The composition according to claim 7, wherein the black liquor has at least 50% solids by weight.

9. The composition according to claim 7, wherein the water-soluble polymer has general structure R1-R2-R3, wherein R2 is a polycarboxylate, R1 and R3 are independently hydrogen or an end group, and at least one of R1 and R3 is the end group $\text{—S—CH}_2\text{CH}_2\text{COOH}$.

10. The composition according to claim 7, wherein the water-soluble polymer comprises a homopolymer or copolymer of acrylic acid.

11. The composition according to claim 7, wherein the concentration of the water-soluble polymer is 100 ppm or greater.

12. The composition according to claim 7, wherein the water-soluble polymer has a weight average molecular weight of 2000 to 12000 daltons.

13. The composition according to claim 7, wherein the water-soluble polymer is a homopolymer or copolymer of acrylic acid chain terminated with 3-mercaptopropionic acid.

14. A system for recovering waste material from a kraft pulp process for paper production comprising an evaporator for concentrating a weak black liquor to a heavy black liquor, wherein the evaporator comprises black liquor and a scale-inhibiting amount of a water-soluble polymer, wherein the water-soluble polymer comprises a polycarboxylate chain and a 3-mercaptopropionic acid end group.

15. The system according to claim 14, wherein the black liquor has at least 50% solids by weight.

16. The system according to claim 14, wherein the water-soluble polymer has general structure R1-R2-R3, wherein R2 is a polycarboxylate, R1 and R3 are independently hydrogen or an end group, and at least one of R1 and R3 is the end group $\text{—S—CH}_2\text{CH}_2\text{COOH}$.

17. The system according to claim 14, wherein the water-soluble polymer comprises a homopolymer or copolymer of acrylic acid.

18. The system according to claim 14, wherein the concentration of the water-soluble polymer is 100 ppm or greater.

19. The system according to claim 14, wherein the water-soluble polymer has a weight average molecular weight of 2000 to 12000 daltons.

20. The system according to claim 17, wherein the water-soluble polymer is a homopolymer or copolymer of acrylic acid chain terminated with 3-mercaptopropionic acid.

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