



(51) International Patent Classification:

D21C 9/10 (2006.01) *D21C 9/16* (2006.01)
D21C 9/14 (2006.01) *D21C 9/02* (2006.01)

(21) International Application Number:

PCT/US2017/022443

(22) International Filing Date:

15 March 2017 (15.03.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/309,282 16 March 2016 (16.03.2016) US

(71) Applicant: **ECOLAB USA INC.** [US/US]; 1 Ecolab Place, St. Paul, Minnesota 55102 (US).(72) Inventors: **DUGGIRALA, Prasad Y.**; 2403 Sisters Ct., Naperville, Illinois 60564 (US). **SHEVCHENKO, Sergey M.**; 931 Park Hill Circle, Aurora, Illinois 60502 (US).

(74) Agent: **BISHOP, Joshua D.**; Leydig, Voit & Mayer, Ltd., Two Prudential Plaza, Suite 4900, 180 North Stetson Avenue, Chicago, Illinois 60601 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,

[Continued on next page]

(54) Title: LOW CAPITAL BLEACHING OF CHEMICAL PULP

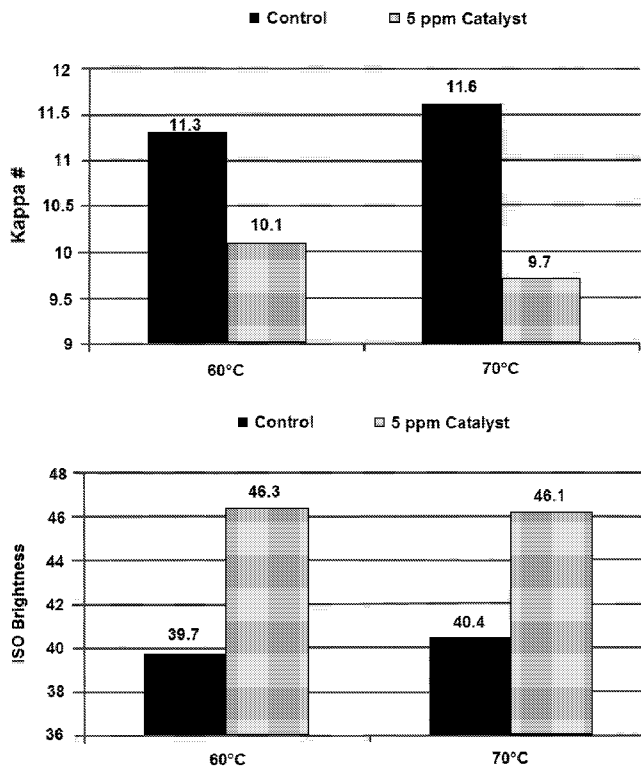


FIG. 1

(57) Abstract: Bleaching methods and formulations for bleaching/delignification processes for chemical pulp are provided. The bleaching methods utilize peroxide and an organomanganese complex under aqueous caustic conditions, increasing bleaching efficiency of the overall bleaching/delignification process. Chemical pulp having increased brightness can be obtained at decreased temperatures and with reduced stage time, resulting in reduced chemical consumption and improved energy efficiency.



DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, **Published:**

LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE,
SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

— with international search report (Art. 21(3))

LOW CAPITAL BLEACHING OF CHEMICAL PULP

[0001] This application is an international (*i.e.*, PCT) application claiming the benefit of U.S. Provisional Patent Application No. 62/309,282, filed March 16, 2016, the contents of which are incorporated by reference herein in their entirety.

FIELD OF INVENTION

[0002] The invention is directed to a method of improving efficiency of a chemical pulp bleaching process.

BACKGROUND OF THE INVENTION

[0003] Chemical pulps such as kraft or sulfite commonly possess dark color, the extent of which depends on the wood source, degree of delignification, and the papermaking processes utilized. Generally, the papermaking industry utilizes bleaching chemicals to improve the optical properties of finished paper and paper products. Bleaching involves chemical alteration of the light-absorbing structures in pulp, as well as removal of residual lignin (*i.e.*, delignification) and is an extension of the delignification started in the digestion stage. Multistage bleaching processes generally include stages such as oxygen-alkali delignification, oxygen-peroxide alkali extraction, chlorine dioxide bleaching, and peroxide bleaching. The resulting pulp can be evaluated using brightness measurements, which are used to assess the whiteness of paper materials through measurement of the amount of light reflected by the pulp.

[0004] Many bleaching sequences comprise oxygen delignification, a first chlorine dioxide stage (“D0”) followed by an alkali extraction stage with hydrogen peroxide and a second chlorine dioxide stage (“D1”). Chlorine dioxide stages can be used for bleaching of wood pulp in elemental chlorine-free (“ECF”) bleaching sequences because chlorine dioxide produces few carcinogenic organochlorine compounds, and thus is currently preferred over the use of elemental chlorine. However, the use of chlorine dioxide has disadvantages. For example, chlorine dioxide stages are acutely toxic. Generally, chlorine dioxide stages are moderately acidic (*e.g.*, pH 2.5–5), which usually necessitates one or more subsequent alkali extraction stages to aid in lignin removal from chemical pulp. Generally, the chlorine dioxide stages utilize hydrogen peroxide to provide additional brightness to the chemical pulp. A

higher number of bleaching stages results in an increase in process time and material costs as well as degradation of the chemical pulp, resulting in a reduction in pulp yield and strength.

BRIEF SUMMARY OF THE INVENTION

[0005] In an embodiment, a method of bleaching alkali oxidized chemical pulp is provided. The method comprises treating alkali oxidized chemical pulp with peroxide and an organomanganese complex under aqueous caustic conditions, which is done subsequent to an acidic oxidative bleaching stage, to form an enhanced chemical pulp. In a preferred embodiment, the chemical pulp is a brownstock chemical pulp.

[0006] In another embodiment, a method of enhancing chemical pulp is provided. The method comprises treating chemical pulp under acidic oxidative conditions to form an acidic oxidized chemical pulp. The acidic oxidized chemical pulp is washed with aqueous caustic solution to form an alkali oxidized chemical pulp. The alkali oxidized chemical pulp is treated with peroxide and an organomanganese complex to form an enhanced chemical pulp.

[0007] In another embodiment, a thermally stable aqueous formulation for bleaching of a chemical pulp is provided. The formulation comprises an organomanganese complex and water, wherein the aqueous formulation has a pH of from about 3 to about 7 and the organomanganese complex is present at a concentration of from about 0.0001% to about 1% by weight based on weight of the aqueous formulation.

[0008] In another embodiment, an aqueous formulation for bleaching of a chemical pulp is provided. The formulation comprises an organomanganese complex, a peroxide, and water, wherein the organomanganese complex is present at a concentration of from 0.0001% to about 1% and the peroxide is present at a concentration of from about 5% to about 60% by weight based on weight of the aqueous solution.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1 is a bar graph that illustrates the effect of temperature on Kappa number and brightness for an embodiment of the inventive methods.

[0010] FIG. 2 is a bar graph that illustrates the effect of time on Kappa number and brightness for an embodiment of the inventive methods.

[0011] FIG. 3 is a bar graph that illustrates brightness, Kappa number, and viscosity for an embodiment of the inventive methods.

[0012] FIG. 4 is a bar graph that illustrates the effect of the peroxide concentration of an embodiment of the inventive methods on D0 hardwood pulp pre-treated with aqueous caustic solution.

[0013] FIG. 5 is a bar graph that illustrates the effect of various conditions on a D0EpD1 sequence for an embodiment of the inventive methods.

[0014] FIG. 6A is a bar graph that illustrates the effect of aqueous caustic conditions and exposure time on brightness for hardwood pulp for an embodiment of the inventive methods.

[0015] FIG. 6B is a bar graph that illustrates the effect of aqueous caustic conditions and exposure time on brightness for softwood D0 pulp for an embodiment of the inventive methods.

[0016] FIG. 7 is a bar graph that illustrates the effect of catalyst concentration on brightness for an embodiment of the inventive methods.

[0017] FIG. 8A is a bar graph that illustrates comparatively the effects of increased hydroxide concentration as a means to improve brightness, viscosity and yield in softwood post-D0 pulp for an embodiment of the inventive methods.

[0018] FIG. 8B is a line graph that illustrates comparatively the effects of increased hydroxide concentration as a means to improve brightness and viscosity in softwood post-D0 pulp for an embodiment of the inventive methods.

[0019] FIG. 9 is a bar graph that illustrates the effect of reagent and catalyst concentration on brightness of D0 softwood pulp for an embodiment of the inventive methods.

[0020] FIG. 10 is a bar graph that illustrates the effect of caustic pre-treatment of a chemical pulp on brightness for an EoPcD0 sequence for an embodiment of the inventive methods and illustrates a potential reduction in chlorine dioxide consumption.

[0021] FIG. 11 is a bar graph that illustrates the effect of an oxygen delignification stage on brightness before and after a chlorine dioxide stage for an embodiment of the inventive methods.

[0022] FIG. 12 is a bar graph that illustrates the effect of catalyst on a multistage sequence that allows for the elimination of a chlorine dioxide stage (D2) for an embodiment of the inventive methods.

[0023] FIG. 13 is a plot that illustrates stability of catalyst formulations stored for certain periods of time for one or more embodiment of the inventive methods and/or formulas.

[0024] FIG. 14 is a bar graph that illustrates changes in catalyst feeding and their effects on brightness at certain temperatures.

[0025] FIG. 15A is a line graph that illustrates how changes in catalyst loading affects brightness for one or more embodiments of the inventive methods in a field trial.

[0026] FIG. 15B is a bar graph that illustrates how changes in catalyst loading affects brightness for one or more embodiments of the inventive methods in a field trial.

[0027] FIG. 15C is a bar graph that illustrates how changes in catalyst loading and temperature affect Eop brightness for one or more embodiments of the inventive methods in a field trial.

[0028] FIG. 15D is a bar graph that illustrates how changes in catalyst loading affects pulp brightness before and after a D1 stage in a field trial.

DETAILED DESCRIPTION OF THE INVENTION

[0029] The invention is based on application of a manganese-based catalyst in pulp bleaching stages involving peroxide. Applicants have discovered methods of bleaching chemical pulp that either eliminates the need for certain stages or reduces the amount of bleaching agent required. The present methods involve exposure of chemical pulp from a papermaking process to manganese complex-based catalysis of peroxide bleaching under aqueous caustic conditions, which generally refers to high-pH (*e.g.*, pH > 7) conditions undertaken in certain steps of bleaching and/or enhancing chemical pulp. In certain embodiments of the methods provided herein, chemical pulp (*e.g.*, acidic oxidized chemical pulp) may be washed with aqueous caustic solution (*i.e.*, under aqueous caustic conditions) to form alkali oxidized chemical pulp. In certain embodiments of the methods described herein, the aqueous caustic conditions have (or aqueous caustic solution has) a pH of from about 8 to 14, or from about 8 or from about 9, or from about 10, to 14, or to about 13, or to about 12. In certain embodiments of the methods described herein, the aqueous caustic solution has a pH of from about 8 to 14, or from about 8 or from about 9, or from about 10, to 14, or to about 13, or to about 12. In certain embodiments of the methods provided herein, the aqueous caustic conditions are the result of an express alkali extraction. For purposes of this disclosure, the terms “caustic” and “alkali” are used interchangeably.

[0030] The methods of the present invention allow for process modifications that provide higher efficiency and unexpected benefits as compared to other bleaching methods. Applicants have surprisingly discovered that the methods described herein provide benefits

including (a) shorter peroxide bleaching stages at lower temperature that improve yield and provide stronger pulp, (b) a reduction in the amount of bleaching chemicals across all stages without sacrificing brightness, (c) substitution of oxygen stages with the inventive organomanganese-catalyzed bleaching stage, and (d) elimination of certain stages that are deemed unnecessary to achieve certain quality metrics, including chlorine dioxide stages.

[0031] A problem perceived with certain existing catalyst-based bleaching methods is that, while some improve pulp brightness in target processes, the brightness gain alone does not justify the expense. The methods disclosed herein involve manganese-based catalysis of a pulp bleaching stage involving hydrogen peroxide with overall process modifications that have been shown to provide higher efficiency and unexpected benefits. Applicants have discovered, among other things, that organomanganese-catalyzed bleaching stages can be performed at lower temperatures than conventional bleaching stage temperatures. The organomanganese-catalyzed bleaching stage can be performed at temperatures as low as about 50° C without substantial erosion of pulp brightness. It was surprisingly and unexpectedly discovered that brightness in some pulps increases or does not change with a decrease in process temperature to, *e.g.*, from about 5° C to about 55° C. Thus, the present invention provides chemical pulp of sufficient brightness under thermally milder and more energy-efficient conditions than traditional bleaching stages. This is an important benefit, because reduction in process temperature can result in a substantial improvement in energy efficiency. Moreover, the low temperatures of the present invention can reduce pulp degradation that often occurs at higher temperatures, resulting in bleaching processes that produce chemical pulp in higher yield.

[0032] In some instances, the inventive methods can require as little as 20 minutes or less to reach maximum brightness. By comparison, additional process time beyond 20 minutes in those instances resulted in a small increase in pulp brightness. In certain embodiments, the use of the present bleaching technology allows for about 10 to about 15 minutes bleaching when utilized in a bleaching tube. In an embodiment, reaction tubes are used instead of bleaching tanks. The reaction tubes contain slowly moving pulp, which effects the bleaching process. This improvement has been shown to increase throughput without any decrease in brightness.

[0033] In certain embodiments, the present invention improves the multistage bleaching/delignification sequence for chemical pulp based on the application of an organomanganese complex in the stages of the process that involve hydrogen peroxide under aqueous caustic

conditions. The result is a modification that includes eliminating and modifying stages of the process based on increased brightness and efficiency. The examples are: (a) replacing D0ED1 sequence with D0EPc process, where EPc stands for the peroxide bleaching with the catalyst (Pc) after express alkali extraction (E), thus eliminating the D1 stage; (b) substituting the conventional D0EopD1 sequence with D0EPc eliminating oxygen and the second chlorine dioxide stage; (c) substituting conventional D0EopD1 sequence with D0EoPc using the Eo stage for activation of pulp at the following Pc stage that results in sufficient brightness to eliminate a second chlorine dioxide stage; (d) substituting oxygen delignification (O) of brownstock pulp with catalyzed peroxide extraction (Epc) process, thus eliminating oxygen; (e) activation of pulp toward a first chlorine dioxide stage (D0) by introducing the catalyst into a preceding alkali peroxide stage at the medium brightness range (approximately 50–70 ISO brightness units), thus allowing for reduction of chlorine dioxide load or even elimination of a subsequent chlorine dioxide stage; (f) activation of D0 pulp towards subsequent alkali peroxide bleaching, and additional activation of the catalyst via express alkali extraction (the phrase “express alkali extraction” is used to describe fast thorough mixing of the D0 pulp with a warm (*e.g.*, from about 40° C to about 90° C) caustic solution followed by immediate dewatering and/or washing prior to the Pc (Epc) stage, and/or washing pulp with warm caustic solution via a shower); (g) substituting conventional P and Eop stages with rapid/short retention lower-temperature Pc (Epc) bleaching stages (*e.g.*, utilizing reaction tubes instead of conventional bleach towers), which have been shown to result in less damage to the fiber thus providing higher throughput, improved energy efficiency, and increased pulp strength (fiber modification).

[0034] The methods disclosed herein can be performed using any suitable organomanganese complex. In certain preferred embodiments, the organomanganese complex is a mononuclear or binuclear complex of Mn (III) and/or Mn (IV) organic complex with one or more O²⁻ bridge. In certain preferred embodiments, the organomanganese complex is an organomanganese-triazacyclononane complex. In certain preferred embodiments, the manganese complex is $\text{Mn}^{2+} \mu\text{-(acetato-}\kappa\text{O}:\kappa\text{O}')][\mu\text{-[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine-}\kappa\text{N1},\kappa\text{N4},\kappa\text{N7}]]]\text{di-}\mu\text{-oxodi-X}^-$. The aforementioned complex can comprise any suitable organic or inorganic anion (X⁻). In certain embodiments, the anion is a halogen such as fluoride, chloride, bromide, and/or iodide. In certain preferred embodiments, X⁻ is selected from a halogen, sulfate, acetate, and citrate. In certain preferred embodiments, the organomanganese complex is $\text{Mn}^{2+} \mu\text{-(acetato-}$

$\kappa O:\kappa O')$][μ -[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine- $\kappa N1,\kappa N4,\kappa N7$]]]di- μ -oxodi-chloride (1:2). The term “catalyst,” as used herein, indicates an organomanganese complex, and when used in the Examples set forth herein, “catalyst” refers to Mn^{2+} μ -(acetato- $\kappa O:\kappa O')$][μ -[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine- $\kappa N1,\kappa N4,\kappa N7$]]]di- μ -oxodi-chloride (1:2).

[0035] The organomanganese complex can be utilized at any suitable concentration in the organomanganese-catalyzed bleaching stage. In certain embodiments, the organomanganese complex is at a concentration of from about 0.001 ppm to about 100 ppm. In certain embodiments, the organomanganese complex is at a concentration of from about 0.001 ppm to about 50 ppm. In certain preferred embodiments, the organomanganese complex is at a concentration of from about 0.001 ppm to about 20 ppm. Thus, in certain preferred embodiments, the organomanganese complex is at a concentration of from about 0.001 ppm to about 20 ppm, from about 0.001 ppm to about 10 ppm, from about 0.01 to about 10 ppm, from about 0.01 ppm to about 8 ppm, from about 0.01 ppm to about 6 ppm, from about 0.01 ppm to about 5 ppm, from about 0.001 to about 4 ppm, from about 0.001 ppm to about 3 ppm, from about 0.01 ppm to about 3 ppm, or from about 0.01 ppm to about 2 ppm, or from about 0.1 ppm to about 2 ppm, or from about 1 ppm to about 2 ppm.

[0036] The inventive methods can include any suitable peroxide. In certain embodiments, the peroxide is an organic peroxide or an inorganic peroxide. In certain embodiments, the peroxide is selected from organic peroxides such as benzoyl peroxides, or inorganic peroxides such as hydrogen peroxide. In certain preferred embodiments, the peroxide is hydrogen peroxide.

[0037] The peroxide can be added in any suitable form and at any concentration. In certain preferred embodiments, the peroxide is added to the chemical pulp as a solution. In certain preferred embodiments, the peroxide is added as a solution to the chemical pulp at a concentration of from about 5% to about 60% by weight based on the weight of solution. Thus, in certain preferred embodiments, the peroxide is added as a solution to the chemical pulp at a concentration of from about 5% to about 60%, from about 10% to about 60%, from about 15% to about 60%, from about 20% to about 60%, from about 25% to about 60%, from about 30% to about 60%, from about 35% to about 60%, from about 40% to about 60%, from about 45% to about 60%, or from about 50% to about 60% by weight based on the weight of solution. In certain other preferred embodiments, the peroxide is added as a solution to the chemical pulp at a concentration of about 50% or more. Thus, in certain other preferred

embodiments, the peroxide is added as a solution to the chemical pulp at a concentration of about 50% or more, about 60% or more, or about 70% or more.

[0038] In certain preferred embodiments, the organomanganese complex and peroxide are added to the chemical pulp together as an aqueous solution. It has been discovered that higher brightness is obtained when the manganese complex is added to a peroxide line comprising a concentrated hydrogen peroxide solution. In particular, it was found that the efficiency of the treatment increases when the catalyst is added to a more concentrated hydrogen peroxide solution. However, in certain other embodiments, the organomanganese complex and the peroxide are added separately to the chemical pulp.

[0039] In certain preferred embodiments, an organomanganese catalyst solution having a concentration of from about 0.0001% to about 2%, or to about 1%, or to about 0.5%, or to about 0.1%, is mixed with concentrated hydrogen peroxide prior to contacting with the chemical pulp. In certain preferred embodiments, an organomanganese catalyst solution having a concentration of from about 0.0001% to about 0.05% is mixed with the concentrated hydrogen peroxide prior to contacting with the chemical pulp. In certain preferred embodiments, an organomanganese catalyst solution having a concentration of from about 0.001% to about 0.05% is mixed with concentrated hydrogen peroxide prior to contacting with the chemical pulp. In certain preferred embodiments, an organomanganese catalyst solution having a concentration of from about 0.001% to about 0.02% is mixed with concentrated hydrogen peroxide prior to contacting with the chemical pulp. In certain preferred embodiments, an organomanganese catalyst solution having a concentration of from about 0.001% to about 0.01% is mixed with concentrated hydrogen peroxide prior to contacting with the chemical pulp. In certain preferred embodiments, vigorous mixing is applied when the solution of the catalyst is mixed with hydrogen peroxide. In certain preferred embodiments, the time between the mixing and feeding the mixture to pulp does not exceed 10 minutes. In certain preferred embodiments, vigorous mixing is applied when the solution of the catalyst is mixed with hydrogen peroxide. In certain embodiments, the time between the mixing and feeding the mixture to pulp does not exceed 1 minute.

[0040] Any suitable caustic can be used in the organomanganese-catalyzed bleaching stage. In certain embodiments, the caustic is an inorganic base or an organic base. In certain embodiments, the base is an alkali metal or alkaline earth metal hydroxide or salt. In certain embodiments, the base is an alkaline earth metal hydroxide or salt selected from magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, and combinations

thereof. In certain preferred embodiments, the base is an alkali metal hydroxide or salt selected from sodium hydroxide, potassium hydroxide, lithium hydroxide, rubidium hydroxide, cesium hydroxide, and combinations thereof.

[0041] The methods of the present invention can be performed in the presence or absence of oxygen. Oxygen refers to any added oxygen or oxygen-containing gas. In certain preferred embodiments, an individual stage or process does not comprise the use of added oxygen. Such an embodiment may be advantageous, as one can avoid the challenges associated with the use of oxygen (*e.g.*, safety and handling).

[0042] The organomanganese-catalyzed bleaching stage of the present invention can be performed at any suitable temperature necessary to achieve a requisite brightness. It has been discovered that the inventive methods are effective at relatively low process temperatures. In certain embodiments, the organomanganese-catalyzed bleaching stage is performed at a temperature of about 100° C or less. In certain embodiments, the organomanganese-catalyzed bleaching stage is performed at a temperature of about 90° C or less. In certain preferred embodiments, the organomanganese-catalyzed bleaching stage is performed at a temperature of about 80° C or less. Thus, in certain preferred embodiments, the organomanganese-catalyzed bleaching stage is performed at a temperature of about 80° C or less, about 75° C or less, about 70° C or less, about 65° C or less, about 60° C or less, about 55° C or less, or about 50° C or less.

[0043] The methods of the present invention provide organomanganese-catalyzed bleaching stages that require residence times that are much faster than typical residence times required under standard mill conditions. For example, standard mill conditions generally require 60–90 minutes. In certain embodiments, the organomanganese-catalyzed bleaching stage is complete in about 60 minutes or less, or in about 50 minutes or less, or in about 40 minutes or less. In certain preferred embodiments, the organomanganese-catalyzed bleaching stage is complete in about 30 minutes or less. Thus, in certain embodiments, the organomanganese-catalyzed bleaching stage is complete in about 30 minutes or less, or in about 25 minutes or less, or in about 20 minutes or less, or in about 15 minutes or less.

[0044] As discussed above, in certain embodiments, the organomanganese-catalyzed bleaching stages of the present invention can be performed using express low-temperature bleaching by replacing bleach towers with reactor tubes, *i.e.*, “bleaching tubes.” In certain embodiments, the target brightness can be achieved in about 20 minutes or less at temperatures as low as 50 °C, thus providing improved energy efficiency, yield, throughput,

and fiber quality (*e.g.*, increased pulp strength). Thus, conventional P and Eop stages can be substituted with rapid/short retention lower-temperature organomanganese catalyzed bleaching stages by, *e.g.*, utilizing one or more reaction tubes instead of conventional bleach towers.

[0045] In certain embodiments, the chemical pulp is further treated with a phase transfer agent. In certain embodiments, the phase transfer agent is selected from quaternary ammonium salt, phosphonium salt, crown ether, and polyethylene glycol examples of which being tetra-*n*-butylammonium bromide, methyltrioctylammonium chloride, benzyltrimethylammonium chloride, and hexadecyltributylphosphonium bromide. The phase transfer agent can be added to the chemical pulp together with the organomanganese catalyst and/or peroxide or separately.

[0046] The present invention can be used to bleach any chemical pulp. In certain preferred embodiments, the chemical pulp is kraft pulp. In certain embodiments, the chemical pulp is selected from kraft pulp, sulfite pulp, recycled pulp, and any combination of such pulps. In an embodiment, the invention provides a method for improving a papermaking process through modification of a multistage bleaching of chemical pulp. The method comprises an organomanganese-catalyzed bleaching stage comprising treating chemical pulp with an organomanganese complex and a peroxide in the presence of a base and optionally oxygen; a chlorine dioxide stage performed immediately following the organomanganese-catalyzed bleaching stage, wherein the chlorine dioxide stage comprises treating the chemical pulp with chlorine dioxide at a concentration of from about 0.01% to about 2% by weight based on weight of the chemical pulp.

[0047] In certain embodiments, the amount of chlorine dioxide needed to obtain pulp of sufficient brightness is less than would be required in the absence of a preceding organomanganese-catalyzed bleaching stage. It has been discovered that an organomanganese-catalyzed bleaching stage performed prior to a chlorine dioxide stage can allow for a reduction in the amount of chlorine dioxide needed by up to about 20% or more while maintaining sufficient brightness. Thus, in certain embodiments, an organomanganese-catalyzed bleaching stage performed prior to a chlorine dioxide stage reduces the overall amount (*e.g.*, total for all stages) of chlorine dioxide needed by about 20% or more, about 30% or more, about 40% or more, about 50% or more, about 60% or more, about 70% or more, or about 80% or more.

[0048] As discussed above, the organomanganese-catalyzed bleaching stage can reduce the amount of chlorine dioxide needed in a subsequent chlorine dioxide stage. In certain embodiments, the chlorine dioxide stage comprises chlorine dioxide at a concentration of about 5% or less by weight based on the weight of the chemical pulp. Thus, in certain embodiments, the chlorine dioxide stage comprises chlorine dioxide at a concentration of from about 0.01% to about 5%, from about 0.01% to about 4%, from about 0.01% to about 3%, from about 0.01% to about 2%, from about 0.01% to about 1%, from about 0.01% to about 0.08%, from about 0.01% to about 0.06%, from about 0.01% to about 0.05%, from about 0.01% to about 0.04%, from about 0.01% to about 0.02%, or from about 0.01% to about 0.1% by weight based on the weight of the chemical pulp. In certain preferred embodiments, the method comprises a chlorine dioxide stage comprising chlorine dioxide at a concentration of from about 0.01% to about 1% by weight based on weight of the chemical pulp.

[0049] In certain preferred embodiments, the organomanganese complex is present in the organomanganese-catalyzed bleach stage at a concentration of from about 0.001 ppm to about 20 ppm, the peroxide is present in the organomanganese-catalyzed bleach stage at a concentration of from about 0.01% to about 5% by weight, and the organomanganese-catalyzed bleaching stage is performed for about 60 minutes or less, with ppm concentrations and weight percentages each based on the weight of the chemical pulp.

[0050] In certain preferred embodiments, the organomanganese complex and peroxide are added to the chemical pulp as an aqueous solution comprising organomanganese complex at a concentration of from about 0.001% to about 5% and peroxide at a concentration of from about 5% to about 60% by weight based on the weight of solution.

[0051] In certain preferred embodiments, the organomanganese-catalyzed bleaching stage is performed in a bleaching tube at a temperature of about 55 °C or less and reaches completion in about 20 minutes or less.

[0052] In certain preferred embodiments, the chemical pulp has medium brightness and the chlorine dioxide stage is not immediately followed by an additional chlorine dioxide stage.

[0053] In an embodiment, the invention provides a method for improving a papermaking process through modification of a multistage bleaching of chemical pulp, the method comprising in the following order: a chlorine dioxide stage comprising treating chemical pulp with chlorine dioxide, an express alkali extraction (an example of washing with aqueous

caustic solution) comprising contacting the chemical pulp with a caustic solution, and an organomanganese-catalyzed bleaching stage comprising treating the chemical pulp with an organomanganese complex and a peroxide in the presence of caustic, which in certain embodiments is under aqueous caustic conditions.

[0054] The following are non-limiting examples of sequence modifications that result in pulp having improved properties:

[0055] (A) For a D0-E-D1 sequence, the second chlorine dioxide stage (D1) can be replaced with an organomanganese-catalyzed bleaching stage (Epc) and a standard caustic extraction stage (E) with express extraction (caustic wash, E'). Thus, the resulting D0-E'-Epc method comprising a chlorine dioxide stage (D0), caustic wash and an organomanganese-catalyzed bleaching stage (Epc) does not comprise a second chlorine dioxide stage.

[0056] (B) For a D0-Eop-D1 sequence, employment of express alkali extraction (caustic wash, E') combined with an organomanganese-catalyzed bleaching stage allows for the elimination of the need for the second chlorine dioxide stage (D1) and oxygen leading to a simplified procedure D0E'Pc.

[0057] It has been surprisingly and unexpectedly discovered that express alkali extraction of chemical pulp after a D0 stage prior to an organomanganese-catalyzed bleaching stage improves reactivity of the D0-treated chemical pulp towards (a) hydrogen peroxide itself and (b) the manganese catalyst applied with hydrogen peroxide, resulting in a substantial increase in pulp brightness. Otherwise, the D0-treated chemical pulp could be insufficiently reactive in the presence of the catalyst to provide justification for the use of the catalyst. For example, only a quick (*e.g.*, ≤ 1 minute) warm caustic wash at 2 wt% sodium hydroxide at 65° C is needed to provide significant improvement in brightness. A quick warm caustic wash tends to reduce alkali brightness loss and provide higher pulp yield, as pulp tends to degrade in the presence of caustic. Without wishing to be bound by theory, the experimental results suggest that express alkali extraction improves the response of pulp through pulp swelling as well as removal of uronic acids and degraded lignin, which constitute chromophores and consume peroxide.

[0058] Moreover, it was surprisingly and unexpectedly discovered that a two-stage alkali process results in higher differentiation and brightness as compared to a simple increase in hydroxide concentration in a one-stage process (*see, e.g.*, FIGs. 8 and 9).

[0059] As discuss above, an organomanganese-catalyzed bleaching stage can allow for the elimination of the need for a second chlorine dioxide stage (D1) and/or third chlorine

dioxide stage (D2) and/or oxygen. Thus, in certain embodiments, a chlorine dioxide stage does not immediately follow the organomanganese-catalyzed bleaching stage. In certain embodiments, the express alkali extraction and organomanganese-catalyzed bleaching stage does not comprise the use of oxygen. However, in certain embodiments, the express alkali extraction is performed in the presence of oxygen.

[0060] Any suitable caustic solution can be used to perform the express alkali extraction. In certain embodiments, the caustic solution comprises an inorganic base or an organic base. In certain embodiments, the caustic solution comprises an alkali or alkaline earth metal hydroxide or salt. In certain embodiments, the caustic solution comprises an alkali metal hydroxide or salt selected from sodium hydroxide, potassium hydroxide, lithium hydroxide, rubidium hydroxide, cesium hydroxide, and combinations thereof.

[0061] In certain preferred embodiments, the express alkali extraction is performed by mixing the chemical pulp with an aqueous caustic solution having a temperature of from about 40° C to about 90° C, and optionally dewatering and washing the chemical pulp before treating the pulp with the organomanganese complex and peroxide. As discussed above, sufficient brightness can be obtained with relatively short extraction times (*e.g.*, 10 minutes or less). In certain embodiments, express alkali extraction is performed by contacting a chemical pulp with an aqueous caustic solution for about 10 minutes or less. Thus, in certain embodiments, express alkali extraction is performed by contacting a chemical pulp with an aqueous caustic solution for about 10 minutes or less, about 8 minutes or less, about 6 minutes or less, about 5 minutes or less, about 4 minutes or less, about 2 minutes or less, or about 1 minute or less. In certain preferred embodiments, express alkali extraction is performed by contacting the chemical pulp with an aqueous caustic solution for about 1 minute or less.

[0062] The aqueous caustic solution used in the express alkali extraction may be re-used. In certain embodiments, the aqueous caustic solution is reused in one or more express alkali extractions from two to ten times. In certain embodiments, express alkali extraction is performed using an aqueous caustic solution that has been used from two to ten times.

[0063] In certain embodiments, the organomanganese-catalyzed bleaching stage reduces the amount of chlorine dioxide needed in the chlorine dioxide stage by 50% or less. Thus, in certain embodiments, the organomanganese-catalyzed bleaching stage reduces the amount of chlorine dioxide needed in the chlorine dioxide stage by about 50% or less, about 40% or less, about 30% or less, about 20% or less, about 10% or less, or about 5% or less. In certain

embodiments, the organomanganese-catalyzed bleaching stage reduces the amount of chlorine dioxide needed in the chlorine dioxide stage by 50% or more.

[0064] In another embodiment, the invention provides a method for improving a papermaking process through modification of a multistage bleaching of chemical pulp, the method comprising performing delignification of a chemical pulp (*e.g.*, brownstock pulp) subsequent to a cooking process and immediately prior to a bleaching process (*e.g.*, prior to a chlorine dioxide stage), wherein the delignification is performed by treating the chemical pulp with a manganese complex and a peroxide in the presence of a base, and optionally oxygen gas.

[0065] For example, bleaching experiments on Eo chemical pulp (*e.g.*, hardwood pulp) has demonstrated that a multistage EoPcD0 sequence results in activation of the pulp towards subsequent stages in the intermediate bleaching range. In other words, a brightness gain is higher at the following D stage when the organomanganese complex is applied in a previous alkali peroxide stage. Generally, “stage synergism” is not expected when both stages are oxidative. In certain embodiments, a reduction of about 50% chlorine dioxide at a D stage may be obtained without a consequential loss in brightness. In certain embodiments, the method does not comprise a chlorine dioxide stage either immediately following a D stage or later in the bleaching sequence. Thus, a D-treated (*e.g.*, D0-treated) chemical pulp is an example of an acidic oxidated chemical pulp.

[0066] In certain embodiments, express alkali extraction is also achieved through an oxygen delignification stage. Thus, even on less reactive D0-treated hardwood chemical pulp, an organomanganese-catalyzed bleaching stage after oxygen delignification yields an improvement in catalytic brightness (*see, e.g.*, FIG. 7).

[0067] Generally, oxygen delignification of brownstock pulp immediately follows cooking and precedes bleaching stages. Generally, residual lignin is removed in a reactor under aqueous caustic conditions and pressurized oxygen, with kappa number being the most important criterion of performance. Kappa number is an indication of the residual lignin content or the bleachability of wood pulp. Kappa number is determined by the number of milliliters of 0.1-N potassium permanganate solution that can be absorbed by 1 gram of oven-dry pulp under conditions specified in the ISO 302:2004 standard.

[0068] It has been found that in the presence of peroxide, the effect of the organomanganese complex on oxygen delignification can be significant. Applying the organomanganese complex with hydrogen peroxide alone could bring about the same effect

that is achieved through application of oxygen, in terms of both brightness and kappa number. Moreover, application of the organomanganese complex improves selectivity in bleaching, yielding increased brightness and decreased kappa number at increased pulp viscosity (*see* FIG. 3). If peroxide concentration is sufficient, an organomanganese-catalyzed bleaching process may be utilized in addition to or instead of oxygen (*e.g.*, Eo or Eop stages). Thus, in certain embodiments, the method is performed in the absence of oxygen.

[0069] In another embodiment, the invention provides an aqueous formulation for bleaching of a chemical pulp comprising an organomanganese complex and water, wherein the aqueous formulation has a pH of from about 3 to about 7 and the organomanganese complex is at a concentration of from about 0.001% to about 5% by weight based on the weight of the aqueous solution. In certain preferred embodiments, the formulation comprises about 0.5% to about 3% organomanganese complex actives and has a pH of from about 4 to about 6.

[0070] The organomanganese complex can be thermally unstable under certain weather conditions, which limits its use at some pulp mill locations. For example, application sites are normally not protected from outdoor temperatures. Decomposition of Mn^{2+} μ -(acetato- $\kappa\text{O}:\kappa\text{O}'$)[μ -[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine- $\kappa\text{N}1,\kappa\text{N}4,\kappa\text{N}7$]]]di- μ -oxodi-chloride (1:2) in an aqueous solution can occur at sustained temperatures of about 35–40° C for 1–2 days. Therefore, it is especially important that the organostability of the organomanganese complex is taken into account. In certain preferred embodiments, the organomanganese complex is introduced into pulp in a form of a dilute solution that provides sufficient storage stability at elevated temperatures. In certain embodiments of the formulation, the formulation is ready-to-deliver and can be stored without substantial degradation for an extended period of time (*e.g.*, 2 months or more) at temperatures of about 35–40° C.

[0071] The proposed combination of concentration and pH ranges is optimal from the points of feeding, storage and transportation. The product can be formulated at an external facility or, preferably, on site. A critical aspect of the formulation's stability is the pH adjustment to an acidic range using an organic acid and/or an inorganic acid, which may include, *e.g.*, acetic acid, citric acid, lactic acid, sulfuric acid, hydrochloric acid, and/or phosphorous acid. The pH of the formulation is adjusted in view of a continuous shift typical of the product. The formulation can be at any suitable pH. In certain preferred embodiments, the formulation has a pH of from about 4 to about 6. In certain embodiments, the formulation

has a pH of about 4, or of about 5, or of about 6. In certain preferred embodiments, a strong acid such as sulfuric acid is used to lower the pH of the formulation to about 4 to about 6. In certain embodiments, the formulation is given enough time during preparation for the pH adjustment. In certain preferred embodiments, the initial pH of the formulation is about 4 so that it would not exceed 6.5 after exposure to mill conditions.

[0072] In certain embodiments, the formulation comprises an organomanganese complex and water. In certain embodiments, the formulation consists essentially of an organomanganese complex and water. In certain embodiments, the formulation consists of an organomanganese complex and water.

[0073] Any suitable water source can be used with the present inventive methods. In certain embodiments, the water is mill white water. In certain embodiments, the water is tap water or deionized water.

[0074] The formulation can comprise any suitable organomanganese complex. In certain embodiments, the manganese complex is a mononuclear or binuclear complex of Mn(III) and/or Mn(IV) organic complex with one or more O^{2-} bridge. In certain preferred embodiments, the manganese complex is a manganese-triazacyclononane complex. In certain preferred embodiments, the manganese complex is $Mn^{2+} \mu-(acetato-\kappa O:\kappa O')[\mu-[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine-\kappa N1,\kappa N4,\kappa N7]]]di-\mu-oxodi-X^-$. The aforementioned complex can comprise any suitable organic or inorganic anion (X^-). In certain embodiments, the anion is a halogen such as fluoride, chloride, bromide, and/or iodide. In certain preferred embodiments, X^- is a chloride anion. In certain preferred embodiments, X^- is selected from a halogen, sulfate, acetate, and citrate. In certain preferred embodiments, the organomanganese complex is $Mn^{2+} \mu-(acetato-\kappa O:\kappa O')[\mu-[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine-\kappa N1,\kappa N4,\kappa N7]]]di-\mu-oxodi-chloride (1:2)$.

[0075] The formulation can comprise organomanganese complex at any suitable concentration. In certain embodiments, the organomanganese complex is present in the formulation at a concentration of from about 0.001% to about 5%. Thus, in certain preferred embodiments, organomanganese complex is present in the formulation at a concentration of from about 0.001% to about 5%, from about 0.001% to about 4%, from about 0.001% to about 3%, from about 0.001% to about 2%, from about 0.001% to about 1%, from about 0.001% to about 0.5% by weight based on the weight of formulation. In certain preferred

embodiments, the organomanganese complex is present in the formulation at a concentration of from about 0.5% to about 3% by weight of actives based on weight of the formulation.

[0076] In another embodiment, the invention provides an aqueous formulation for bleaching of a chemical pulp comprising an organomanganese complex, a peroxide, and water, wherein the organomanganese complex is at a concentration of from 0.0001% to about 1% and the peroxide is at a concentration of from about 5% to about 60% by weight based on weight of the aqueous solution.

[0077] As discussed herein, it has been found that delivery form and technique can affect the performance of the organomanganese complex and industrial utility of the methods set forth herein. In certain embodiments, the organomanganese complex is fed as a dilute solution into, preferably, a peroxide line. If delivery into a peroxide line is not possible, then the organomanganese complex can be delivered into the chemical pulp line after the chemical pulp has been treated with base and peroxide. If the organomanganese complex is delivered directly into the pulp, thorough mixing of the organomanganese complex with pulp slurry is recommended. In certain embodiments, a high consistency mixer, *e.g.*, an Andritz mixer Model HCM3HH, is used to provide even distribution of the catalyst in pulp. In certain preferred embodiments, the peroxide is concentrated. In certain preferred embodiments, the ready-to-deliver catalyst formulation comprises about 0.5 to about 3% actives and has pH adjusted to around about 4 to about 6. In certain preferred embodiments, the deliverable formulation is prepared on site from the solid product and tap water. In the absence of the aforementioned steps, faster product decomposition has been observed under common pulp mill conditions.

[0078] In certain embodiments, it was also found that the organomanganese complex is preferably introduced into pulp in a form of a solution into the hydrogen peroxide feeding line, the higher concentration of peroxide the better. In certain preferred embodiments, the peroxide is at a concentration of from about 30% to about 50%. Introducing the organomanganese complex with the peroxide increases efficiency in the methods set forth herein. The organomanganese complex can also be introduced into pulp as a solution. In certain embodiments, the organomanganese catalyst solution is mixed with pulp before the bleaching process begins. In certain preferred embodiments, the organomanganese complex is fed into the peroxide line as a solution. In certain preferred embodiments, the organomanganese complex is not fed into the caustic line because the catalyst can be deactivated.

[0079] The following definitions are provided to determine how terms used in this application, and in particular, how the claims are to be construed. The organization of the definitions is for convenience only and is not intended to limit any of the definitions to any particular category.

[0080] “Reaction tube” refers to a tube containing pulp combined with a bleaching solution, where pulp moves through the tube at an elevated temperature (*e.g.*, 50–90°C). A difference between a standard bleaching chest and a reaction tube is that the reaction tube provides for continuous pulp bleaching during the relatively short time when the pulp moves through the tube.

[0081] “Chemical pulp” refers to a mass of fibers resulting from the reduction of wood or other fibrous raw material into its component parts during cooking phases with various chemical liquors, in such processes as sulfate, sulfite, soda, NSSC, etc.

[0082] “Chlorine dioxide state” refers to a step or steps in a multistage bleaching process (*i.e.*, “D-stages”) where chlorine dioxide solution is combined with pulp, allowed to react, and then washed as one of the operations making up a multistage pulp bleaching system.

[0083] “Express alkali extraction” refers to the relatively short-time contacting of pulp with relatively large quantity of warm aqueous caustic solution followed by dewatering (*e.g.*, 10% consistency pulp is mixed with 1:5 volume of 1–10% caustic in water at about 40 to about 90°C, and then dewatered back to 10%). Generally, an express alkali extraction stage is performed in the absence of peroxide and organomanganese complex.

[0084] “Medium brightness” refers to pulp having a ISO brightness of about 50 to about 70.

[0085] The following examples further illustrate the inventive concepts of the present disclosure but should not be construed as in any way limiting its scope.

EXAMPLES

[0086] All percentages in the Examples are given on a weight percent of dry pulp basis. In the Examples, the following terms shall have the indicated meaning. Br for ISO brightness R457 (TAPPI 525); Ye for E313 yellowness; WI for E313 Whiteness. For the purposes of the examples and procedures set forth herein, “catalyst” refers to an organomanganese complex, and, specifically for the Examples, refers to $\text{Mn}^{2+} \mu\text{-(acetato-}\kappa\text{O}:\kappa\text{O}')][\mu\text{-[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine-}\kappa\text{N1},\kappa\text{N4},\kappa\text{N7}]]]\text{di-}\mu\text{-oxodi-chloride (1:2)}$, which is an example of an organomanganese complex.

PROCEDURE 1 – Peroxide Bleaching

[0087] Procedure 1 is a procedure for peroxide bleaching of chemical pulp in accordance with a portion of an embodiment of the invention. The catalyst (*e.g.*, organomanganese complex) used for the experimental Examples is $\text{Mn}^{2+} \mu\text{-(acetato-}\kappa\text{O:}\kappa\text{O')}] [\mu\text{-[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine-}\kappa\text{N1,}\kappa\text{N4,}\kappa\text{N7}]]]$ di- μ -oxodichloride (1:2).

[0088] Pulp samples from various mills were tested. Based on initial pulp consistency, 10 g (based on o.d. pulp) of sample was taken. Next, samples were put in Kapak bags and diluted to a total volume of 100 g, which provided pulp of 10% consistency.

[0089] Hydrogen peroxide (3% solution) was dosed at 0.5–2% by weight, and sodium hydroxide (3% solution) was dosed at 1–3% by weight based on o.d. pulp. An organomanganese complex sample diluted to 1:50000 was applied at 1–5 ppm (active base) based on dry pulp. The order of addition was as follows unless indicated otherwise. Sodium hydroxide was added to the pulp first, followed by the catalyst, and then hydrogen peroxide. After a pH measurement was taken, the bag was sealed and pulp mixed by pounding and pressing the bag. Subsequently, the samples were placed in a water bath at 70° C, unless indicated otherwise. After 40 minutes (unless indicated otherwise), the samples were removed from the water bath, placed in cold water and allowed to cool. After about 10 minutes, the samples were washed in a Buchner funnel lined with cheesecloth with 3L of water. Excess water was squeezed from the samples. The samples were weighed and divided in half. One half of each sample was used for making brightness pads; the other half of each sample was saved for second stage bleaching with chlorine dioxide, when needed.

[0090] It was discovered that that feeding the organomanganese complex with caustic can cause decomposition and loss of activity. The catalyst can be added to pulp before or after peroxide. Additional benefit was discovered when the catalyst was fed to the pulp with the peroxide via the peroxide line. In laboratory tests simulating the latter process, the catalyst was added as a 1:20 solution of the standard formulation (2% actives) in water (total dilution 0.1%) to concentrated hydrogen peroxide solution at a target peroxide/catalyst ratio. The solution was held for 1 min and then diluted to 3% peroxide that was added to alkali oxidized chemical pulp at the target dosage.

[0091] In order to make brightness pads, the samples were diluted to 1L in a plastic beaker and stirred for about 10 minutes each. One drop of 5-N sulfuric acid was added in order to eliminate residual hydroxide. Then, the samples were passed through filter paper,

placed on metal plates and pressed for 5 minutes to remove excess water. The samples were then left in a constant humidity and temperature room (23° C, 50% humidity) overnight. Brightness was measured with a Technodyne Color Touch 2 (Model ISO) instrument.

PROCEDURE 2 - Oxygen and Oxygen-Peroxide Delignification

[0092] Procedure 2 is a procedure for oxygen and oxygen-peroxide delignification of chemical pulp in accordance with a portion of an embodiment of the invention.

[0093] Pulp samples were prepared as described above based on 3% consistency, 10.5 g o.d. pulp. The chemicals were added to dilute pulp in an open Parr reactor, then the reactor was closed and, when applicable, pressurized with oxygen to 100 psi. The slurry was mixed at the “max” rate, believed to be about 300–400 rpm, and heated to the target temperature that took 15–20 min dependent on the target temperature. Time at the target temperature was counted from the moment that the temperature was 5° C less than the target (e.g., 95° C for 100° C target) to 40 min. Then the reactor was cooled, depressurized, and the pulp processed as described above.

PROCEDURE 3 - Chlorine Dioxide Bleaching

[0094] Procedure 3 is a procedure for chlorine dioxide bleaching of chemical pulp in accordance with a portion of an embodiment of the invention. Chlorine dioxide solution prepared in the laboratory was stored in a refrigerator and titrated before the bleaching. For chlorine dioxide bleaching, 5g samples (based on o.d. pulp) obtained from the previous step (hydrogen peroxide bleaching) were diluted to 10% consistency in plastic bags. The pH of these pulp samples was adjusted to about 4.5 with 5-N sulfuric acid before addition of chlorine dioxide. Chlorine dioxide was dosed (usually, at 0.5% based on o.d. pulp) and added right after pH adjustment. The pH of these samples was from 2.5 to 2.9. The bags were sealed; the samples mixed and kept in a water bath for 1 hour at 70° C. Subsequently, the samples were cooled to 25° C and processed in the same way as described above for Procedure 1.

PROCEDURE 4 - Express Alkali Extraction

[0095] Procedure 4 is a procedure for express alkali extraction of chemical pulp in accordance with a portion of an embodiment of the invention.

[0096] Express alkali extraction was done in certain samples before a peroxide bleaching stage. For such certain samples, usually 10 g samples (based on o.d. pulp) were diluted to 5% consistency in plastic bags. Then, 2% NaOH, based on dry pulp, was added as a 3% solution to the bags and the samples mixed. The samples were then placed in a water bath at 65°C, diluted to 1 L of water and squeezed with cheesecloth (*i.e.*, no excessive wash). In further tests, the samples were washed with a warm aqueous caustic solution. In even further tests, the samples were treated with caustic and dewatered to the target bleaching consistency without a wash. Samples prepared according to Procedure 4 were later used in peroxide bleaching as described in Example 1 herein.

PROCEDURE 5 – Brightness Determination

[0097] Procedure 5 provides background information related to brightness determination of chemical pulp in accordance with a portion of an embodiment of the invention.

[0098] Generally, brightness measurements are used for pulp characterization and process assessment. “ISO Brightness” is a term used to describe the whiteness of pulp or paper, on a scale from 0% (absolute black) to 100% (relative to an MgO standard, which has an absolute brightness of about 96%) by the reflectance of blue light (457 nm wavelength) from the sheet.

Process Modification Examples

[0099] Examples of process modification and corresponding results are as follows. FIG. 1 shows that, when organomanganese catalyst is used in peroxide stage, the temperature of the process can be reduced without negatively affecting brightness. Generally, standard mill conditions can require between 60 and 90 minutes to achieve target brightness. FIG. 2 demonstrates that bleaching develops quickly in the presence of organomanganese catalyst, resulting in maximum brightness at a much faster rate than under standard mill conditions. This result is advantageous because reducing temperature and time leads to increased pulp preservation, which translates into increased yield and strength (*e.g.*, increased viscosity) of bleached pulp. FIG. 3 shows that selectivity of bleaching and delignification are improved, resulting in increased brightness, decreased kappa numbers, and increased viscosity.

[0100] Express alkali extraction significantly improves response of D0-treated chemical pulp. FIG. 4 shows that a significant improvement in brightness is achieved in the presence of catalyst when D0-treated chemical pulp is subjected to alkali extraction prior to bleaching,

even at relatively low concentrations of hydrogen peroxide (0.5% vs. 1%) on D0-treated hardwood chemical pulp.

[0101] FIG. 5 shows that softwood D0-treated chemical pulp is more responsive the catalyst and alkali activation further increases the effect.

[0102] FIGs. 6A and 6B demonstrate that a short caustic wash tends to improve bleachability and reactivity toward the catalyst for both Eo (hardwood) and D0 (softwood) chemical pulp. It was discovered that increased time of treatment had no effect on the result, and 1 min treatment (*e.g.*, washing with a warm aqueous caustic solution) provided significant improvement in brightness. Advantageously, washing with a short warm aqueous caustic solution does not lead to alkali brightness loss. The results described herein allow for a bleaching scheme of improved efficiency, with an aqueous caustic wash followed by alkali peroxide bleaching comprising a catalyst, *e.g.*, an organomanganese complex.

[0103] Express alkali extraction can be achieved also through the oxygen delignification stage. FIG. 7 demonstrates that, even on less reactive D0 hardwood pulp, peroxide bleaching that is post-oxygen delignification and that utilizes a catalyst improves brightness in a D0EoEpc sequence.

[0104] Generally, express alkali extraction affects catalyst performance more than the mere pH increase absent the catalyst. FIGs. 8A and 8B show a comparative study of two- and one-stage Pc process at the same hydroxide concentration (pre-treatment at 2% caustic followed by 2% caustic / 2% peroxide bleaching vs. 4% caustic / 2% peroxide bleaching). The figures demonstrate a clear advantage of the two-stage process — higher differentiation and higher brightness. The results illustrated in FIGs. 8A and 8B show that a much greater brightness (81.0 versus 75.6 ISO Brightness units) and shorter stage time (20 versus 90 minutes) is obtained when compared to control samples. Additionally, reducing bleaching time provides a benefit in yield and strength (*i.e.*, viscosity).

[0105] FIG. 9 shows that improvement in brightness can be achieved even at a relatively low peroxide dose and catalyst loading, *e.g.*, at 0.5% hydrogen peroxide and 1–2 ppm catalyst.

[0106] Generally, oxygen delignification of brownstock pulp immediately follows cooking and precedes bleaching stages. Under aqueous caustic conditions and pressurized oxygen in a reactor, oxygen delignification removes residual lignin, with kappa number being an important criterion of performance. In the presence of peroxide, which is optional, catalyst in oxygen delignification can provide significant benefit. Moreover, the catalyst improves

selectivity of bleaching and delignification, resulting in increased brightness, decreased kappa number, and increased viscosity of the pulp, as illustrated in FIG. 3. With sufficient peroxide concentration (in this particular instance about 2% hydrogen peroxide), an Epc process may replace oxygen (Eo, Eop), as oxygen may no longer be necessary in multistage bleaching.

[0107] FIGs. 10 and 11 demonstrate that multistage EoPcD0 bleaching experiments on Eo hardwood pulp results in pulp activation toward subsequent stages in an intermediate bleaching range as exemplified by an increased brightness at the subsequent D-stage than at the target peroxide stage. As noted herein, “stage synergism” is not expected when both stages (*e.g.*, peroxide stage and D-stage) are oxidative. Potential reduction in chlorine dioxide consumption at the D-stage may exceed 50 wt% based on examples presented herein.

[0108] Differentiation achieved at the Ep stage remains when D1 has a relatively high brightness range as well, which allows for reduced chlorine dioxide consumption, or even possibly the elimination of one or more chlorine dioxide stages. Elimination of one or more chlorine dioxide stages would avoid pH readjustment for the one or more chlorine dioxide stages that would be eliminated. FIG. 12 shows the effect of the catalyst on an E2 Stage (D1 hardwood chemical pulp) that allows for a modified procedure, thereby eliminating a D-stage (*e.g.*, Do-Ep-D1-E2-D2 becomes Do-Ep-D1-Epc).

[0109] A solution of catalyst in water is thermally unstable under certain conditions and therefore cannot be used in every pulp mill, particularly in summer months, as decomposition has been shown to occur at 35° C to 40° C in 1–2 days. In certain embodiments, the catalyst is introduced into pulp via a dilute solution (*e.g.*, from about 0.5 wt% to about 3 wt% as actives, having a pH of from about 4 to about 6). FIG. 13 provides examples of conditions that have been shown to allow for sufficient storage stability under elevated temperatures.

Efficiency Improvement Examples

[0110] FIGs. 14A–C show that greater brightness is obtained when catalyst is introduced as a solution into the hydrogen peroxide feeding line prior to addition to the chemical pulp. It was discovered that higher concentration of peroxide gives increased brightness (*e.g.*, 30–50 wt%). Introducing the catalyst with the peroxide has been shown to provide improved efficiency (*e.g.*, improved energy efficiency via decreased process temperatures and/or improved chemical efficiency via decreased chemical consumption). Catalyst can also be introduced into pulp in a form of a solution after the caustic mixed with pulp or after the caustic and peroxide mixed with pulp.

[0111] Laboratory findings were confirmed in a full-scale week-long mill trial (kraft pulp, feeding the organomanganese catalyst as a solution to a peroxide line). Trial data are presented in FIG. 15.

[0112] The following tests demonstrate how catalyst can be used in specific stages to improve process efficiency, for example, to allow for shorter reaction time(s), decreased process temperature(s), reduction in bleaching agent consumption (*e.g.*, chlorine dioxide at a subsequent D1 stage up to 50%), and/or allow for the use of express bleaching (*e.g.*, via reaction tube(s)), in accordance with embodiments of the present invention. “Program” and “Test (no.)” refer to samples that include catalyst. The catalyst utilized was Mn^{2+} μ -(acetato- $\kappa O:\kappa O'$)[μ -[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine- $\kappa N1,\kappa N4,\kappa N7$]]]di- μ -oxodi-halide (1:2).

[0113] Test 1- *Eop Stage*

Conditions: Laboratory test, 3 wt% brownstock pulp, 2 wt% hydrogen peroxide, 100 psi oxygen, 100° C, 40 minutes + 18 min ramping, 10 ppm by weight catalyst

Data: Control 1 (no catalyst) versus Test 1 (with catalyst): Brightness of Control 1 54.6 ISO Brightness Units versus brightness of Test 1 63.5 ISO Brightness Units; Kappa value: Control 1 7.8 versus Test 1 7.3.

Results and Discussion: There was an immediate effect on the process observed in the presence of the catalyst. In particular, the Brightness increases and the Kappa number decreases in the presence of the catalyst. The data suggests potential reduction in chemical consumption and elimination of oxygen (*e.g.*, replacement of Eo stage with Epc stage).

[0114] Test 2 - *Ep (Eop) Stage*

Conditions: Laboratory test, 10 wt% brownstock pulp, 2 wt% sodium hydroxide, 2 wt% hydrogen peroxide, 70° C, 5 ppm catalyst.

Data: Control 2 - Brightness (ISO Brightness Units) - 41.8 (20 min), 43.3 (40 min), 42.8 (60 min)

Test 2 - Brightness (ISO Brightness Units): 47.6 (20 min), 47.6 (40 min), 48.3 (60 min)

Control 2 - Kappa: 11.9 (20 min), 11.7 (40 min), 11.7 (60 min)

Test 2 - Kappa: 10.1 (20 min), 10.8 (40 min), 10.4 (60 min)

Results and Discussion: A significant time saving can be achieved simultaneously with increased brightness and Kappa number; higher yield and strength are expected due to decreased pulp degradation because of shorter exposure to hydroxide.

[0115] Test 3 - *Ep (Eop)*

Conditions: lab test, 10 wt% brownstock pulp, 2 wt% sodium hydroxide, 2 wt% hydrogen peroxide, 40 min, 5 ppm catalyst.

Data: Control 3 - Brightness (ISO Brightness Units): 40.4 (70° C), 39.7 (60° C)

Test 3 - Brightness (ISO Brightness Units): 46.1 (70° C), 46.3 (60° C)

Control 3 - Kappa: 11.6 (70° C), 11.3 (60° C)

Test 3 - Kappa: 9.7 (70° C), 10.1 (60° C)

Results and Discussion: Energy efficiency is improved simultaneously with increased brightness and Kappa number; higher yield and strength are expected due to decreased pulp degradation because of milder conditions. Both time and temperature can be decreased.

[0116] Tests 4a and 4b – *EoEp(c)D1*

Conditions: lab test, 10 wt% Eo softwood chemical pulp, 1 wt% hydrogen peroxide, 2 wt% sodium hydroxide, 70° C, 40 min, 5 ppm catalyst, followed by a D1 stage.

Data: Control 4a versus Test 4a: Brightness (ISO Brightness Units) Control 4a 52.0 versus Test 4a 62.7 (0.5 wt% chlorine dioxide at D1)

Control 4b versus Test 4b: Brightness (ISO Brightness Units) Control 4b 55.9 versus Test 4b 64.8 (1 wt% chlorine dioxide at D1)

Results and Discussion: A similar increase in brightness is achieved with 50% reduction of chlorine dioxide consumption. Low-chlorine dioxide D1 or elimination of D1 with proper chemical balance is possible.

[0117] Tests 5a and 5b – *EoEp(c)D1*

Conditions: lab test, 10 wt% Eo hardwood chemical pulp, 2 wt% hydrogen peroxide, 2 wt% sodium hydroxide, 70° C, 40 min, 5 ppm catalyst; then followed by a D1 stage (0.6 wt% chlorine dioxide)

Data: Control 5a versus Test 5a: Brightness (ISO Brightness Units) Control 5a 47.2 versus Test 5a 55.2 (*EoEp(c)*)

Control 5b versus Test 5b: Brightness (ISO Brightness Units) Control 5b 54.5 versus Test 5b 65.8 (*EoEp(c)D1*)

Results and Discussion: Brightness gain in the following D1 stage (Test 5b) exceeds brightness gain in the *Ep(c)* stage proper (11.3 vs. 8 ISO Brightness Units) –synergy likely due to lignin activation; potential reduction in chlorine dioxide consumption.

Modification Examples

[0118] This Example demonstrates how catalyst can be used to redesign multistage bleaching processes in accordance with embodiments of the present invention.

[0119] Test 6—*Eo/Eop*

Conditions: lab test, 3 wt% chemical pulp, 2 wt% hydrogen peroxide, 100 psi oxygen, 100° C, 40 minutes + 18 minutes ramping, 10 ppm catalyst.

Data: Peroxide alone versus Peroxide + O₂ versus Peroxide + Program: Brightness (ISO Brightness Units) 43.1 : 54.6 : 54.1.

Kappa 9.8 : 7.8 : 8.1

Results and Discussion: Eop can be potentially replaced with Epc (no oxygen) that would improve strength and yield, and activate D0-treated chemical pulp towards the next D1 stage.

[0120] Tests 7a and 7b—*Ep*

Conditions: lab test, 10 wt% D0-treated softwood pulp, 2 wt% sodium hydroxide, 2 wt% hydrogen peroxide, 70° C, 40 minutes, 5 ppm catalyst.

Data: Control 7a versus Test 7a “direct” (e.g., no pre-treatment): Brightness (ISO Brightness Units) Control 7a 72.5 versus Test 7a 75.8

Control 7b versus Test 7b after 1 minute, 70° C, pre-treatment with 2 wt% sodium hydroxide: Brightness (ISO Brightness Units) Control 7b 74.1 versus Test 7b 79.0

Results and Discussion: Process modification, EEpc sequence brings a significant brightness increase that may potentially either eliminate subsequent D1 stage or allow significant reduction in chlorine dioxide consumption.

[0121] Tests 8a and 8b — *Ep*

Conditions: lab test, 10 wt% D0 softwood chemical pulp, 10 minutes pre-treatment with 2 wt% sodium hydroxide at 70° C, 2 wt% sodium hydroxide, 2 wt% hydrogen peroxide, 70° C, 5 ppm catalyst.

Data: Control 8a versus Test 8a, 20 minutes bleaching: Brightness (ISO Brightness Units) Control 8a 73.7 versus Test 8a 81.0; Yield Control 8a 93.1% versus Test 8a 92.3%

Control 8b versus Test 8b, 90 minutes bleaching: Brightness (ISO Brightness Units) Control 8b 75.6 versus Test 8b 81.8; Yield Control 8b 88.1% versus Test 8b 87.7%

Results and Discussion: Process modification, EEpc sequence brings increased brightness that may provide for the elimination of a subsequent D1 stage or allow for a significant reduction in chlorine dioxide consumption. Test 8a approximately achieved in 20 min what a “standard” 90-min cycle achieved (e.g., Control 8b and Test 8b).

[0122] Test 9 - *D0EoPc*

Conditions: lab test, 10 wt% D0 hardwood pulp, Eo, 1 wt% sodium hydroxide, 1.5 wt% hydrogen peroxide, varied catalyst concentration, 70° C, 40 minutes.

Data: Brightness (ISO Brightness Units): Control 9a 70.9, Test 9a1 (1 ppm catalyst) 74.2, Test 9a2 (3 ppm catalyst) 76.2

Control 9b versus Test 9b (3 ppm catalyst), 90 minute bleaching: Brightness (ISO Brightness Units) Control 9b 75.6 versus Test 9b 81.8; Yield Control 9a 88.1% versus Control 9b 87.7%

Results and Discussion: Multistage bleaching with catalyst at the last stage: a significant improvement in brightness was achieved, likely because the treated chemical pulp was activated at Eo stage. As a result, a decreased dose of catalyst was required.

EXAMPLE 9 – Field Trial

[0123] A one-week trial of catalyst (for this example, Mn^{2+} μ -(acetato- $\kappa\text{O}:\kappa\text{O}'$)) $[\mu$ -[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine- $\kappa\text{N}1,\kappa\text{N}4,\kappa\text{N}7$]]]di- μ -oxodichloride (1:2)) confirmed the catalytic effect expected based on laboratory studies. At 0.8 wt% hydrogen peroxide, application of the catalyst at 4 ppm (2 ppm actives basis) improved brightness 2.5 ISO Brightness Units. The effect was observed also at decreased catalyst and peroxide doses. Bleaching at reduced temperature by 20° F (*i.e.*, approximately 11° C) in presence of catalyst brought brightness better than in the baseline. Thus, the primary objective of the trial was satisfied.

[0124] Secondary objectives of the trial were to assess potential improvements in decreased chlorine dioxide consumption and energy efficiency. Chlorine dioxide consumption could be reduced to at least 5 lbs. per ton chemical pulp (dry), with more work on the D1 stage. The improvement in energy efficiency will be more site-dependent from plant to plant because it is not always possible to decrease the temperature for each stage of a multistage bleaching plant.

[0125] The one-week trial was designed to establish the utility of the technology in a conventional five-stage bleach plant. The bleach plant sequence is: D0, Ep, D1, E2, and D2. The catalyst was added to the hydrogen peroxide stream being delivered to the first extraction stage and fed into the dilution water delivered into the 50 wt% hydrogen peroxide feed line. The final concentration of the hydrogen peroxide acting on the pulp was 35 wt%.

[0126] Trial data are illustrated in FIG. 15. The trial data support the assumption that, under trial conditions (*i.e.*, no process changes, minimal changes of conditions), 2-ISO Brightness Unit gain at target catalyst doses could be expected.

[0127] Mill trials always include periods of instability, and averages should be measured through periods of unchanging conditions to make correct comparisons. Raw brightness data though are illustrative of the effect of the catalyst subsequent to an acidic bleaching stage. Average data through consistent periods of the same trial stages show that the immediate gain increased from 1.9 to 2.5 ISO Brightness Units when catalyst dose is increased. Brightness decreased when feeding stopped, followed by an increase upon resuming catalyst feeding. The effect of concentration remained almost the same. Total gain can reach 3.9 ISO Brightness Units at 4.4 ppm (2.2 ppm catalyst based on active ingredients). The ability to reduce temperature when the catalyst was applied decreased brightness by around 0.5 ISO Brightness Units, which provided a gain versus baseline at 3.3 ISO Brightness Units.

[0128] The use of the terms “a” and “an” and “the” and “at least one” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The use of the term “at least one” followed by a list of one or more items (for example, “at least one of A and B”) is to be construed to mean one item selected from the listed items (A or B) or any combination of two or more of the listed items (A and B), unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (*i.e.*, meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0129] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

CLAIMS:

1. A method of bleaching alkali oxidized chemical pulp comprising:
treating alkali oxidized chemical pulp with peroxide and an organomanganese complex under aqueous caustic conditions subsequent to an acidic oxidative bleaching stage to form an enhanced chemical pulp.
2. A method of enhancing chemical pulp comprising:
treating chemical pulp under acidic oxidative conditions to form an acidic oxidized chemical pulp;
washing the acidic oxidized chemical pulp with aqueous caustic solution to form an alkali oxidized chemical pulp; and
treating the alkali oxidized chemical pulp with peroxide and an organomanganese complex to form an enhanced chemical pulp.
3. The method of claim 2, wherein the aqueous caustic solution is at a temperature of from about 40° C to about 90° C.
4. The method of claims 2 or 3, wherein the washing step is an express alkali extraction.
5. The method of any one of claims 2–4, wherein the washing step is performed at atmospheric pressure.
6. The method of any one of claims 2–5, wherein the washing step is performed for about 10 minutes or less.
7. The method of claim 6, wherein the washing step is performed for about 2 minutes or less.
8. The method of claim 7, wherein the washing step is performed for about 1 minute or less.
9. The method of any one of claims 2–8, wherein the treating the alkali oxidized chemical pulp step is performed at a temperature of about 75° C or less.

10. The method of any one of claims 2–9, wherein the treating the alkali oxidized chemical pulp step is performed at a temperature of about 55° C or less.

11. The method of any one of claims 2–10, wherein the treating the alkali oxidized chemical pulp step is performed in a reaction tube.

12. The method of any one of claims 1–11, further comprising treating the enhanced chemical pulp under acidic oxidative conditions.

13. The method of claim 12, wherein the acidic oxidative conditions of treating the enhanced chemical pulp result from treating the enhanced chemical pulp with chlorine dioxide.

14. The method of any one of claims 1–13, wherein the organomanganese complex is at a concentration of from about 0.0001 ppm to about 20 ppm, and the peroxide is at a concentration of from about 0.01% to about 5% by weight, relative to dry pulp in the chemical pulp.

15. The method of any one of claims 1–14, wherein the organomanganese complex is a manganese-triazacyclononane complex.

16. The method of any one of claims 1–14, wherein the organomanganese complex is $\text{Mn}^{2+} \mu\text{-(acetato-}\kappa\text{O:}\kappa\text{O')}] [\mu\text{-[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine-}\kappa\text{N1,}\kappa\text{N4,}\kappa\text{N7}]]] \text{di-}\mu\text{-oxodi-X}^-$.

17. A thermally stable aqueous formulation for bleaching of a chemical pulp comprising an organomanganese complex and water, wherein the aqueous formulation has a pH of from about 3 to about 7 and the organomanganese complex is at a concentration of from about 0.0001% to about 3% by weight based on weight of the aqueous formulation.

18. The formulation of claim 17, wherein the organomanganese complex is $\text{Mn}^{2+} \mu\text{-(acetato-}\kappa\text{O:}\kappa\text{O')}] [\mu\text{-[1,1'-(1,2-ethanediyl)bis[octahydro-4,7-dimethyl-1H-1,4,7-triazonine-}\kappa\text{N1,}\kappa\text{N4,}\kappa\text{N7}]]] \text{di-}\mu\text{-oxodi-X}^-$.

19. The formulation of claim 17 or 18, wherein the organomanganese complex is at a concentration of from about 0.001% to about 2%, by weight based on the weight of aqueous solution and wherein the formulation has a pH of from about 4 to about 6.

20. The formulation of any one of claims 17–19, further comprising peroxide.

1/20

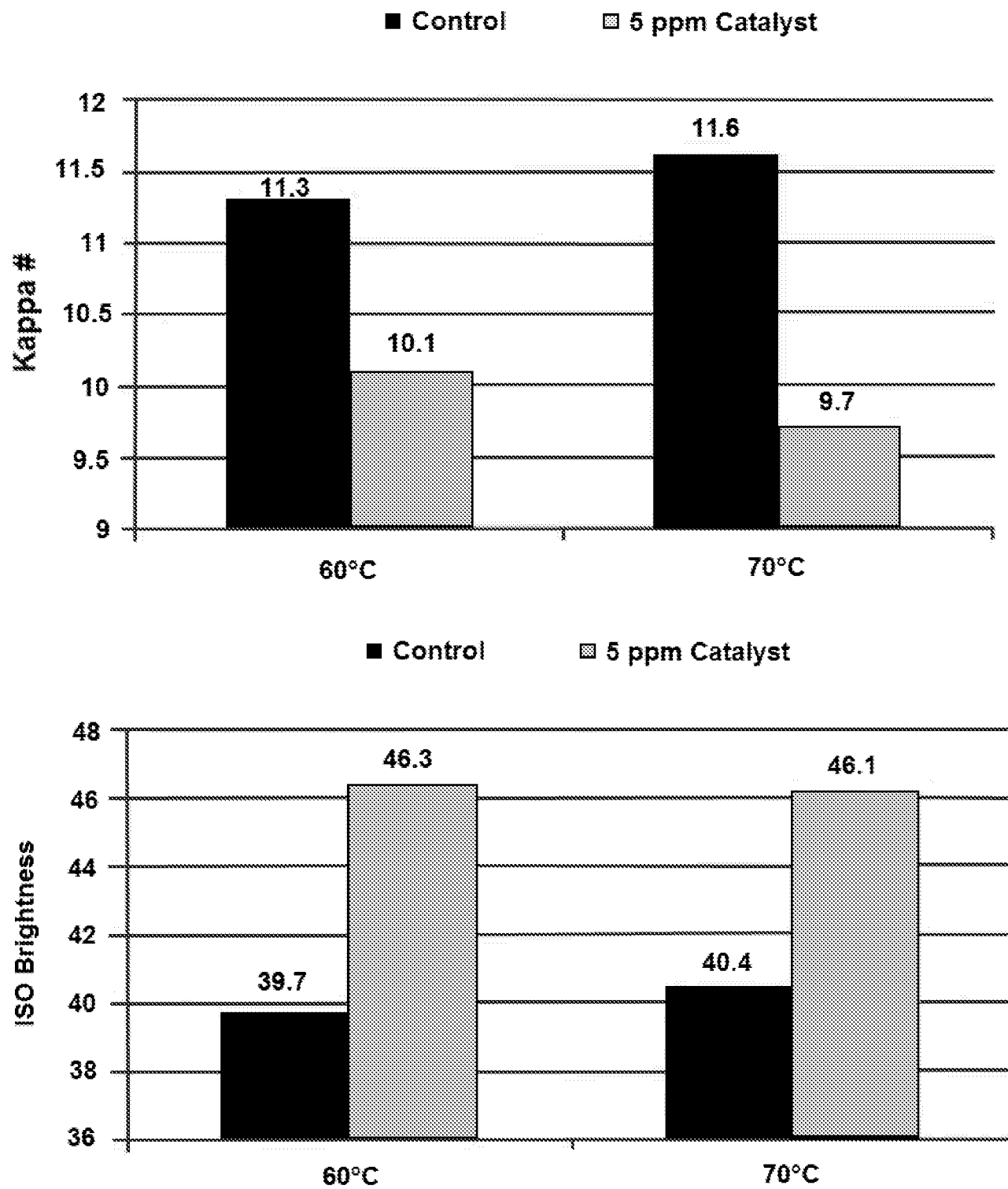


FIG. 1

2/20

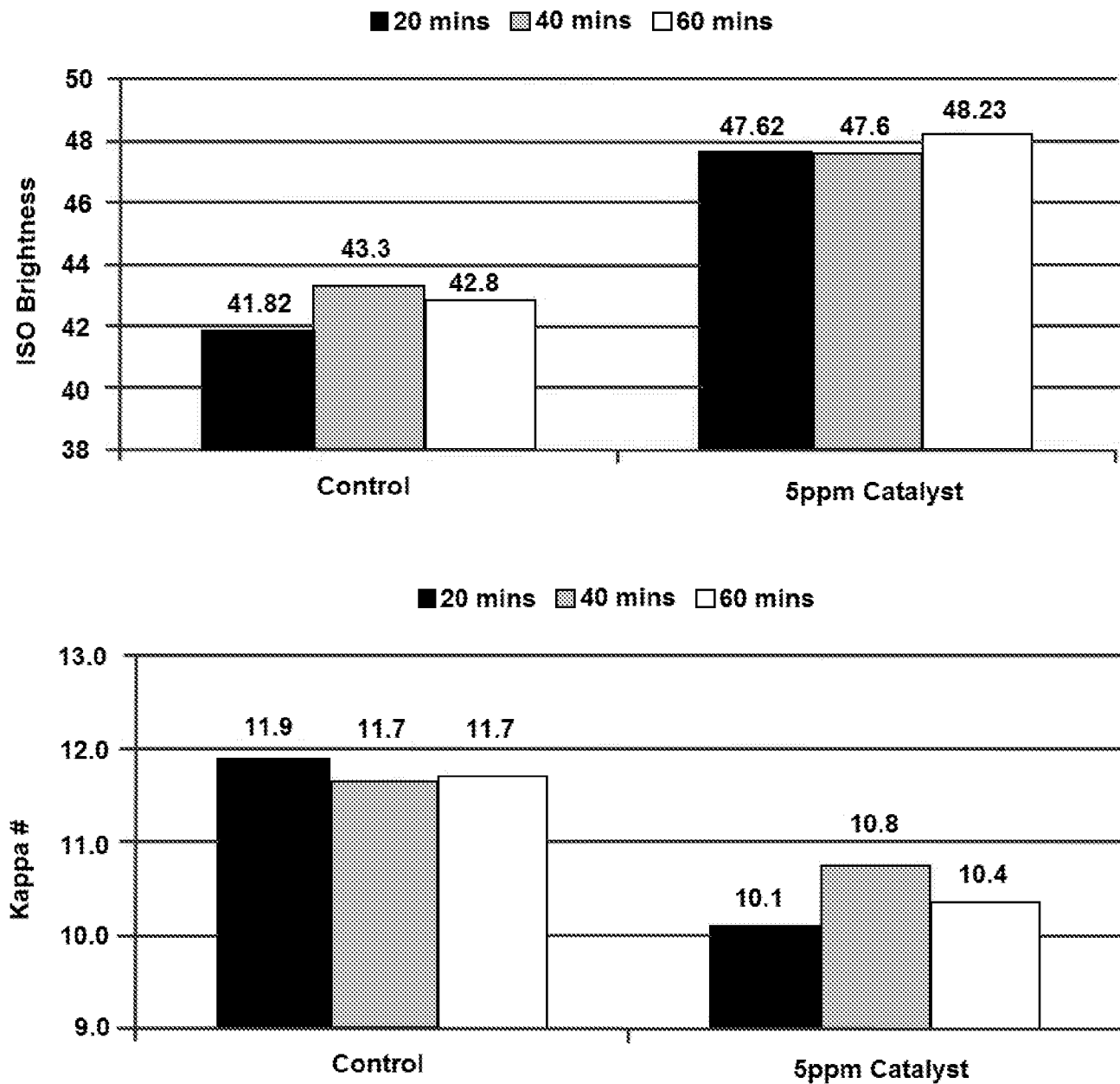


FIG. 2

3/20

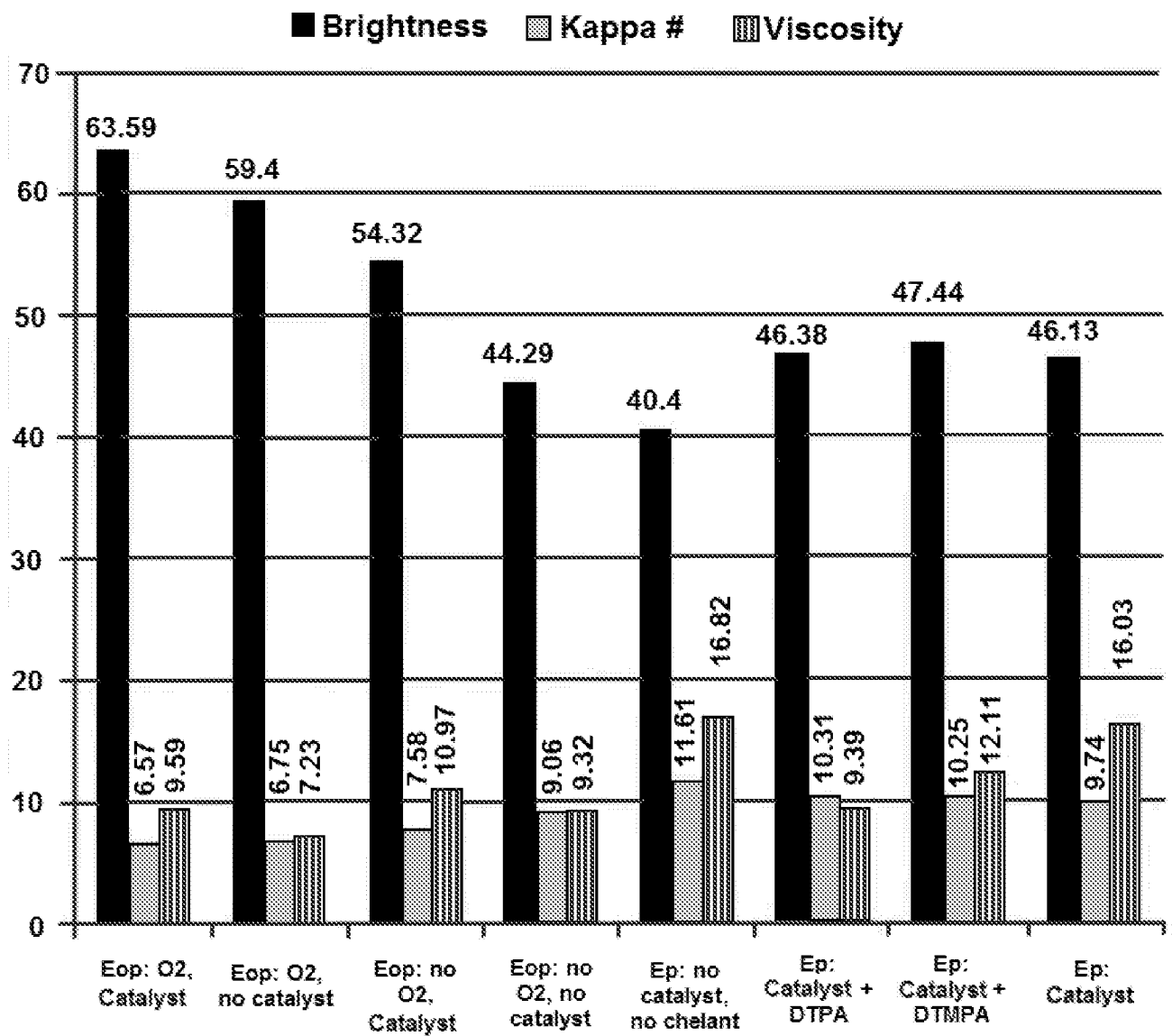


FIG. 3

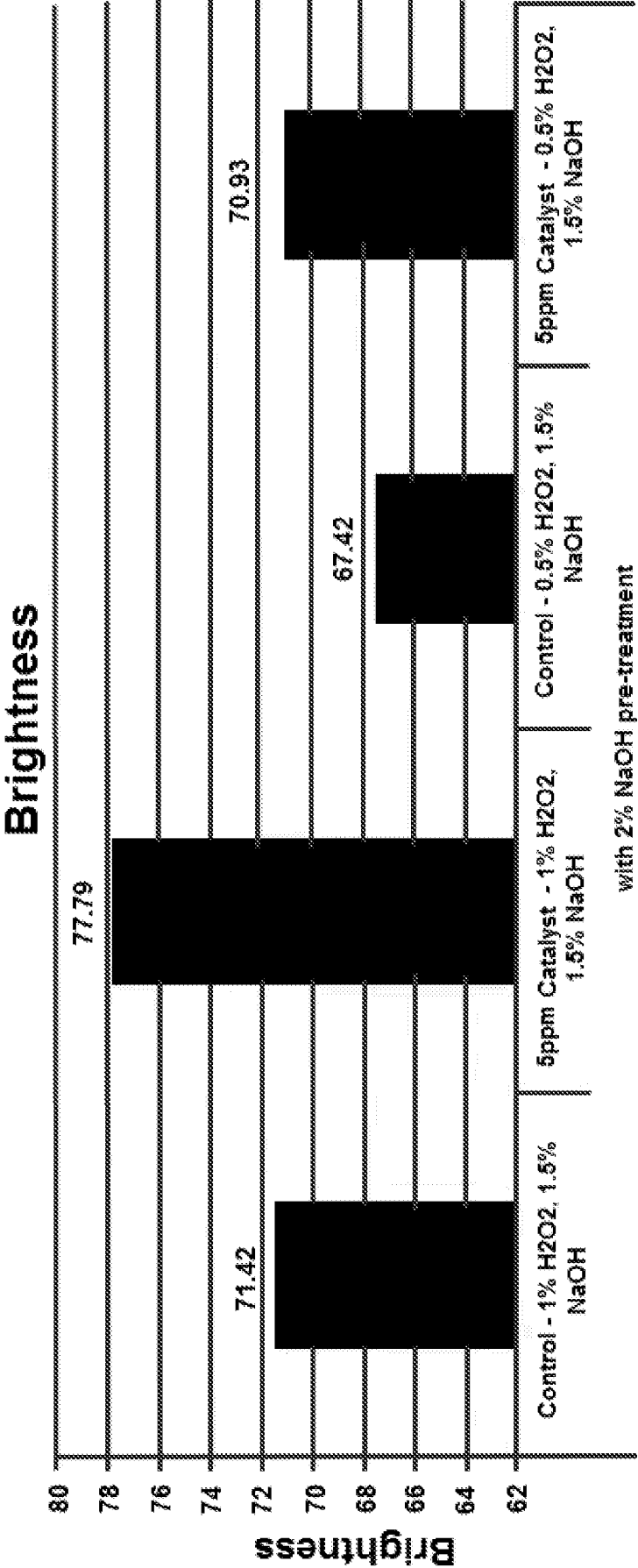


FIG. 4

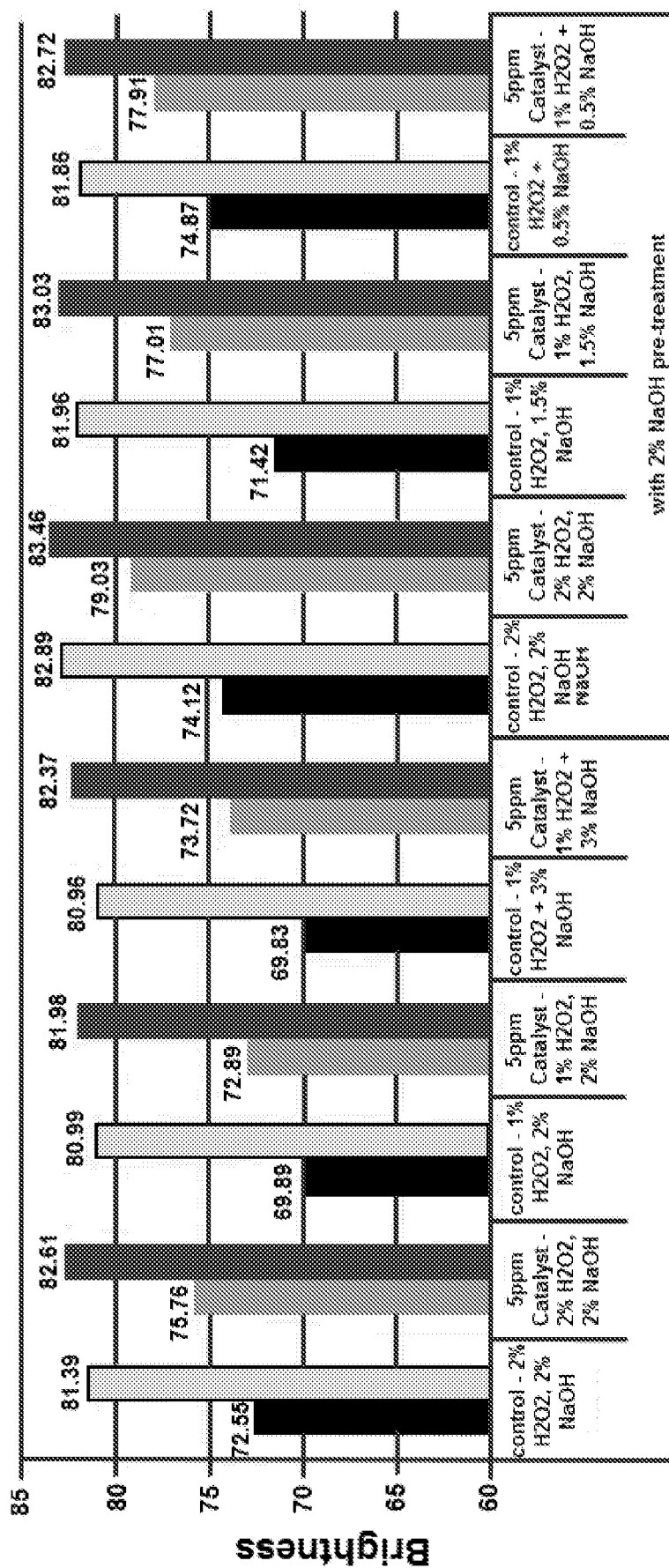


FIG. 5

6/20

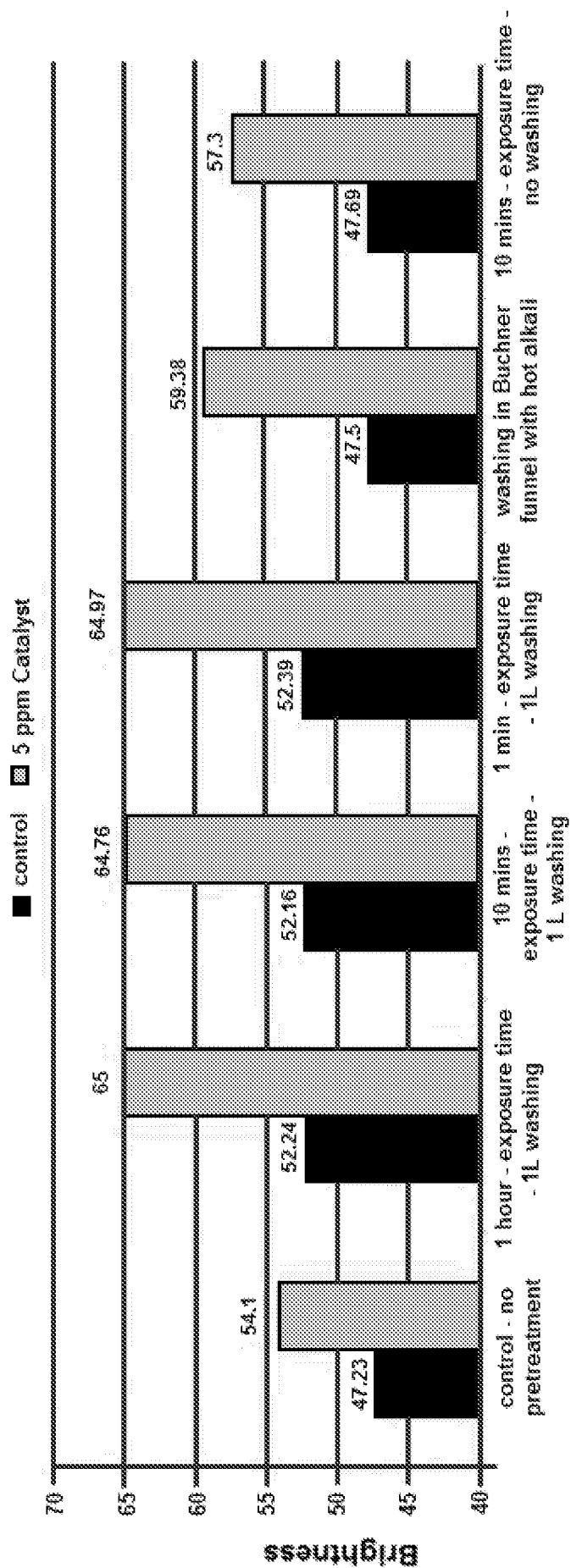


FIG. 6A

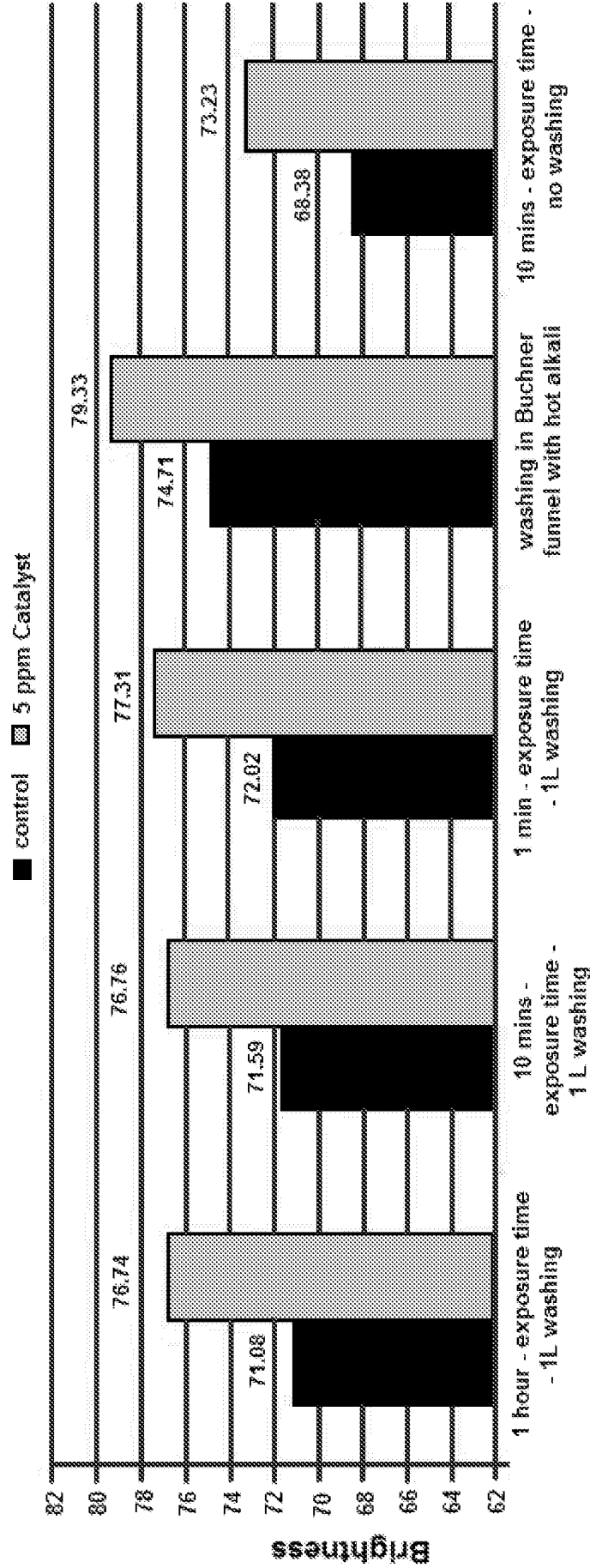
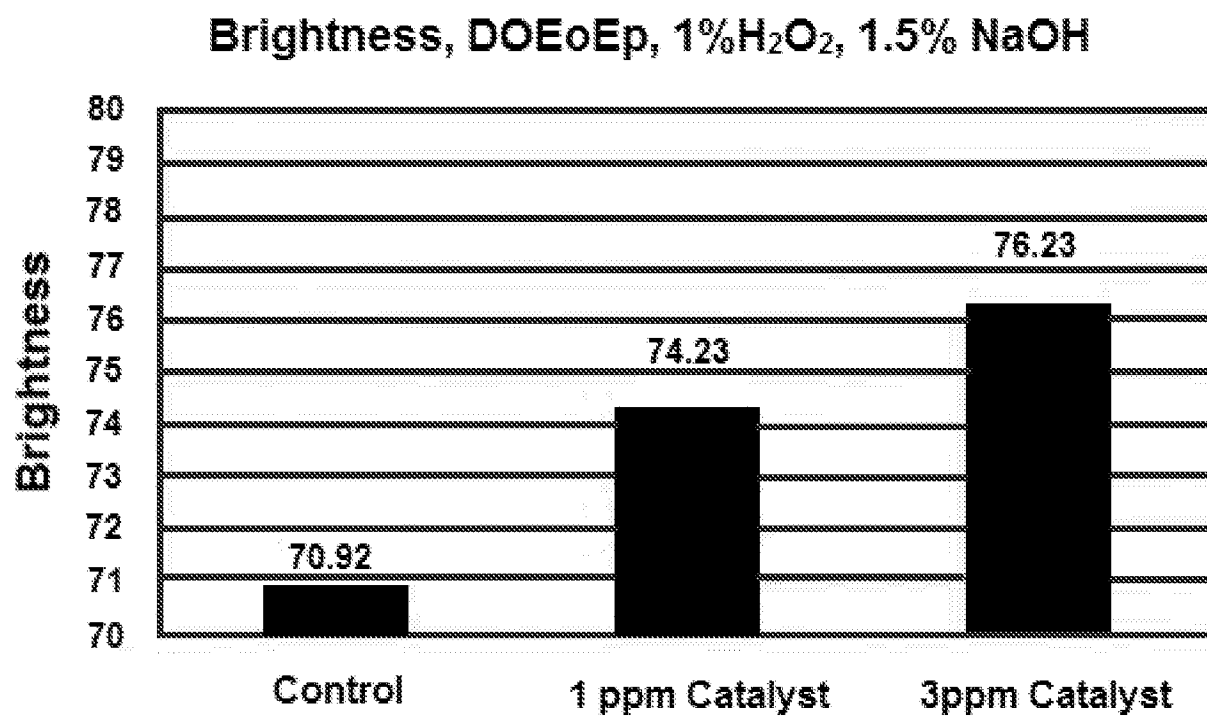


FIG. 6B

8/20

**FIG. 7**

9/20

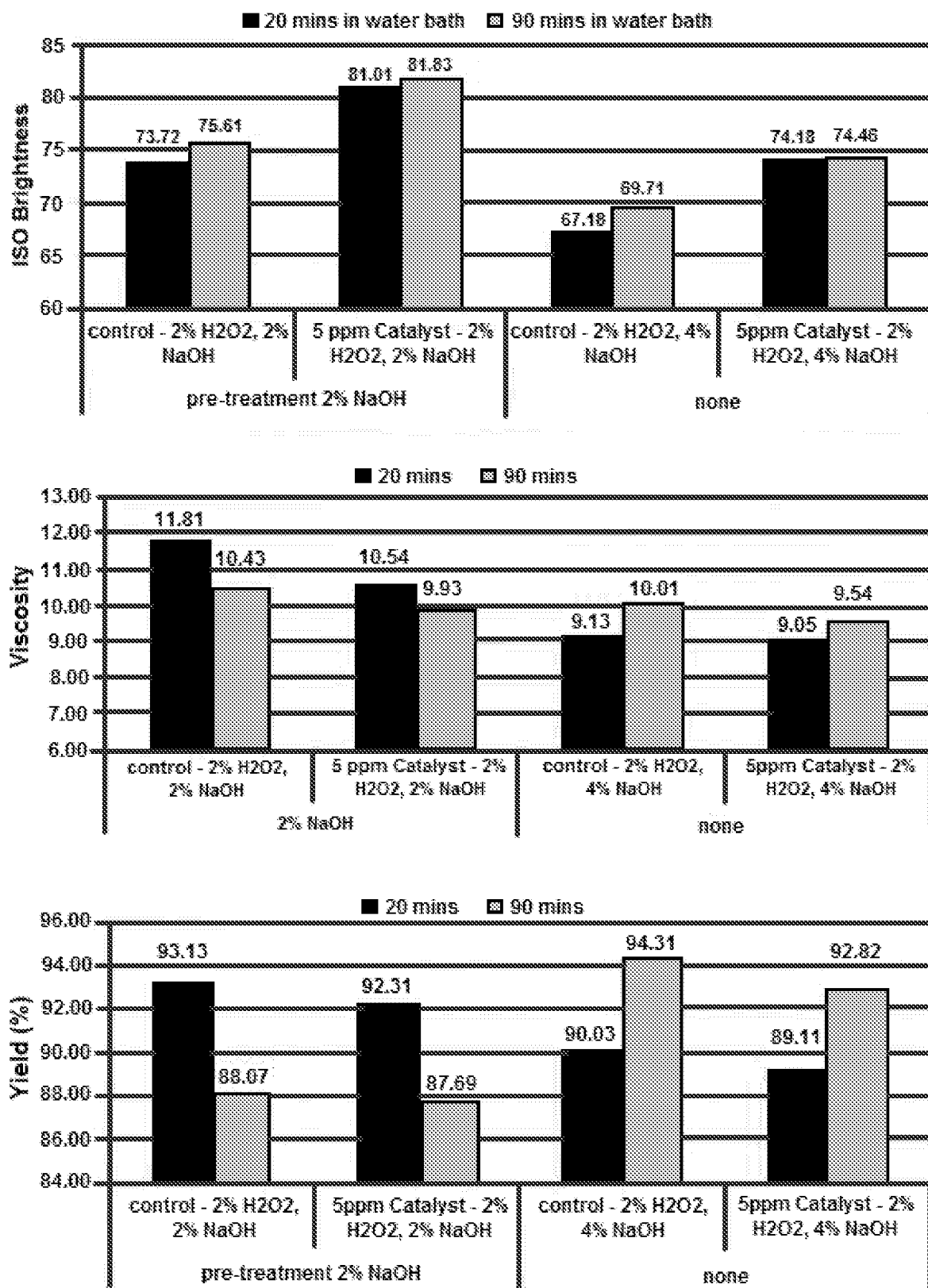


FIG. 8A

10/20

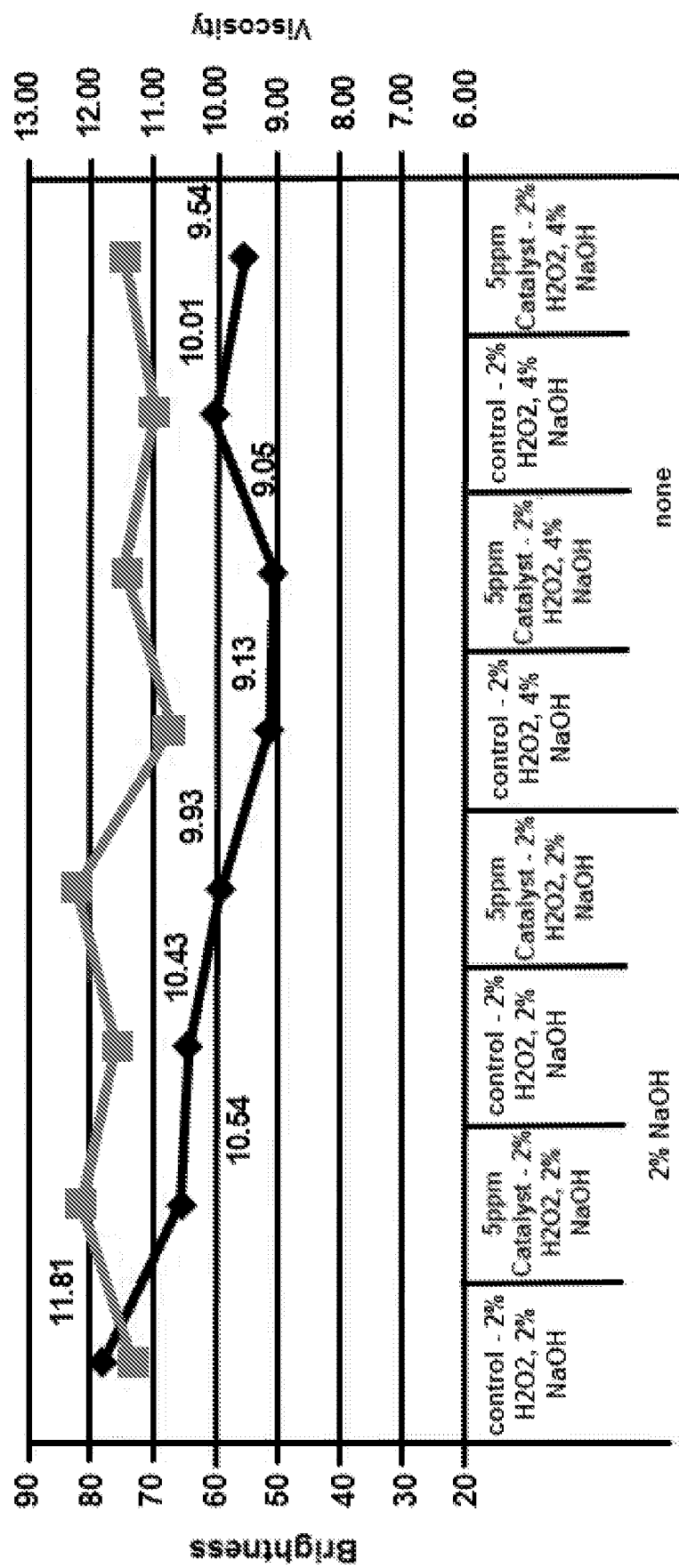


FIG. 8B

11/20

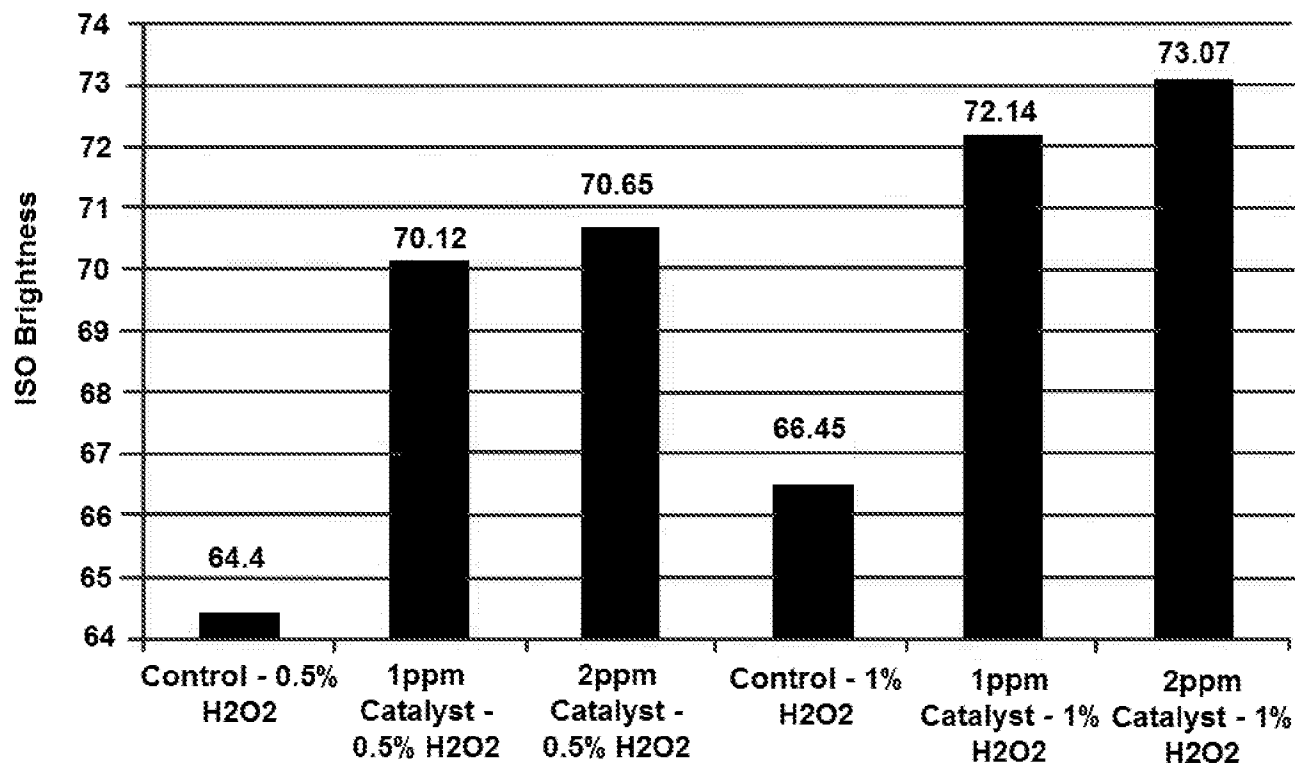


FIG. 9

12/20

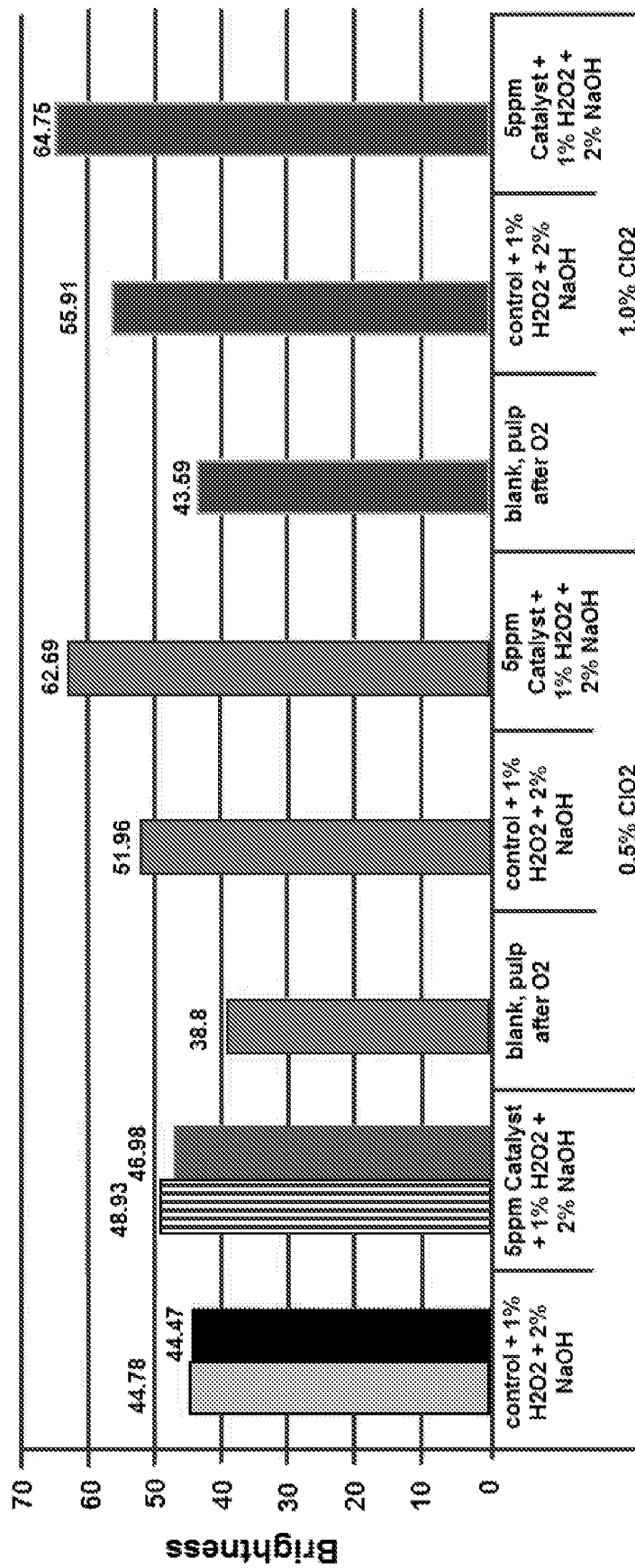


FIG. 10

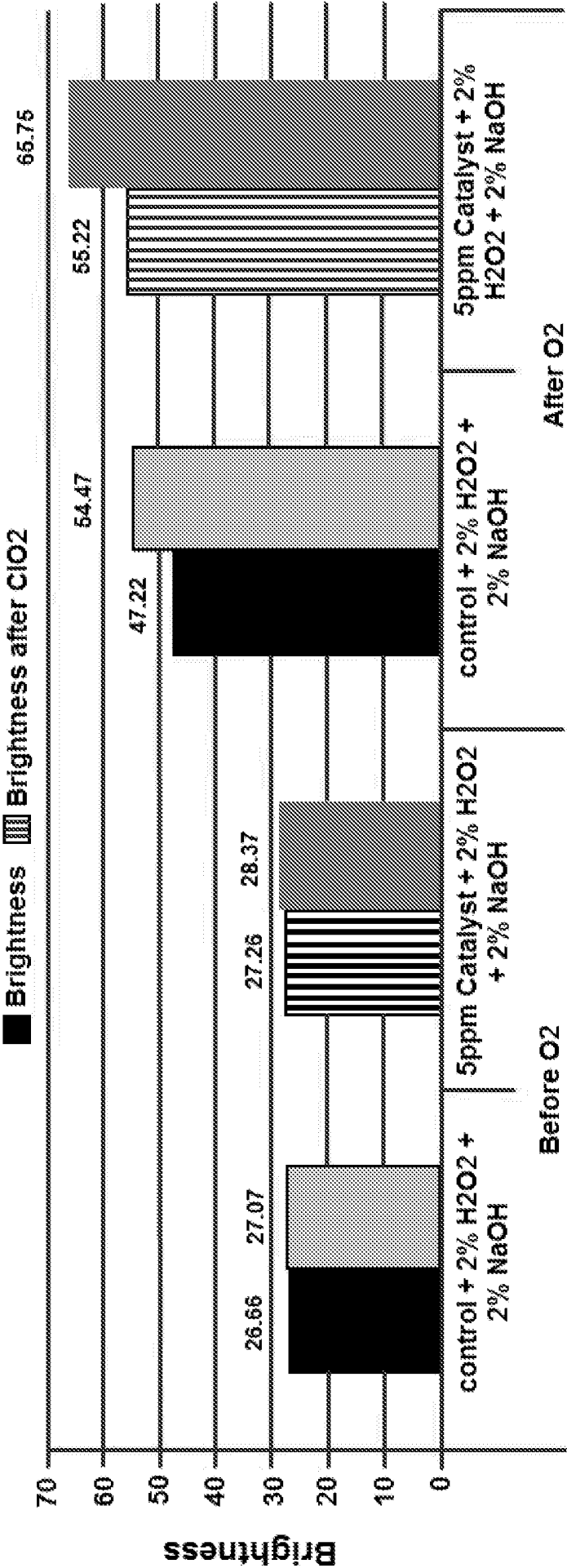


FIG. 11

14/20

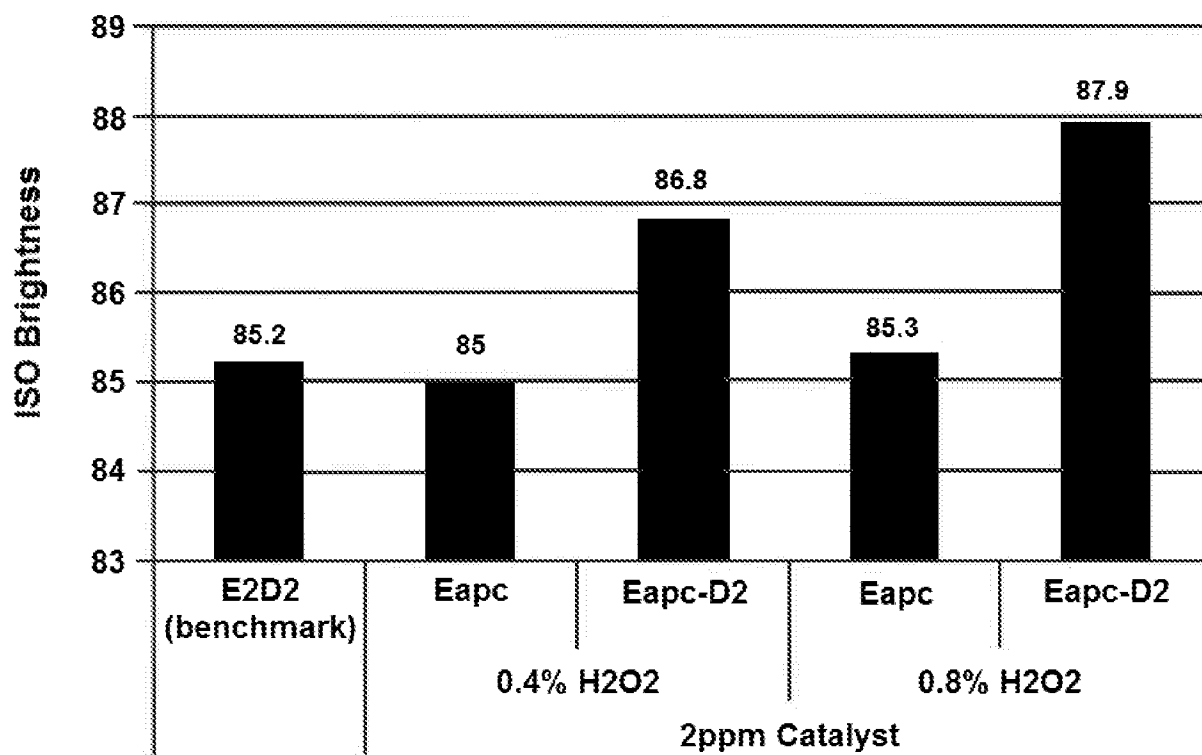


FIG. 12

15/20

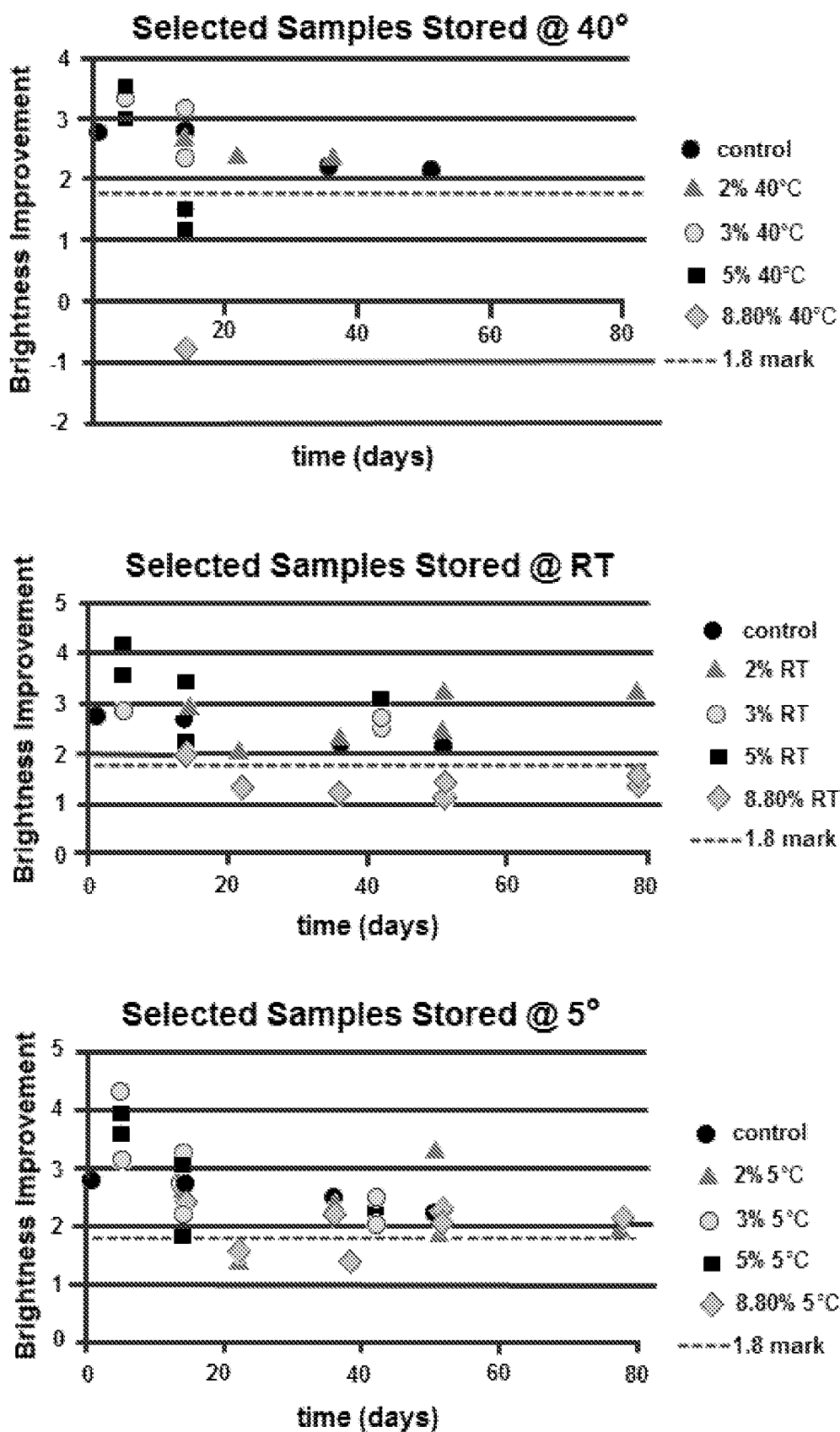


FIG. 13

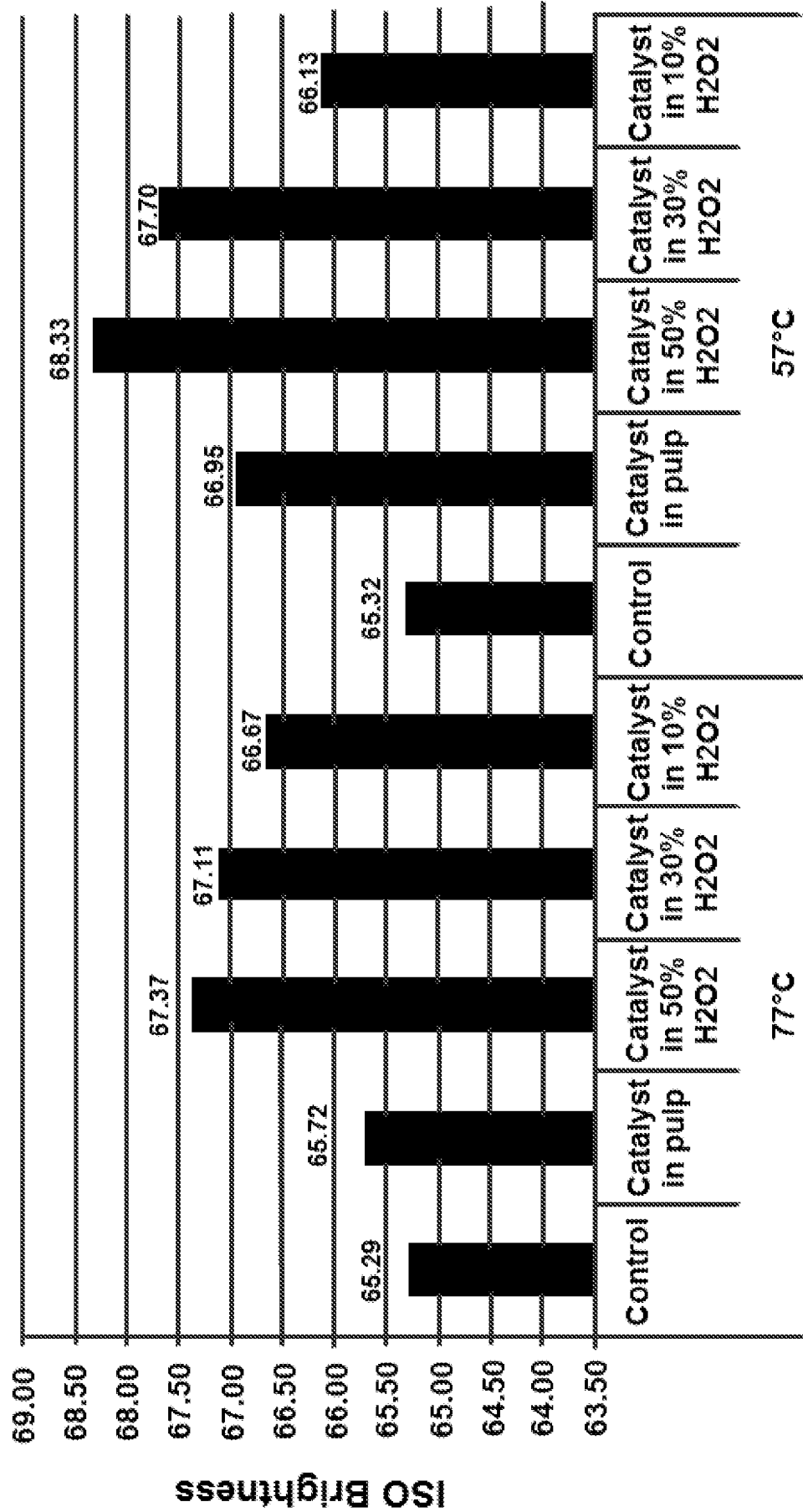


FIG. 14

17/20

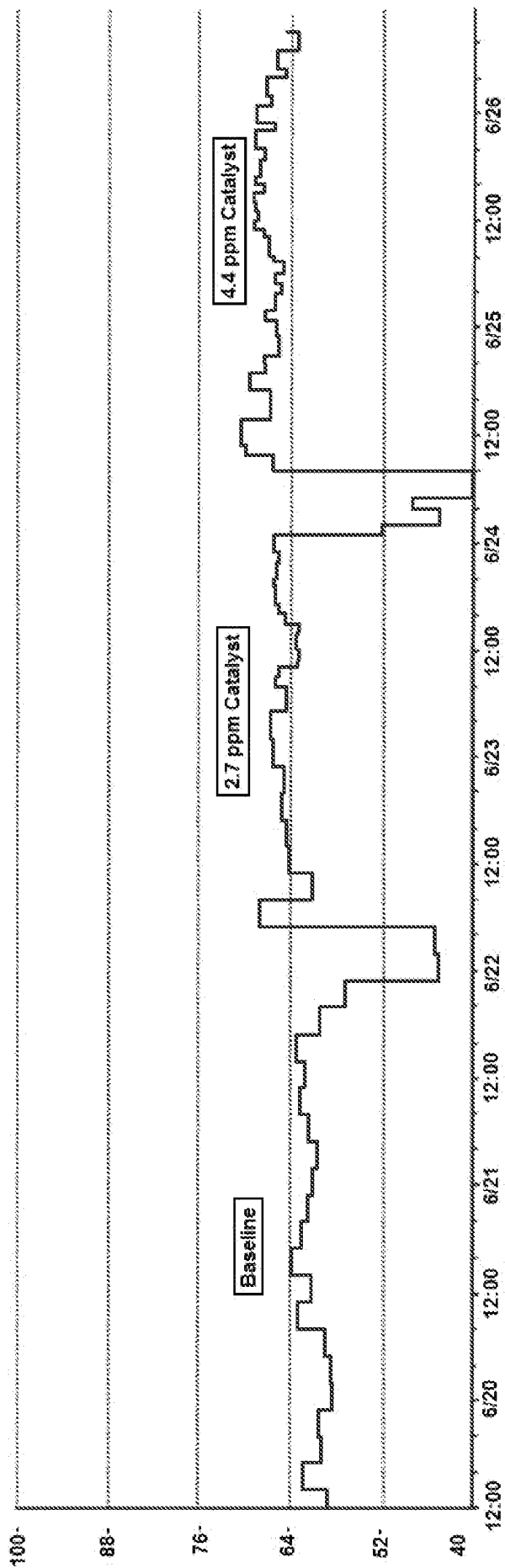


FIG. 15A

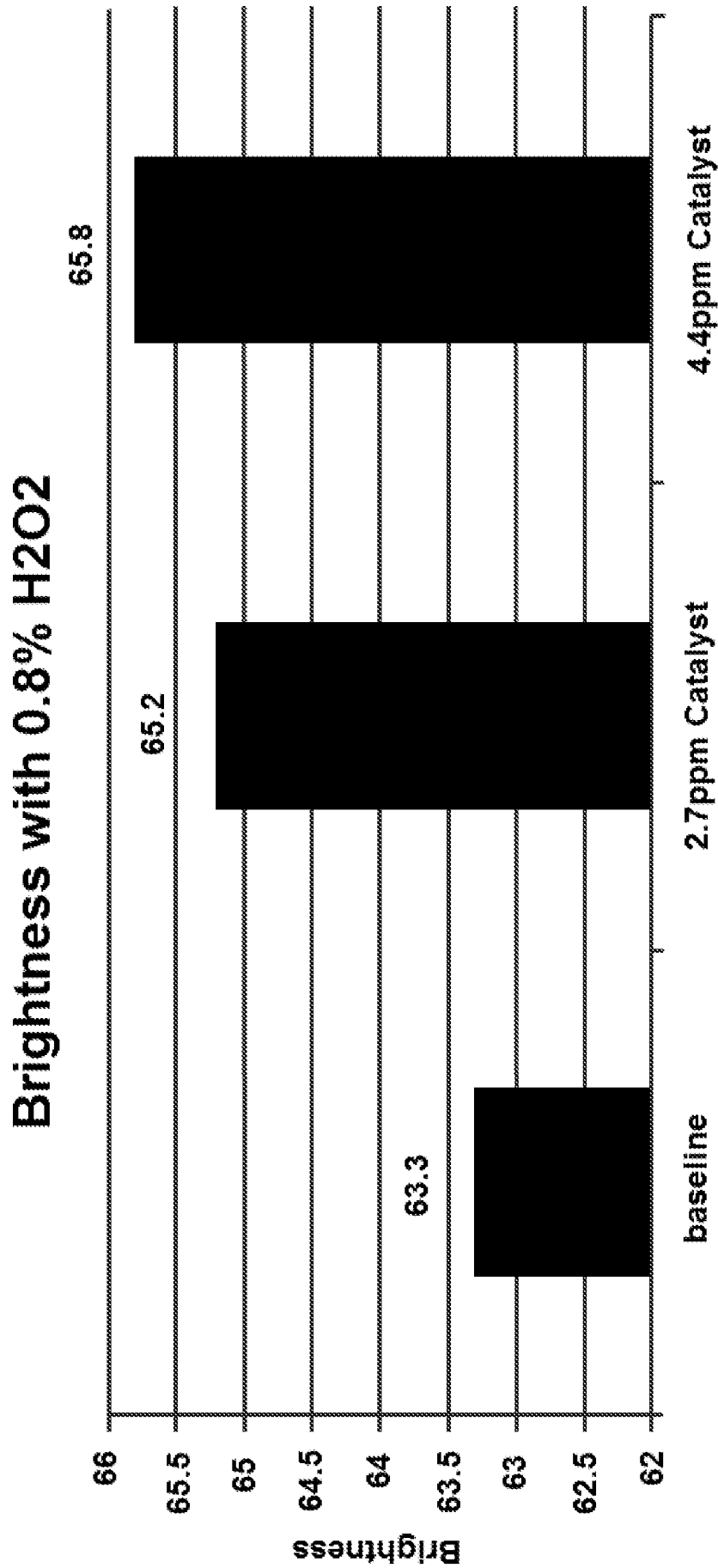


FIG. 15B

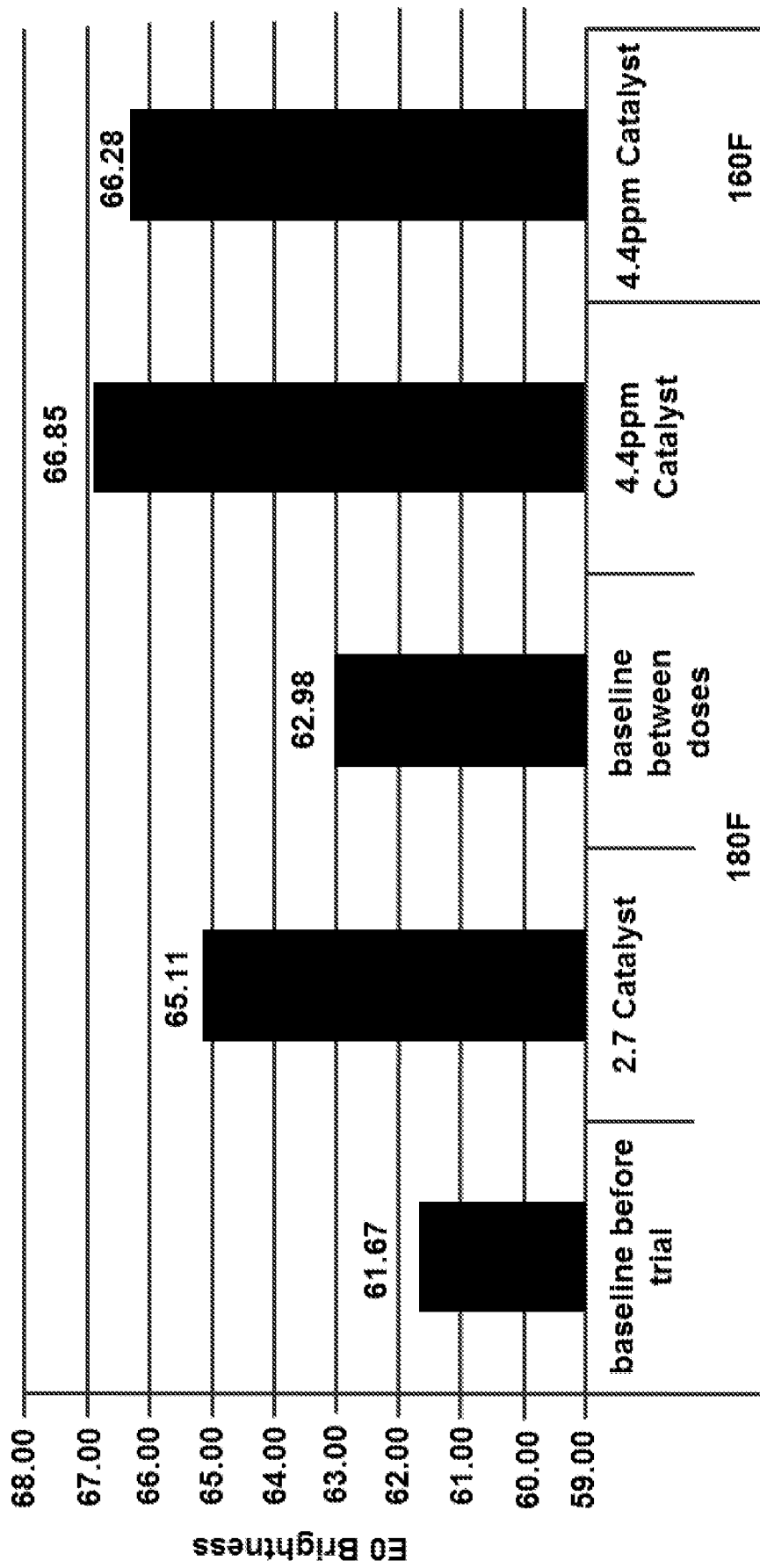


FIG. 15C

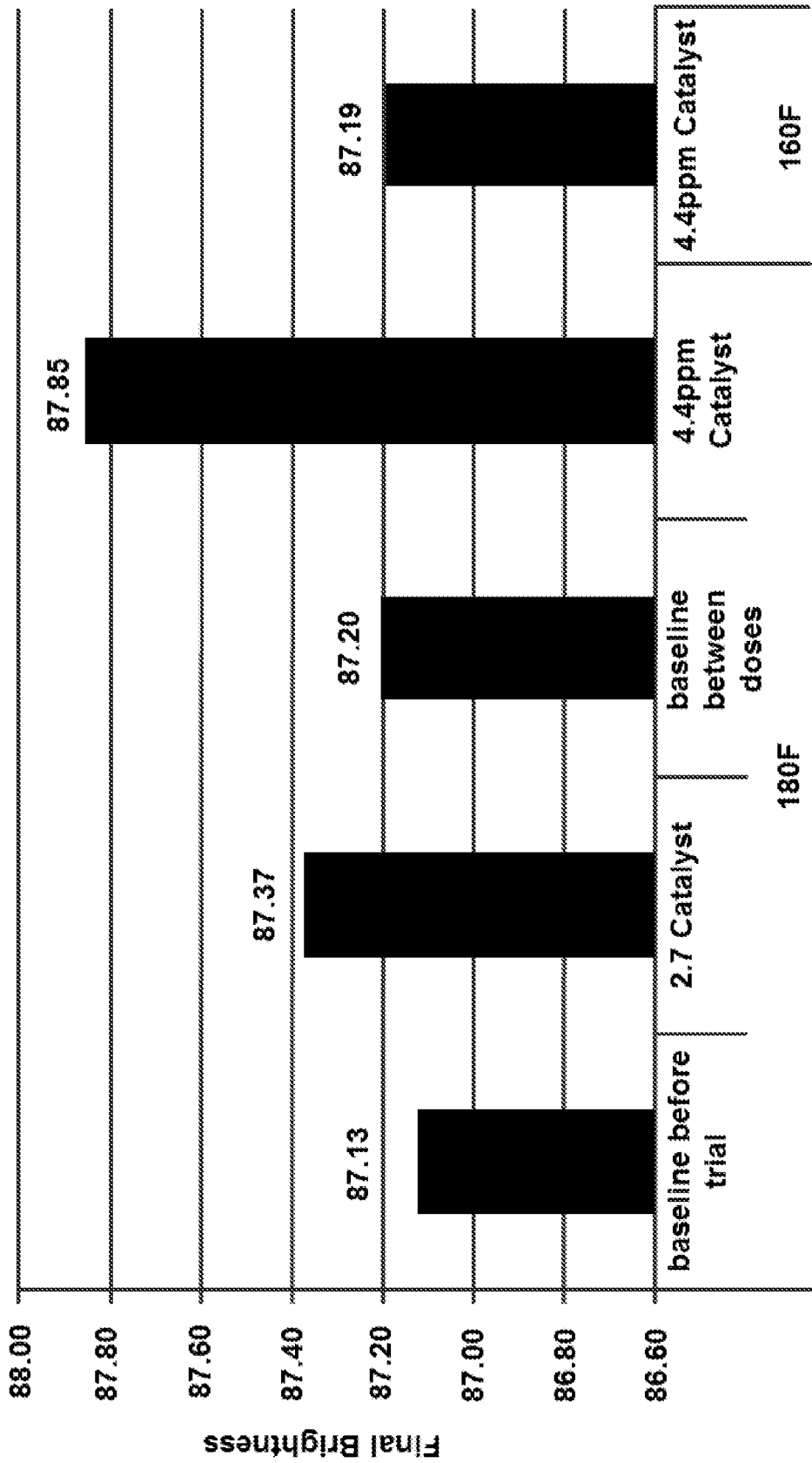


FIG. 15D

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/022443

A. CLASSIFICATION OF SUBJECT MATTER INV. D21C9/10 D21C9/14 D21C9/16 D21C9/02 ADD.		
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) D21C		
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) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/126111 A1 (HAGE RONALD [NL] ET AL) 23 May 2013 (2013-05-23)	1,2, 9-11, 14-16 3-8,12, 13
Y	paragraphs [0015], [0061], [0064], [0065], [0082] paragraph [0073] - paragraph [0077] claims 1-20; table 1 paragraph [0030] - paragraph [0032] paragraph [0091] - paragraph [0099] -----	
X	US 2014/213436 A1 (HAGE RONALD [NL] ET AL) 31 July 2014 (2014-07-31) paragraphs [0017], [0018], [0020], [0042], [0055] paragraph [0030] - paragraph [0037] claims 1-12 paragraph [0044] - paragraph [0051] ----- -/--	17-20
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* 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 11 May 2017		Date of mailing of the international search report 19/05/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Billet, Aina

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/022443

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CA 1 246 304 A (CIP INC) 13 December 1988 (1988-12-13) page 9, line 6 - line 20 claims 1-14 -----	3-8
Y	US 5 938 892 A (MAPLES GERALD E [US] ET AL) 17 August 1999 (1999-08-17) column 9, line 42 - column 11, line 20; figure 2 -----	12,13
A	US 5 244 594 A (FAVRE THOMAS L F [NL] ET AL) 14 September 1993 (1993-09-14) claims 1-19 column 1, line 58 - column 2, line 22 -----	1-20
A	WO 02/22944 A1 (ATOFINA [FR]; BRIOIS LAURENCE [FR]; RABION ALAIN [FR]) 21 March 2002 (2002-03-21) claims 1-8 page 6, line 1 - line 20 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/022443

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013126111	A1	23-05-2013	CA 2798917 A1 17-11-2011
			CN 103109015 A 15-05-2013
			EP 2395147 A1 14-12-2011
			EP 2569481 A1 20-03-2013
			ES 2598509 T3 27-01-2017
			HU E030187 T2 28-04-2017
			RU 2012152936 A 20-06-2014
			US 2013126111 A1 23-05-2013
			WO 2011141692 A1 17-11-2011
US 2014213436	A1	31-07-2014	AR 056367 A1 10-10-2007
			AU 2006251406 A1 30-11-2006
			BR PI0610466 A2 22-06-2010
			CA 2608440 A1 30-11-2006
			CN 101253292 A 27-08-2008
			EP 1883730 A1 06-02-2008
			EP 2402087 A1 04-01-2012
			ES 2392347 T3 07-12-2012
			ES 2421289 T3 30-08-2013
			PT 1883730 E 26-09-2012
			PT 2402087 E 22-07-2013
			US 2009205143 A1 20-08-2009
			US 2011275510 A1 10-11-2011
			US 2013260986 A1 03-10-2013
			US 2014213436 A1 31-07-2014
			WO 2006125517 A1 30-11-2006
			ZA 200710210 B 25-02-2009
CA 1246304	A	13-12-1988	AU 1923683 A 05-04-1984
			CA 1246304 A 13-12-1988
			JP S5988988 A 23-05-1984
			ZA 8306912 B 25-07-1984
US 5938892	A	17-08-1999	NONE
US 5244594	A	14-09-1993	AU 622362 B2 02-04-1992
			AU 622363 B2 02-04-1992
			BR 9102085 A 24-12-1991
			BR 9102086 A 24-12-1991
			CA 2042736 A1 22-11-1991
			CA 2042738 A1 22-11-1991
			DE 69125309 D1 30-04-1997
			DE 69125309 T2 03-07-1997
			DE 69125310 D1 30-04-1997
			DE 69125310 T2 03-07-1997
			EP 0458397 A2 27-11-1991
			EP 0458398 A2 27-11-1991
			ES 2100924 T3 01-07-1997
			ES 2100925 T3 01-07-1997
			IN 172881 B 25-12-1993
			IN 173875 B 30-07-1994
			JP 2613707 B2 28-05-1997
			JP H0765074 B2 12-07-1995
			JP H04270798 A 28-09-1992
			JP H06269676 A 27-09-1994
			NO 911942 A 22-11-1991
			NO 911943 A 22-11-1991
			US 5244594 A 14-09-1993

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/022443

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 5246621 A	21-09-1993
WO 0222944	A1 21-03-2002	AU 8999301 A	26-03-2002
		FR 2813896 A1	15-03-2002
		WO 0222944 A1	21-03-2002