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(54) **Title:** SEQUESTERING AGENTS

(57) **Abstract:** A sequestering agent composition includes a (co)polymer of acrylic acid. The acrylic acid copolymers may be selected from a copolymer of acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid, a copolymer of acrylic acid and hydroxyethyl methacrylate, and a copolymer of acrylic acid and 3-allyloxy-1,2-propanediol. Also disclosed are processes for preventing the build-up of undesirable mineral scale or deposits in an aqueous solution in pulping, comprising adding the sequestering agent to the aqueous solution.



SEQUESTERING AGENTS

Field of the invention

[0001] The present invention relates to calcium control in the pulp and paper industries. More particularly the present invention relates to calcium sequestering agents comprising a (co)polymer of acrylic acid.

Background of the invention

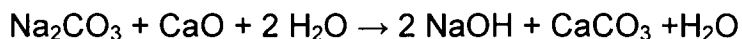
[0002] Residual calcium in the pulp mill, in the form of calcium carbonate (CaCO_3), has long been a problem in the pulp and paper industry. It results in pitch formation in the pulp mill, which can adversely affect washing efficiency. The excess CaCO_3 also causes scale buildup in digesters where the wood is cooked. Flocculants are often used to remove excess CaCO_3 from the green and white liquors, but often times excess CaCO_3 is allowed to move through the pulp mill regardless of what program is in place.

[0003] If the white liquor could be treated to modify CaCO_3 scale buildup in digesters or prevent scale formation all together, costly shutdowns to clean digesters could be delayed or significantly shortened saving the pulp mill time and money. CaCO_3 that does not go to the washers is not present to form calcium soaps and CaCO_3 deposits which cost the mill time and money in clean-up, costly pitch control programs, increased bleaching costs, and loss of pulp quality.

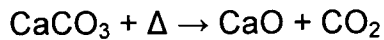
[0004] Calcium control in pulp mills is critical. The calcium comes from the lime (CaO) added during the regeneration of caustic soda (NaOH).

[0005] Black liquor is burned and Na_2CO_3 is a byproduct. Lime is added to the Na_2CO_3 solution which will generate CaCO_3 and NaOH , but the CaCO_3 stays suspended in what is now called the White Liquor. CaCO_3 although is sparingly soluble in the pulp mill black liquor will still form insoluble calcium soaps which will act as collectors for additional hydrophobic materials in the pulping system. This is known as pitch and is very problematic and expensive in pulp mills.

[0006] Sodium hydroxide (NaOH) is recovered in the re-causticizing plant in the pulp mill. This is done by the following reactions:



[0007] The CaCO_3 precipitates out of solution and is recovered to be reduced to CaO again by burning.



[0008] Not all of the CaCO_3 precipitates out of solution and is suspended
5 in the Green and White Liquors (caustic solutions). Green liquor is converted to White Liquor via clarification of the Green Liquor as described below in the next paragraph. The White Liquor is added back to the digester to cook the wood chips into pulp. The calcium carry over to the digester is undesired because it can cause scale build-up in the digester leading to bad heat transfer thus higher fuel costs
10 and inefficiencies in the pulping process. It can also lead to the formation of insoluble calcium soaps on the Brown Stock Washing process in the system leading to dirt or pitch outbreaks which will interfere with the pulp washing and bleaching process.

[0009] The CaCO_3 suspension in the Green and White Liquor is usually
15 clarified by the use of polymeric settling aids. The settling aids are typically anionic polymers added directly to the green and white liquors to settle the suspended CaCO_3 in the liquors. These settling aids are not always effective which leaves room for an alternate approach for handling unwanted calcium.

[0010] If the suspended calcium salts remaining after the polymer add
20 could be effectively sequestered or chelated prior to the white liquor being added to the digester, there would be a significant reduction in digester scaling and pitch or dirt formation which would mean a reduction in down time to clean the Brown Stock Washing system and to de-scale the digester(s) saving the mill significant amounts of money.

25 **Brief description of the invention**

[0011] One method of minimizing the CaCO_3 formation is through the application of a chelant or sequestering agent, which can keep calcium and magnesium in solution. An effective chelant, which will remove the calcium from
30 interacting harmfully in the pulp mill system, would be an extreme cost benefit to the pulp and paper making process.

[0012] In the present invention it was discovered that certain (co)polymers of acrylic acid are efficient as sequestering agents for example in the pulp and paper industries. The concept is to tie up the divalent ions, such as calcium, so that

they do not build up and cause harm to the system. The chemistry is used to bind to the divalent ion and prevent it from precipitating and collecting as scale.

[0013] The present invention provides a process for preventing the build-up of undesirable mineral scale or deposits in an aqueous solution in pulping with a sequestering agent comprising a (co)polymer of acrylic acid. More particularly, the present invention provides a process for preventing the build-up of undesirable mineral scale or deposits in an aqueous solution in pulping, the process comprising: adding a sequestering agent or a composition containing thereof to the aqueous solution, wherein the sequestering agent comprises a (co)polymer of an acrylic acid; and sequestering the divalent ions in the aqueous solution.

[0014] The present invention also provides a sequestering agent or a composition containing thereof containing a (co)polymer of acrylic acid.

[0015] In one embodiment the acrylic acid (co)polymer is a copolymer of acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid.

[0016] In another embodiment the acrylic acid (co)polymer is a copolymer of acrylic acid and hydroxyethyl methacrylate.

[0017] In another embodiment the acrylic acid (co)polymer is a copolymer of acrylic acid and 3-allyloxy-1,2-propanediol.

[0018] It is an advantage of the present invention that the sequestering agents are biodegradable and the use of traditional harmful agents can be avoided.

[0019] It is another advantage of the present invention that the sequestering agents have high chelating values.

Detailed description of the invention

[0020] Chelation is the ability of a ligand, in this case dispersant, to coordinate to a single metal ion through two or more ligation sites. Generally speaking, a chelating ligand has much stronger coordination strength than a monodentate ligand having only one ligation site. Usually these ligands are organic compounds, and are called chelants, chelators, chelating agents, or sequestering agents. Sequestering means enclosing a metal ion by one or more polydentate ligands, as in a chelate complex. Polyacrylates and various derivatives thereof have been synthesized and have shown to provide an affinity for calcium and

magnesium sequestering, thus providing prevention the precipitation of divalent ions, such as calcium and magnesium salts, which is very much undesirable. As a further definition: a scale inhibitor is generally a reagent that prevents scale from precipitating. A scale inhibitor can be a chelant or a sequestering agent, but on the other hand all the chelants or sequestering agents are not always scale inhibitors.

[0021] The present invention provides a process or a method for preventing the build-up of undesirable mineral scale or deposits in an aqueous solution in pulping, the process comprising adding a sequestering agent or a composition containing thereof to the aqueous solution, wherein the sequestering agent comprises a (co)polymer of an acrylic acid, to sequester the divalent ions in the aqueous solution. In one embodiment the divalent ions are selected from calcium and magnesium. In the pulping applications especially the sequestering of calcium is important. Generally the aim of the sequestering is to keep the divalent ion(s) in the solution and to prevent the precipitation thereof. Further examples of divalent ions are manganese, copper, iron, barium, strontium, beryllium, chromium, ruthenium, iridium, tantalum, cobalt, nickel, zinc, cadmium, mercury, aluminum, lead, titanium, uranium, gadolinium, platinum, gold and silver ions. The sequestering agent composition contains at least one sequestering agent described herein. The sequestering agent composition may contain also other suitable agents, which may promote the chelation or preventing the precipitation of the divalent ions, for example flocculants, such as anionic, cationic or nonionic flocculants. Also any excipients, solvents, diluents, pH adjusting agents (sodium hydroxide, ammonium hydroxide etc.) or the like may be included. Typically the sequestering agent composition is provided as a liquid.

[0022] The sequestering agent or the composition containing thereof may be utilized in any suitable application in pulp or paper industry. The term "pulping" as used herein refers generally to applications in the field of pulp and paper industry and related fields. The pulp may be mechanical, thermomechanical, chemithermomechanical, chemical, recycled, organosolv or any other suitable pulp.

[0023] The sequestering agent or the composition containing thereof may be added to any suitable process stage of pulping, bleaching, washing, flotation or other related applications in pulp mill, such as in the pulper, in the digester, in the white liquor clarifier or at the bleach stage. The sequestering agents may be added prior to bleaching of the pulp. In one embodiment of the process the sequestering agent composition is added to a digester, or for example prior to adding the white

liquor. In one embodiment of the process the sequestering agent composition is added to the white liquor clarifier. This will prevent the CaCO_3 from reaching the digester.

[0024] The aqueous solution as used herein refers to any suitable aqueous solution or liquid, such as a liquid selected from an aqueous liquid, a soil, a liquid comprising sediments or sludge, a slurry and a leachate. Further examples of liquids are, but are not limited to, water, waste water, industrial water, sludge or solids suspension, pulp suspension or any other liquid, such as a solvent or other chemical. The sequestering agent or the composition thereof may be added in an amount sufficient to chelate a desired proportion of the divalent ions present in the solution, such as most or substantially all of them, for example at least 90% (w/w) of divalent ions.

[0025] In one embodiment the polymeric sequestering agent is a polymer of acrylic acid (100% AA), which has the biodegradability of over 60%.

[0026] The "(co)polymer" as used herein refers to homopolymers of acrylic acid alone and to copolymers of acrylic acid and one or more other monomer(s). The copolymer has generally a low average molecular weight, such as about 20,000 Daltons or less. Generally the molecular weights disclosed herein are average molecular weights. In one embodiment the copolymer is a copolymer of acrylic acid and a monomer selected from 2-acrylamido-2-methyl propane sulfonic acid (AMPS), hydroxyethyl methacrylate (HEMA) and 3-allyloxy-1,2-propanediol (AOP).

[0027] In one embodiment the copolymer comprises a copolymer of acrylic acid (AA) and 2-acrylamido-2-methyl propane sulfonic acid (AMPS). The molecular weight of the copolymer of acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid (AA/AMPS) may be, but is not limited to, in the range of about 9,000–20,000 Daltons. The ratio of acrylic acid to 2-acrylamido-2-methyl propane sulfonic acid in the copolymer may be in the range of about 70:30 to 50:50 (w/w). In one embodiment the ratio of acrylic acid to 2-acrylamido-2-methyl propane sulfonic acid in the copolymer is about 60:40 (w/w). In one embodiment the copolymer of acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid has a molecular weight in the range of about 15,000–20,000 Daltons.

[0028] In one embodiment the copolymer of acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid has a molecular weight in the range of about 9,000–20,000 Daltons. It is generally in 45–60% solution of polymer in

water, pH 3–7, clear to yellow viscous liquid. In one embodiment the copolymer of acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid has a molecular weight of about 18,000 Daltons.

[0029] In one embodiment the copolymer comprises a copolymer of acrylic acid (AA) and hydroxyethyl methacrylate (HEMA). The molecular weight of the copolymer of acrylic acid and hydroxyethyl methacrylate (AA/HEMA) may be, but is not limited to, in the range of about 6,000–14,000 Daltons. The ratio of acrylic acid to hydroxyethyl methacrylate in the copolymer may be in the range of about 80:20 to 60:40 (w/w). In one embodiment the ratio of acrylic acid to hydroxyethyl methacrylate in the copolymer is about 70:30 (w/w).

[0030] In one embodiment the copolymer of acrylic acid and hydroxyethyl methacrylate has a molecular weight in the range of about 8,000–9,000, such as in the range of about 8,500–8,700 Daltons, such as about 8,600 (measured as 8,577 in one example) Daltons. It is generally in 45–60% solution of polymer in water, pH 3–7, clear to yellow viscous liquid.

[0031] In one embodiment the copolymer comprises a copolymer of acrylic acid (AA) and 3-allyloxy-1,2-propanediol (AOP). The molecular weight of the copolymer of acrylic acid and allyloxy-1,2-propanediol may be, but is not limited to, in the range of about 5,000–15,000 Daltons. In one embodiment the molecular weight of the copolymer of acrylic acid and allyloxy-1,2-propanediol is in the range of about 8,000–12,000 Daltons. In one embodiment the molecular weight of the copolymer of acrylic acid and allyloxy-1,2-propanediol is about 10,000 Daltons.

[0032] Also other suitable monomers may be included to the copolymers. These may include, but are not limited to, vinyl sulfonic acid or vinyl sulfonate salts; vinyl phosphoric acid or vinyl phosphonate salts; vinylidene diphosphonic acid or salts thereof; methacrylic acid; vinyl acetate; vinyl alcohol; vinyl chloride; unsaturated mono- or dicarboxylic acids or anhydrides, such as maleic anhydride, maleic acid, fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid, crotonic acid, isocrotonic acid, angelic acid, tiglic acid; vinyl chloride; styrene-*p*-sulfonic acid, or styrene sulfonates salts; allyl sulfonate salts; acrylamido-2-methylpropanesulfonic acid (AMPS); hydroxyphosphonoacetic acid (HPA); hypophosphorus acids such as H_3PO_3 , giving units of formula $-\text{PO}(\text{OH})-$; acrylamides, propargyl alcohol having formula $\text{HC}\equiv\text{C}-\text{CH}_2-\text{OH}$; butyr-1,4-diol, hydroxyethylmethacrylate (HEMA); hydroxyethylacrylate (HEA), imidazole; mercaptan; 3-allyloxy-1,2-propanediol (AOP) and mixtures thereof. In certain exemplary embodiments the copolymer consists of only the monomers disclosed in

the embodiments herein, for example they consists of two monomer species, i.e. the copolymer does not contain other additional monomer species.

[0033] The synthesis of the copolymeric sequestering agent can be carried out by any suitable polymerization reaction which is well-known in the art.

5 [0034] Said polymerization reaction can be initiated by any suitable means which results in generation of a suitable free-radical. In the radical polymerization technique the source of free radicals can be any suitable method of generating free radicals such as thermally induced method, redox initiating method, photochemical initiating method or high energy radiation such as electron beam, X or gamma ray
10 radiation. The preferred method of generating free radicals is thermally induced method, such as one carried out at 90°C, but pending on the initiator system the temperature can be lower or higher.

 [0035] In the radical polymerization typical thermal initiators are azo compounds, peroxides or peroxyesters. The polymerization initiators are not
15 limited to any particular species but may be any of the conventional initiators, inclusive redox initiators, azo initiators and peroxides. Among them, the azo initiators are preferred and, as specific examples thereof, there may be mentioned, among others, azonitrile compounds such as 2,2'-azobis(2-methylpropionitrile) (AIBN), azobisdimethylvaleronitrile and azobisdimethylmethoxyvaleronitrile;
20 azoamidine compounds such as 2,2'-azobis(methylpropionamidine)-dihydrochloride (V-50), VA-041, VA-044 and VA-061 (V-50, VA-041, VA-044 and VA-061 are products of Wako Pure Chemical Industries, Ltd.); azoamide compounds such as VA-080, VA-086 and VA-088 (products of Wako Pure Chemical Industries, Ltd.); azoalkyl compounds such as azodi-tert-octane and
25 azoditert-butane; cyanopropylazo-formamide, 4,4'-azobis(cyanovaleric acid), 4,4'-azobis-(cyanopentanoic acid) dimethylazobismethyl propionate, azobishydroxymethyl-propionitrile and the like. Preferred initiators are 2,2'-azobis-(methylpropionamidine)dihydrochloride (V-50), and 4,4'-azobis(cyanopentanoic acid) or 4,4'-azobis(cyanovaleric acid).

30 [0036] One of these radical polymerization initiators for use in the present invention may be used alone, or two or more thereof may be used as a mixture.

 [0037] The molar ratio of the radical polymerization initiator to the monomer is preferably from 0.0001 to 0.1, more preferably from 0.0005 to 0.05, still more preferably from 0.0005 to 0.01.

Examples

[0038] The chelation values of several (co)polymers of acrylic acid were measured with the following protocol and compared to the well-known chelating agent EDTA.

- 5 1) Accurately weigh 2.00 g of respective polyacrylate to a 250 ml beaker and add 50 ml of distilled water. Stir until completely dissolved.
- 2) Adjust the pH of the solution from (1) to 8.0 with 1.0 N NaOH.
- 3) Pipet 10.0 ml of 2.0% soda ash solution into the beaker from (2).
- 4) Adjust the pH of the solution in (3) to 11.0 with 0.2 N NaOH and add distilled
10 water to the 150 ml mark on the beaker.
- 5) Titrate the sample from (4) with a 4.41% calcium acetate monohydrate solution to a distinct, permanent turbidity.
- 6) Maintain the pH of the solution from (5) at 11.0 with 0.2 N NaOH.

15 [0039] The data below was obtained by observing the amount of calcium that can be sequestered by the ligating polymer prior to precipitation. Without chemical assistance there is very little calcium maintained in solution. EDTA can sequester 55.7 times more calcium than in the absence of any sequestering or chelating agent. Most of the polymers tested are significantly better than EDTA meaning at least 2 times more calcium can be sequestered (Table 1). One
20 embodiment of this invention provides AA/AMPS product that can sequester 40 times more calcium than EDTA and biodegrades 23% after 28 days. AA/HEMA can sequester nearly 13 times more calcium than EDTA and biodegrades 36% after 28 days. The AA/AOP (3-allyloxy-1,2-propandiol) polymer can sequester nearly 12 times more calcium than EDTA (no biodegradation study performed).

25 [0040] Table 1. Comparison of various chemistries towards their chelation value by looking at the affinity to calcium and ability to remain soluble in water.

Sample	Calcium Sequestering Relative
Ligand free	1
EDTA (ethylenediamine tetraacetic acid)	55.7
AA/AMPS (acrylic acid/acrylamido-2-methylpropanesulfonic acid copolymer)	2433.3
AA/HEMA (acrylic acid/hydroxyethyl methacrylate copolymer)	713.3
AA/IM (acrylic acid/imidazole copolymer)	202.5
Maleic/DEAP (maleic acid/allylphosphonic acid diethyl ester copolymer)	164.2
Maleic/ AOP (maleic acid/3-allyloxy-1,2-propanediol copolymer)	127.7
AA, RAFT (reversible addition fragmentation transfer polymerized acrylic acid)	234.8
AA/AOP (acrylic acid/3-allyloxy-1,2-propandiol copolymer)	660.7
AA/Maleic (acrylic acid/maleic acid copolymer)	140.5
AA/AM (acrylic acid/acrylamide copolymer)	234.4
AA (acrylic acid)	174.4
SASMAC (maleic acid/anhydride/sodium allyl sulfonate copolymer)	99.7
AA (acrylic acid), phosphite term	201.1
Maleic/Mercaptan (maleic acid/mercaptan copolymer)	224.9
AA/Mercaptan (acrylic acid/mercaptan copolymer)	162.2

[0041] The biodegradation of the copolymers was investigated using Marine BODIS test. Two copolymers (Table 2) AA/AMPS and AA/HEMA had the best chelating ability and biodegradability combination.

[0042] Table 2. The biodegradation of the copolymers.

Copolymer	Biodegradation Day 14	Biodegradation Day 28
AA/AMPS	17%	23%
AA/HEMA	22%	36%

5

[0043] This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to make and use the invention. The patentable scope of the invention is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

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Claims

1. A sequestering agent comprising a (co)polymer of acrylic acid.
2. The sequestering agent of claim 1 wherein the (co)polymer of acrylic acid is a copolymer of acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid.
- 5 3. The sequestering agent of claim 2 wherein the (co)polymer of acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid has a molecular weight in the range of 9,000–20,000 Daltons.
4. The sequestering agent of claim 2 wherein the (co)polymer of acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid has a molecular weight in the range
10 of 15,000–20,000 Daltons, such as about 18,000 Daltons.
5. The sequestering agent of any of the claims 2–4, wherein the ratio of acrylic acid to 2-acrylamido-2-methyl propane sulfonic acid is in the range of 70:30 to 50:50 (w/w).
6. The sequestering agent of any of the claims 2–4, wherein the ratio of acrylic
15 acid to 2-acrylamido-2-methyl propane sulfonic acid is about 60:40 (w/w).
7. The sequestering agent of claim 1 wherein the (co)polymer of acrylic acid is a copolymer of acrylic acid and hydroxyethyl methacrylate.
8. The sequestering agent of claim 7 wherein the (co)polymer of acrylic acid and hydroxyethyl methacrylate has a molecular weight in the range of 6,000–14,000
20 Daltons.
9. The sequestering agent of claim 7 wherein the (co)polymer of acrylic acid and hydroxyethyl methacrylate has a molecular weight in the range of 8,000–9,000 Daltons.
10. The sequestering agent of any of the claims 7–9, wherein the ratio of acrylic
25 acid to hydroxyethyl methacrylate is in the range of 80:20 to 60:40 (w/w).
11. The sequestering agent of any of the claims 7–9, wherein the ratio of acrylic acid to hydroxyethyl methacrylate is about 70:30 (w/w).
12. The sequestering agent of claim 1, wherein the (co)polymer of acrylic acid is a copolymer of acrylic acid and 3-allyloxy-1,2-propanediol.

13. The sequestering agent of claim 12, wherein the copolymer of acrylic acid and 3-allyloxy-1,2-propanediol has a molecular weight in the range of 5,000–15,000 Daltons.
14. A process for preventing the build-up of undesirable mineral scale or deposits in an aqueous solution in pulping, the process comprising:
- 5 adding a sequestering agent of any of the claims 1–13 to the aqueous solution; and
- sequestering divalent ions in the aqueous solution.
15. The process of claim 14 wherein the divalent ions are selected from calcium and magnesium.
- 10 16. The process of claim 14 or 15, comprising adding the sequestering agent prior to adding white liquor.
17. The process of claim 14 or 15, comprising adding the sequestering agent prior to bleaching of the pulp.
- 15 18. The process of claim 14 or 15, comprising adding the sequestering agent to a digester.
19. The process of claim 14 or 15, comprising adding the sequestering agent to a white liquor clarifier.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2012/000365

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C02F 5/00 (2012.01)

USPC - 210/701

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - C02F 5/00 (2012.01)

USPC - 210/696, 697, 698, 699, 700, 701; 162/70, 72, 73, 168.1, 168.2, 199

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase, Google Patents

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---	US 6,329,484 B1 (LOSASSO) 11 December 2001 (11.12.2001) entire document	1-6 -----
Y		7-13
Y	US 2009/0082535 A1 (NAKANO et al) 26 March 2009 (26.03.2009) entire document	7-11
Y	US 4,872,995 A (CHEN et al) 10 October 1989 (10.10.1989) entire document	12, 13

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 June 2012

Date of mailing of the international search report

06 JUL 2012

Name and mailing address of the ISA/US

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2012/000365

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 14-19
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.