(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 November 2020 (19.11.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/231315 A1

(51) International Patent Classification:
D01F 13/02 (2006.01) *D01F 2/02* (2006.01)
C08B 16/00 (2006.01) *D01D 5/06* (2006.01)

(21) International Application Number:
PCT/SE2020/050475

(22) International Filing Date:
08 May 2020 (08.05.2020)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1950576-7 15 May 2019 (15.05.2019) SE

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(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, JO, 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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(54) Title: RECOVERY OF CHEMICALS IN CELLULOSE SPINNING

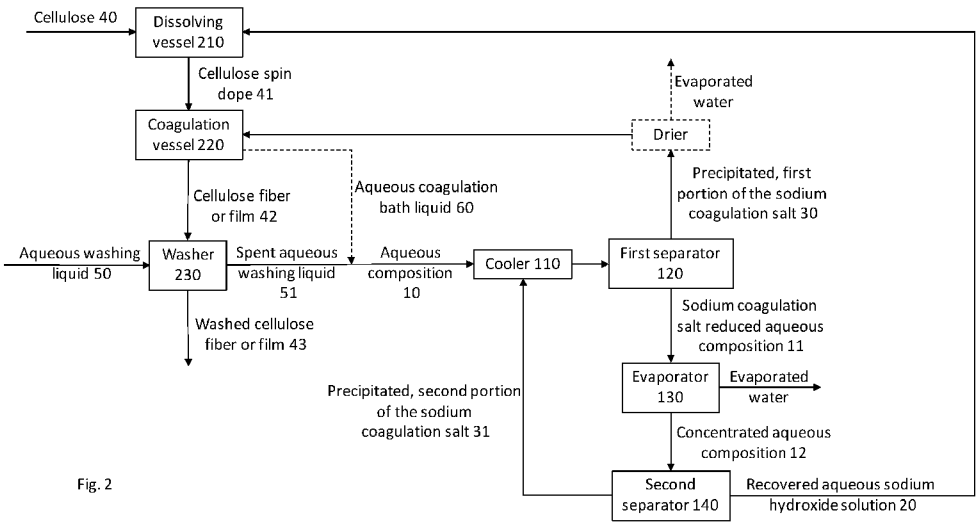

Fig. 2

(57) **Abstract:** A process for separately recovering sodium hydroxide (NaOH) and a sodium coagulation salt, respectively, from an aqueous composition (10) comprising a dissolved sodium coagulation salt and dissolved sodium hydroxide (NaOH) and having a pH of more than 7. The process comprises the steps of: cooling the aqueous composition (10) to precipitate a first portion of the sodium coagulation salt (30), to provide a sodium coagulation salt reduced aqueous composition (11) comprising dissolved sodium hydroxide (NaOH); separating the precipitated, first portion of the sodium coagulation salt (30) from the sodium coagulation salt reduced aqueous composition (11) to provide recovered sodium coagulation salt; evaporating water from the sodium coagulation salt reduced aqueous composition (11), thereby increasing the concentration of sodium hydroxide (NaOH) and remaining sodium coagulation salt; and precipitating and separating a second portion of the sodium coagulation salt (12) from the concentrated aqueous composition (12),

[Continued on next page]

WO 2020/231315 A1

(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, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, 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).

Published:

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

thereby providing a recovered aqueous sodium hydroxide solution (20).

RECOVERY OF CHEMICALS IN CELLULOSE SPINNING

Field of the invention

The present invention relates to a process for recovering sodium hydroxide (NaOH) and a sodium coagulation salt, respectively, from an aqueous composition comprising a dissolved sodium coagulation salt, having been used in an aqueous coagulation bath liquid for alkaline fiber or film spinning, and dissolved sodium hydroxide (NaOH), having been used in dissolving cellulose to provide a cellulose spin dope for fiber or film spinning in an aqueous coagulation bath liquid for alkaline fiber or film spinning, the aqueous coagulation bath liquid comprising a dissolved sodium coagulation salt.

The invention further relates to a process for extruding cellulose dissolved in aqueous sodium hydroxide (NaOH) into a coagulation bath comprising a sodium coagulation salt to form cellulose fibers or films. The process comprises recovering the sodium hydroxide (NaOH) and the sodium coagulation salt, respectively.

Background

Fibers and films have large application areas in the textile and packaging industries. For example, cellulose fibers have for long been used in textile industry for making fabric. Most commonly, the cellulose has been obtained from cotton. There is however a growing interest also in other sources of cellulose, such as wood.

An interesting alternative for obtaining regenerated cellulose fibers is the regeneration of cellulose fibers from solutions of dissolved non-derivatized cellulose, e.g. dissolving pulp. By using non-derivatized cellulose, use of e.g. CS_2 (carbon disulphide) which is used in the viscose process may be avoided. To some extent non-derivatized cellulose is soluble in cold aqueous sodium hydroxide and aqueous sodium hydroxide has been used as cellulose solvent in experimental procedures, though no industrial process being economically feasible is available so far.

Experimental spin dopes comprising cellulose dissolved in aqueous sodium hydroxide have been wet-spun into a coagulation bath comprising aqueous sulfuric acid. Such a procedure suffers, however, from requiring vast amounts of sodium hydroxide and produces, as a rest product, sodium sulfate. Further, such a process suffers from low cellulose concentrations in the spin dope. Thus, this process does not constitute a viable industrial process.

Furthermore, there are processes using alkaline spin baths disclosed in the art. A recent example of such a process is disclosed in WO 2018/169479, which relates to a method for making a regenerated cellulosic fiber composition. Further, there have been disclosed visionary processes using alkaline spin baths where recycling of chemicals is suggested (e.g. WO 2015/000820).

In experimental scale, dissolving cellulose in an aqueous sodium hydroxide solution to produce a spin dope, which is further fed into a coagulation bath comprising an aqueous coagulation sodium salt solution, e.g. Na_2CO_3, has been evaluated. The regenerated fibers from the sodium hydroxide solution form a wet, swollen tow in the coagulation bath, which is subsequently drawn out of from the bath. When the tow is removed, it brings along some of the salts present in the coagulation bath. Thus, a make-up feed to the coagulation bath is necessary. Hence, additional coagulation salt needs is to be added to the coagulation bath to maintain the required concentration of the salt. In order to provide an economical and realizable process, the coagulation salt, as well as the sodium hydroxide, are preferably to be re-cycled. However, in the coagulation bath, the coagulation salt is mixed with sodium hydroxide. The tow thus brings along coagulation salt as well as sodium hydroxide. The sodium hydroxide is also of interest to re-cycle for use in dissolving cellulose to a spin dope. In order to allow for re-cycling of the sodium hydroxide, it needs to be essentially free from coagulation salt.

In WO 2017/178532 a process for forming cellulose fibers or film from dissolved cellulose is disclosed. The process comprises the steps of: dissolving cellulose in an aqueous sodium hydroxide salt solution to provide a cellulose spin dope; extruding the cellulose spin dope into a coagulation bath liquid comprising an aqueous coagulation sodium salt solution to provide cellulose fibers or film. The process further comprises withdrawing a portion of the coagulation bath comprising coagulation sodium salt and sodium hydroxide (NaOH) and cooling the withdrawn portion of the coagulation bath to precipitate solid coagulation sodium salt to recover sodium hydroxide (NaOH) substantially free from the coagulation salt. The recovered sodium hydroxide (NaOH) may be used in dissolving cellulose to provide a cellulose spin dope, as it is essentially free from the coagulation salt. The process thus discloses an interesting process for forming cellulose fibers or film from dissolved cellulose. However, in order to efficiently recover sodium hydroxide (NaOH), the withdrawn portion of the coagulation bath should be cooled to less than -10°C, preferably to between -20°C and -30°C. Such extensive cooling may be less preferred in an industrial

process. Further, separation of the three phases (i.e. ice, aqueous sodium hydroxide, and precipitated sodium carbonate) is a bit demanding in industrial scale.

Thus, there is a need in the art for an efficient process for separately recovering sodium hydroxide (NaOH) and a sodium coagulation salt, respectively, used in alkaline fiber or film spinning.

Summary of the invention

Consequently, according to a first aspect there is provided a process for separately recovering sodium hydroxide (NaOH) and a sodium coagulation salt (e.g. sodium carbonate; Na_2CO_3 or sodium sulphate Na_2SO_4), respectively, from an aqueous composition comprising a dissolved sodium coagulation salt and dissolved sodium hydroxide (NaOH). In the process, the sodium coagulation salt is a salt having been used in an aqueous coagulation bath liquid for alkaline fiber or film spinning, i.e. fiber or film spinning at a pH higher than 7.0. The dissolved sodium hydroxide (NaOH) has been used in dissolving cellulose to provide a cellulose spin dope for fiber or film spinning in an aqueous coagulation bath liquid for alkaline fiber or film spinning. The aqueous composition has a pH of more than 7. The process comprises the steps of:

- cooling the aqueous composition to precipitate a first portion of the sodium coagulation salt, to provide a sodium coagulation salt reduced aqueous composition comprising dissolved sodium hydroxide (NaOH);
- separating the precipitated, first portion of the sodium coagulation salt from the sodium coagulation salt reduced aqueous composition to provide recovered sodium coagulation salt for subsequent use as make up in an aqueous coagulation bath liquid to comprise a sodium coagulation salt, wherein the aqueous coagulation bath liquid is for use in alkaline fiber or film spinning;
- evaporating water from the sodium coagulation salt reduced aqueous composition, thereby increasing the concentration of sodium hydroxide (NaOH) to form a concentrated aqueous composition;
- precipitating and separating a second portion of the sodium coagulation salt from the concentrated aqueous composition, thereby providing a recovered aqueous sodium hydroxide solution comprising dissolved sodium hydroxide (NaOH) for use in dissolving cellulose to provide a cellulose spin dope fiber or film spinning.

The removed second portion of sodium coagulation salt may comprise sodium hydroxide (NaOH). According to an embodiment, the second portion of the sodium coagulation salt is thus recirculated to be treated together with the aqueous composition

in the step of cooling the aqueous coagulation bath liquid to precipitate a first portion of the sodium coagulation salt. By such a re-circulation, the fact that the second portion of sodium coagulation salt may comprise sodium hydroxide (NaOH) is compensated for and the overall yield of the recovery is improved, while still providing essentially pure sodium hydroxide (NaOH) and a sodium coagulation salt (e.g. sodium carbonate; Na_2CO_3 or sodium sulphate; Na_2SO_4), respectively.

According to an embodiment, the aqueous composition comprises spent aqueous washing liquid resulting from washing a fiber, or a film, spun from a cellulose spin dope, comprising dissolved cellulose and sodium hydroxide (NaOH). The spin dope may optionally comprise dissolved zinc oxide (ZnO), as zinc is known to promote dissolution of cellulose in cold alkali and especially to prevent gelling. The cellulose spin dope is typically spun into an aqueous coagulation bath liquid comprising a sodium coagulation salt (e.g. sodium carbonate; Na_2CO_3 or sodium sulphate; Na_2SO_4). The presence of the sodium coagulation salt cause the cellulose to precipitate as a fiber or a film. Once the fiber, or the film, is removed from the coagulation bath it will comprise sodium hydroxide (NaOH) and sodium coagulation salt, which may be washed away (at least partly) by extraction with an aqueous washing liquid. The spent aqueous washing liquid may comprise 2 to 6 wt.%.% NaOH, 8 to 12 wt.% sodium coagulation salt, and optionally 0.2 to 0.6 wt.% zinc in ionic form.

Further, the aqueous composition may, according to an embodiment, comprise an aqueous coagulation bath liquid, comprising a sodium coagulation salt. Typically, the aqueous coagulation bath liquid has been used in alkaline fiber or film spinning of a cellulose spin dope comprising dissolved cellulose, sodium hydroxide (NaOH), and optionally zinc oxide (ZnO). The aqueous coagulation bath liquid may comprise 3 to 9 wt.%, such as 5.0 to 6.5 wt.%, NaOH, 16 to 26 wt.%, such as 19 to 24 wt.%, sodium coagulation salt, and optionally 0.2 to 1.5 wt.% ZnO.

According to an embodiment, the aqueous composition to recover sodium hydroxide (NaOH) and the sodium coagulation salt, respectively, from comprises:

- 2 to 10 wt.% sodium hydroxide (NaOH), such as 3 to 6 wt.% sodium hydroxide (NaOH);
- 8 to 22 wt.% sodium coagulation salt, e.g. sodium carbonate (Na_2CO_3) and/or sodium sulphate (Na_2SO_4), such as 9 to 15 wt.% sodium coagulation salt, e.g. sodium carbonate (Na_2CO_3) and/or sodium sulphate (Na_2SO_4),; and
- optionally zinc oxide (ZnO), the zinc oxide (ZnO) being recovered with the sodium hydroxide (NaOH).

The solubility of the sodium coagulation salt in the aqueous composition decreases with decreasing temperature. By cooling the aqueous composition, the sodium coagulation salt may partly be precipitated, without precipitating sodium hydroxide (NaOH) thus remaining dissolved. The temperature of the aqueous composition to recover sodium hydroxide (NaOH) and a sodium coagulation salt from, may be in the range 20 to 30°C. In order to precipitate sodium coagulation salt, the temperature may be lowered to 5°C or less, such as 3°C or less. However, it is preferred, according to an embodiment, that the temperature of the aqueous composition, in the step of cooling it, remains above the freezing point of the aqueous composition, whereby essentially no water is frozen to ice. In precipitating the sodium coagulation salt, the temperature may be lowered to a temperature in the range 5°C to -5°C, e.g. to about 0°C.

While various sodium coagulation salts may be recovered by the present process, the typical sodium coagulation salt is sodium carbonate (Na_2CO_3). Further, the sodium coagulation salt may be sodium sulfate (Na_2SO_4) or a combination of sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4). In embodiments, wherein the sodium coagulation salt is sodium carbonate (Na_2CO_3), the first portion of sodium coagulation salt may be precipitated as sodium carbonate decahydrate ($Na_2CO_3 \times 10{\cdot}H_20$). Sodium carbonate decahydrate ($Na_2CO_3 \times 10{\cdot}H_20$) has the advantage of forming large crystals being easy to separate. If to recycle the sodium carbonate decahydrate ($Na_2CO_3 \times 10{\cdot}H_20$), it may be preferred to dry it in order to reduce the water content, as the fairly high relative amount of water (10 mole water per mole Na_2CO_3) may result in dilution of e.g. a coagulation bath liquid. The water balance of a coagulation bath liquid may further be controlled in other ways as well, e.g. by evaporation.

The precipitated first portion of sodium coagulation salt may be separated from the sodium coagulation salt reduced aqueous composition by means of a separation technique selected from the group consisting of centrifugation, decantation, and filtration (e.g. by a filter press or by a filter belt), or combinations thereof. The separated, precipitated first portion of the sodium coagulation salt may comprise some sodium hydroxide (NaOH), such as less than 1.5 wt.%, such as less than 1.0 wt.% sodium hydroxide (NaOH).

Once the first portion of the sodium coagulation salt has been removed, water is removed from the sodium coagulation salt reduced aqueous composition to increase the concentration of the remaining salts, including sodium hydroxide (NaOH) and

remaining sodium coagulation salt. By concentrating the sodium coagulation salt reduced aqueous composition, further sodium coagulation salt may be precipitated, i.e. as a second portion of sodium coagulation salt, and removed. The evaporation of water may be continued until the concentration of sodium hydroxide (NaOH) in the concentrated aqueous composition is at least 25 wt.%, such as at least 26 wt.%, 27 wt.%, 28 wt.%, 29 wt.%, or 30 wt.%, preferably at least 28 wt.%, 29 wt.%, or 30 wt.%, more preferably at least 30 wt.%. In the step of precipitating the second portion of the sodium coagulation salt from the concentrated aqueous composition, the temperature of the concentrated aqueous composition may be lowered. More efficient precipitating may be provided by concentrating the aqueous composition at elevated temperature and precipitating the sodium coagulation salt at reduced temperature. The temperature in evaporating water may be 40 to 100°C, such as 50 to 80°C. Further, the temperature of the concentrated aqueous composition in precipitating the second portion of sodium coagulation salt may be -10 to 35°C, such as 0 to 30°C or 15 to 25°C.

The step of concentrating the sodium coagulation salt reduced aqueous composition and the step of precipitating and separating a second portion of the sodium coagulation salt from the concentrated aqueous composition may be effectuated in a manner such that the mass ratio of sodium coagulation salt:sodium hydroxide (NaOH) in the recovered aqueous sodium hydroxide solution is 0.05:1 or less, such as 0.04:1 or less, or 0.03:1 or less. Such a low content of the sodium coagulation salt implies that the sodium hydroxide (NaOH) readily may be used in dissolving cellulose to provide a spin dope.

In the step of evaporating water from the sodium coagulation salt reduced aqueous composition, the composition is typically heated as evaporation is an endothermic process. Further, sub-atmospheric pressure may be applied in the step of evaporating water, whereby water may be evaporated at lower temperature.

As already outlined, the separated second portion of the sodium coagulation salt may comprise sodium hydroxide (NaOH) as well. Rather than discarding the second portion, it may be returned to the disclosed recovery process to recover further sodium hydroxide (NaOH) and a sodium coagulation salt, respectively, therefrom.

According to another aspect, there is provided a process for forming cellulose fibers or film from dissolved cellulose. The process comprises the steps of:

- dissolving cellulose in an aqueous sodium hydroxide (NaOH) solution to provide a cellulose spin dope;

- extruding the cellulose spin dope into an aqueous coagulation bath liquid comprising a dissolved sodium coagulation salt and having a pH of more than 7, the aqueous coagulation bath liquid being present in a coagulation vessel, to provide cellulose fibers or film;
- withdrawing the cellulose fibers or film from the coagulation vessel;
- washing the withdrawn cellulose fibers or film with an aqueous washing liquid to extract sodium hydroxide (NaOH) and sodium coagulation salt therefrom;
- separately recovering sodium hydroxide (NaOH) and the sodium coagulation salt, respectively, from spent aqueous washing liquid resulting from the step of washing the fibers, or the film, and/or from the aqueous coagulation bath liquid used in the step of extruding the cellulose spin dope into an aqueous coagulation bath liquid as described above;
- using recovered sodium hydroxide (NaOH) in the step of dissolving cellulose; and
- using recovered sodium coagulation salt as make up in the aqueous coagulation bath liquid.

In an embodiment, wherein the recovered sodium coagulation salt comprises sodium carbonate (Na_2CO_3), some sodium coagulation salt may not be used as make up in the aqueous coagulation bath liquid. As carbon dioxide is present in the ambient air, some carbon dioxide may dissolve in alkaline stream(s), increasing the concentration of carbonate. In order to avoid gradually increasing the concentration of sodium carbonate (Na_2CO_3), some recovered sodium coagulation salt may not be re-cycled to the aqueous coagulation bath liquid.

In such a process:

- the cellulose spin dope may comprise 4 to 12 wt.%, preferably 5 to 8 wt.% cellulose; and/or
- the cellulose in the cellulose spin dope may have a DP of 140 to 600, such as 180 to 600, 200 to 400, 160 to 400, or 180 to 300; and/or
- the cellulose in the cellulose spin dope may have an intrinsic viscosity according to ISO5351:2010(E) of 115 to 450, such as 150 to 450ml/g, 190 to 300ml/g, 130 to 300 ml/g, or 140 to 230 ml/g; and/or
- the cellulose spin dope may have a viscosity at $1s^{-1}$ of 1 to 500 Pas, preferably 5 to 100 Pas; and/or
- the cellulose in the cellulose spin dope may have a degree of substitution DS of not more than 0.1, preferably not more than 0.05; and/or;

- the cellulose spin dope may comprise 5 to 10 wt.% NaOH, preferably 6.5 to 8.5 wt.% NaOH.

Further, the aqueous sodium hydroxide (NaOH) solution used in the step of dissolving the cellulose may comprise:

- 6 to 18 wt.% NaOH, such as 7.5 to 12 wt.% NaOH; and
- less than 1.0 wt.% sodium coagulation salt, such as less than 0.5 wt.% sodium coagulation salt, preferably even less than 0.3 wt.%; and
- optionally up to 2.7 wt.% zinc oxide (ZnO).

The coagulation bath liquid may comprise 14 to 32 wt.% sodium coagulation salt (e.g. sodium carbonate (Na_2CO_3), preferably 16 to 24 wt.% sodium coagulation salt. As already stated, the sodium coagulation salt is typically sodium carbonate (Na_2CO_3). It may further be e.g. sodium sulfate (Na_2SO_4) or a combination of sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4).

The temperature of the cellulose spin dope upon extruding it into the coagulation bath liquid is 5°C to 30°C, whereas the temperature of the coagulation bath is 20°C to 50°C, preferably 20°C to 30°C.

Further advantageous features of the invention are elaborated in embodiments disclosed herein. In addition, advantageous features of the invention are defined in the claims.

Brief description of the drawings

These and other aspects, features and advantages of which the invention is capable of will be apparent and elucidated from the following description of embodiments of the present invention, reference being made to the accompanying drawing, in which:

Fig. 1 depicts a flow chart for the various process steps in part of an embodiment of a process for separately recovering sodium hydroxide (NaOH) and a sodium coagulation salt;

Fig. 2 depicts the flow chart shown in Fig. 1 in conjunction with a flow chart of the various process steps in an embodiment of a process for cellulose fiber spinning and film forming, employing dissolving pulp in aqueous sodium hydroxide solution to form a spin dope and moving in further into an aqueous coagulation bath liquid;

Fig. 3 shows a diagram depicting a typical wash liquid composition (boxed area) and solubility data for sodium carbonate (Na_2CO_3) in aqueous NaOH at the

temperatures 25°C and 1°C (adopted from A. Tranquard, Rev. Chim. Minerale, 2, No. 3, 449- (1965);

Fig. 4 shows a diagram depicting a typical sodium carbonate (Na_2CO_3) reduced wash liquid composition (boxed area) and solubility data for sodium carbonate (Na_2CO_3) in aqueous NaOH at the temperatures 25°C and 100°C (adopted from A. Tranquard, Rev. Chim. Minerale, 2, No. 3, 449- (1965);

Fig. 5 shows a diagram illustrating the distribution of NaOH and Na_2CO_3 between supernatant (i.e. recovered aqueous sodium hydroxide solution, referred to as: "Recovered aqueous NaOH solution") and sediment (i.e. the second portion of precipitated Na_2CO_3, referred to as: "Second portion of sodium coagulation salt") after "loops" (i.e. repeated treatment after re-cycling of the second portion of precipitated Na_2CO_3); and

Fig. 6 shows a diagram depicting the effect of the sediment composition (i.e. the second portion of precipitated Na_2CO_3), as it is recycled to the cooling crystallization step, on the composition of the wash liquid in each loop cycle.

Detailed description

The general concept of recovering spent sodium hydroxide in cellulose spinning processes has been discussed in WO 2015/000820, wherein the general concept of alkali recovery from a cellulose fiber regeneration step, without substantial neutralization with acids, is disclosed. WO 2015/000820 does however not provide any procedure for regeneration of substantially pure sodium hydroxide with only very low remaining amounts of the salt used in the coagulation bath.

Further, EP 3 231 901 A1 relates to a process for extruding dissolved cellulose to form cellulose fibers or films. An aqueous solution comprising a coagulation sodium salt is employed as a coagulation bath liquid in an extrusion step of the process, which provides regenerated cellulose fibers. In the process, sodium hydroxide to be used for dissolving cellulose is recovered from dispensed coagulation bath liquid by precipitating the coagulation sodium salt.

Since the coagulation bath liquid is drained of its sodium coagulation salt when the tow is removed therefrom, it would be beneficial to also recycle the sodium coagulation salt. If this could be achieved, there would be no, or at least less, need for addition of further sodium coagulation salt to the coagulation bath.

Whereas it is generally known how to precipitate coagulation sodium salts, it is difficult to separate the chemicals from one another at substantial purity so that it may

be recovered and fed back into a suitable step in the process of forming cellulose fibers or films.

For instance, one of the most critical requirements of the separation sequence is having a low concentration of the sodium coagulation salt in the recycled sodium hydroxide solution. The sodium hydroxide solution is to be re-used to dissolve the cellulose starting material and form a cellulose spin dope. If the mass ratio between sodium hydroxide and the sodium coagulation salt is too high in said sodium hydroxide solution, the dissolution of cellulose will result in a spin dope with very poor stability against gelation.

The inventors have surprisingly found that the sodium coagulation salt may be recovered in an efficient manner from an aqueous composition also comprising sodium hydroxide by precipitating it in two separate steps, the first precipitation yielding essentially pure sodium coagulation salt. The second precipitation of sodium coagulation salt provides an essentially pure sodium hydroxide solution with very low content of the sodium coagulation salt. The recovered essentially pure sodium hydroxide solution is sufficiently pure to be used in dissolving cellulose to provide a cellulose spin dope.

It has further been realized that separately recovered sodium hydroxide and the sodium coagulation salt can be reused in a process for forming cellulosic fibers or films. Recovered aqueous sodium hydroxide may thus be recycled into a spin dope and recovered sodium coagulation salt may be recycled into an aqueous sodium coagulation salt solution bath. This recycling of chemicals results in a closed system, which is environmentally friendly and an economically viable process. The sodium hydroxide must be sufficiently free from the coagulation salt to allow for re-use as an efficient solvent cellulose. It would thus be preferred to be able to separately recover substantially pure sodium hydroxide and sodium coagulation salt from an aqueous liquid used in spinning fibers.

Thus, there is, according to an exemplary embodiment of the invention, provided a process for separately recovering sodium hydroxide (NaOH) and a sodium coagulation salt, respectively, from an aqueous composition 10 comprising a dissolved sodium coagulation salt. The salt has been used in an aqueous coagulation bath liquid 60 for alkaline fiber or film spinning, and the dissolved sodium hydroxide (NaOH) has been used in dissolving cellulose 40 to provide a cellulose spin dope 41 for fiber or film spinning in an aqueous coagulation bath liquid 60 for alkaline fiber or film spinning.

The aqueous coagulation bath liquid 60 comprises a dissolved sodium coagulation salt, and has a pH of more than 7. The process comprises the steps of:

- cooling the aqueous composition 10 to precipitate a first portion of the sodium coagulation salt 30, to provide a sodium coagulation salt reduced aqueous composition 11 comprising dissolved sodium hydroxide (NaOH);

- separating the precipitated, first portion of the sodium coagulation salt 30 from the sodium coagulation salt reduced aqueous composition 11 to provide recovered sodium coagulation salt for subsequent use as make up in an aqueous coagulation bath liquid 60 to comprise a sodium coagulation salt, wherein the aqueous coagulation bath liquid 60 is for use in alkaline fiber or film spinning;

- evaporating water from the sodium coagulation salt reduced aqueous composition 11, thereby increasing the concentration of sodium hydroxide (NaOH) to form a concentrated aqueous composition (12); and

- precipitating and separating a second portion of the sodium coagulation salt 31 from the concentrated aqueous composition 12, thereby providing a recovered aqueous sodium hydroxide solution 20 comprising dissolved sodium hydroxide (NaOH) for use in dissolving cellulose 40 to provide a cellulose spin dope fiber or film spinning 41.

Cellulose 40 is dissolved in cold alkali solution, being an aqueous solution of NaOH and optionally ZnO. The cellulose 40 is dissolved in the cold alkali solution under high shear mixing at approximately -4°C to produce a spin dope 41. This is often followed by cellulose regeneration into fibers where the spin dope is fed through spinnerets into an aqueous coagulation bath liquid 60, also referred to as an alkaline spin bath, typically comprising dissolved NaOH (~ 5.7 wt.%), sodium coagulation salt (~ 21 wt.%) and optionally ZnO (~0.7 wt.%).

The regenerated cellulose fibers 42 form a wet swollen tow, which is pulled out of the aqueous coagulation bath liquid 60. However, as mentioned above, the tow entrains aqueous coagulation bath liquid 60 when removed from the bath. A lot of the entrained liquid may be squeezed out of the tow using press rolls. The released liquid may be subject to the present process for recovering sodium hydroxide (NaOH) and the sodium coagulation salt, respectively. Alternatively, the released liquid may be returned to the aqueous coagulation bath. However, the entrainment of liquid still lowers the concentration of the sodium coagulation salt in the aqueous coagulation bath liquid 60. In order to lower the content of metal ions in the fiber tow, the tow is typically washed

in a washing sequence, where an aqueous liquid 50, or water, is used to rinse the tow from remaining NaOH, sodium coagulation salt, and optionally ZnO.

Hence, the ingoing aqueous composition 10 for the separation process described above may be the outgoing generated wash liquid 51 from the washing step. Further, the ingoing aqueous composition 10 may comprise aqueous coagulation bath 60 liquid pressed out from the tow before the washing is initiated. In addition, overflow from the aqueous coagulation bath may form part of the aqueous composition 10.

The aqueous composition 10 hence comprises NaOH, sodium coagulation salt, ZnO (optionally), possibly other metal ions, and organic materials, such as degraded cellulose and hemicellulose residues. As the degraded cellulose and hemicellulose residues may accumulate in the process, it may be necessary to include removal thereof (not shown in Fig. 2).

The aqueous composition 10 may comprise spent aqueous washing liquid 51 resulting from washing a fiber, or a film 42, spun from a cellulose spin dope 41, comprising dissolved cellulose 40, sodium hydroxide (NaOH), and optionally zinc oxide (ZnO), in an aqueous coagulation bath liquid 60 comprising a sodium coagulation salt. Additionally or alternatively, the aqueous composition 10 may comprise an aqueous coagulation bath liquid 60, which in turn comprises a sodium coagulation salt, used in alkaline fiber or film spinning of a cellulose spin dope 42 comprising dissolved cellulose 40, sodium hydroxide (NaOH), and optionally zinc oxide (ZnO).

Furthermore, the aqueous composition 10 to recover sodium hydroxide (NaOH) and the sodium coagulation salt, respectively, typically comprises 2 to 10 wt.%, such as 3 to 6 wt.% sodium hydroxide (NaOH), 8 to 22 wt.%, such as 9 to 15 wt.% sodium coagulation salt, and optionally zinc oxide (ZnO). The zinc oxide (ZnO) is recovered with the sodium hydroxide (NaOH). The sodium coagulation salt may e.g. be sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), or a combination thereof.

As described, it is of importance for the separation process that the concentration of Na_2CO_3 in the recycled NaOH-solution (optionally comprising ZnO) is low. If it is too high, the dissolution of cellulose 40 will result in a spin dope 41 with very poor stability against gelation. Preferably, the mass ratio of sodium coagulation salt:sodium hydroxide (NaOH) in the recovered aqueous sodium hydroxide solution 20 is thus 0.05:1 or less, such as 0.04:1 or less, or 0.03:1 or less. The desired mass ratio may be achieved by precipitating further sodium coagulation salt in the step of precipitating and separating a second portion of the sodium coagulation salt. This may be achieved by concentrating the concentrated aqueous composition further and/or by

lowering the temperature further in precipitating the sodium coagulation salt. Further, also the amount of sodium coagulation salt separated in the first portion of the sodium coagulation salt 30 will affect the relative amount of the sodium coagulation salt in the recovered aqueous sodium hydroxide solution 20.

The solubility of the sodium coagulation salt, e.g. Na_2CO_3, depends on the NaOH concentration and on the temperature of the solution. A typical composition of the aqueous composition 10 to recover NaOH and Na_2CO_3 from is NaOH ~4 wt.% and Na_2CO_3 ~12 w.t%. In **Error! Reference source not found.** the saturation solubility data for Na_2CO_3 as a function of the NaOH concentration at 25°C and 1°C, respectively, is shown. As already mentioned, the mass ratio of Na_2CO_3 to NaOH is of importance to get a stable spin dope 41 solution. Consequently, the recycled solution of NaOH 20 after completed separation of chemicals should have a composition positioned underneath a ratio limit of e.g. 0.04:1, which is shown as the dashed black line in the diagrams in Fig. 3 and 4.

In Fig. 3, at 25°C, the dotted line for the solubility data shows that the NaOH concentration must be about 29-30 wt.% or higher in order to get a Na_2CO_3 solubility below a ratio limit line of 0.04:1 (dashed black line). Thus, direct evaporation of water from the aqueous composition 10 to increase the NaOH concentration would be a possibility. However, direct evaporation of the aqueous composition 10 would cause problems with agitation and heat transfer since the precipitation of Na_2CO_3 crystals results in high viscosities.

However, as shown in Fig. 3, the solubility of Na_2CO_3 is much lower at low temperatures also in reasonably dilute NaOH solutions. This is illustrated by the solid line with triangular data points in **Error! Reference source not found.**Fig. 3, showing the saturation solubility of Na_2CO_3 in NaOH at 1°C. By reducing the temperature to about 0°C, the solubility of Na_2CO_3 in the aqueous composition 10 is low enough to precipitate a first portion of about 80% of Na_2CO_3. When the aqueous composition 10 is cooled in the cooling step, it is typically cooled to a temperature above the freezing point of the aqueous composition, such that essentially no water freezes to ice. This first portion of Na_2CO_3 is preferably precipitated as sodium carbonate decahydrate ($Na_2CO_3 \times 10{\cdot}H_20$), which is advantageous since the decahydrate salt forms big spherical crystals.

Furthermore, the precipitated first portion of sodium coagulation salt 30, such as Na_2CO_3, may be separated from the sodium coagulation salt reduced aqueous composition 11 by means of a separation technique selected from the group consisting

of centrifugation, decantation, and filtration (e.g. by a filter press or by a filter belt), or combinations thereof. The entrainment of NaOH (liquid phase) in the centrifugation process is very small (cf. example 2), and a decahydrate salt ($Na_2CO_3 \times 10 \cdot H_20$) being almost completely free from NaOH may be isolated. Alternative separation means in addition to centrifugation may be filtration, decantation or any other separation technique known by the skilled person.

The first portion of the precipitated sodium coagulation salt (e.g. Na_2CO_3) 30 may then subsequently be used as make up in the aqueous coagulation bath liquid, such that less, or even no, additional Na_2CO_3 does need to be added to the bath.

Even though the first separated portion of precipitated sodium coagulation salt 30 (e.g. Na_2CO_3) may comprise a substantial part of the sodium coagulation salt originally present (e.g. approximately 80% of the sodium coagulation salt) in the aqueous composition, it may not be sufficient to take the aqueous composition 10 below a ratio of e.g. 0.04:1 (cf. dashed black line in Fig. 3) unless the temperature of aqueous composition 10 is lowered well below 0°C. Therefore, an evaporation step, to be followed by a second precipitation of the sodium coagulation salt, may be advantageous. Two separate precipitations steps provide a substantial portion of the sodium coagulation salt in the first step in essentially pure form, allowing for subsequent use as make up a in a coagulation bath liquid.

With reference to Fig. 4, a diagram showing a typical wash liquid composition (black box) and solubility data for Na_2CO_3 in NaOH at 25˚C and 100˚C is shown. Naturally, the removal of Na_2CO_3 during the cooling crystallization step changes the composition of the aqueous composition 10 into a sodium salt reduced aqueous composition 11. A typical sodium salt reduced aqueous composition 11 is shown by the black boundary box in Fig. 4.

The major part of remaining Na_2CO_3 (about 20 %) in the sodium coagulation salt reduced aqueous composition 11 must still be removed in order to allow for using the recovered NaOH in dissolving cellulose. By evaporating water, the concentration of the present salts will increase. Increasing the concentration of NaOH will in turn reduce the solubility of the sodium coagulation salt. Water may be evaporated by simply heating the sodium coagulation salt reduced aqueous composition 11, either at ambient pressure or at reduced pressure (to evaporate water at a lower temperature). If the concentrated aqueous composition becomes sufficiently concentrated, the sodium coagulation salt will start precipitating to allow for separating a second portion of the sodium coagulation salt 31. However, lowering the temperature of the concentrated

aqueous composition will also cause the sodium coagulation salt to precipitate a second portion of the sodium coagulation salt 31. According to an embodiment, water is evaporated at elevated temperature, such at least 50°C, 60 or even 75°C. According to such an embodiment, it may not be necessary to concentrate the aqueous composition such that the sodium coagulation salt starts to precipitate, as lowering the temperature will be sufficient for precipitating the sodium coagulation salt.

As shown by the solid graph line in Fig. 4**Error! Reference source not found.**, heating of the wash liquid to 100°C will increase the solubility of Na_2CO_3 compared to 25°C (dotted graph line). However, as soon as the concentration of NaOH reaches above ~30 wt.%, the wash liquid can be cooled to 25°C, or lower, to ensure sufficient precipitation to reach below a ratio limit of e.g. 0.04:1 (cf. dashed black line in Figs. 3 and 4). Hence, it is not the heating to 100°C *per se* which causes the precipitation of Na_2CO_3, but the fact that the concentration of NaOH increases when water is evaporated. The evaporation forms a concentrated aqueous composition 12, since the aqueous content has been reduced while the absolute amount of NaOH and the sodium coagulation salt, respectively, are maintained at the same levels as prior to the evaporation. As can be seen from the graphs in Fig. 4, the solubility of Na_2CO_3 decreases when the concentration of NaOH increases. Thus, when the concentration of NaOH reaches approximately above 30 wt.%, the solubility of Na_2CO_3 at 25°C is very low and a further substantial portion of it may thus be precipitated.

In order to facilitate the subsequent precipitating and separation of further sodium coagulation salt, the step of evaporating water is preferably continued until the concentration of sodium hydroxide (NaOH) in the concentrated aqueous composition 12 is at least 25 wt.%, such as at least 26 wt.%, 27 wt.%, 28 wt.%, 29 wt.%, or 30 wt.%, preferably at least 28 wt.%, 29 wt.%, or 30 wt.%, more preferably at least 30 wt.%.

As mentioned, the disclosed process has overcome several obstacles to resolve the separate recovery of NaOH and the sodium coagulation salt. The difficulty here is not only to cause precipitation of the second portion of the Na_2CO_3, but to separate the precipitate from the supernatant solution. At concentrations above about 20 wt.% NaOH, the dissolved Na_2CO_3 will precipitate in the form of sodium carbonate monohydrate (Na_2CO_3 x $1{\cdot}H_2O$) instead of the decahydrate form ($Na_2CO_3 \times 10{\cdot}H_20$).

The monohydrate crystals are much smaller compared to the decahydrate crystals and thus harder to separate. These crystals tend to pack into a dense paste during filtration forming a filter cake, which hinders efficient flow of the supernatant solution through the filter. Obviously, the filters need to have small pore sizes to trap

the particles, but such filters are immediately clogged by the paste. Separating the monohydrate particles from supernatant solution by centrifugation is a better option although this method is also somewhat problematic. A lot of liquid phase will remain in the precipitated solid phase.

However, the inventors have surprisingly found a solution to these issues allowing for improving the overall yield of recovered NaOH and sodium coagulation salt, respectively: By recirculating the removed second portion of the precipitated sodium coagulation salt 31, which also comprises sodium hydroxide (NaOH), into the step of cooling the aqueous composition 10 to precipitate the first portion of sodium coagulation salt.

After having removed the second portion of the sodium coagulation salt 31 (e.g. Na_2CO_3), a recovered aqueous sodium hydroxide solution 20 comprising dissolved sodium hydroxide (NaOH) is provided. This solution 20 may be recycled for use in dissolving cellulose to provide a cellulose spin dope fiber or film spinning, as the content of the sodium coagulation salt is very low. Typically the weight ratio of sodium coagulation salt to NaOH is 0.05:1 or less, such as 0.04:1 or less, or 0.03:1 or less.

According to an exemplary embodiment (cf. the flow chart in Fig. 1), an ingoing starting material being an aqueous composition 10 is treated to separately recover aqueous sodium hydroxide as a solution 20 and a first 30 and second 31 portion of the sodium coagulation salt. The aqueous composition 10 comprises an outgoing generated wash waste liquid from a countercurrent washing of a tow and possibly an overflow from a coagulation bath. These combined liquids forming the aqueous composition 10 comprises sodium hydroxide (NaOH), a sodium coagulation salt, which may be sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4) or a combination thereof, optionally zinc oxide (ZnO) and other metal ions, and organic materials such as degraded cellulose and hemicellulose residues.

The aqueous composition 10 shown in Fig. 1 is cooled in a cooler 110, causing a first portion of the sodium coagulation salt 30 to precipitate from the aqueous composition 10. The first portion of the sodium coagulation salt 30 is separated from the solution 10 in a first separator 120, which may, for example, be a centrifuge, a decantation device, or a filter. Approximately 80% of the sodium coagulation salt is precipitated and separated from the aqueous composition 10. Hence, the obtained remaining solution is a sodium coagulation salt reduced aqueous composition 11.

Subsequently, water is evaporated from the sodium coagulation salt reduced aqueous composition 11 in an evaporator 130, resulting in a concentrated aqueous

composition 12. When the water is evaporated from the liquid, the concentration of the compounds therein inherently is increased, as they are not volatile. When heating the sodium coagulation salt reduced aqueous composition 11, water evaporates from the aqueous composition 11, thereby increasing the concentration of sodium hydroxide (NaOH). Optionally the evaporation may be improved by applying sub-atmospheric pressure.

The concentrated aqueous composition 12 still comprises some remaining sodium coagulation salt (approximately 20% of the initial amount) and sodium hydroxide. Thus, a second portion of the sodium coagulation salt 31 is separated from the concentrated aqueous composition 12 through precipitation in a second separator 140. This may be performed either at ambient pressure or at reduced pressure, which causes the second portion of the sodium coagulation salt 31 to precipitate and salt crystals can be separated from the concentrated aqueous composition 12. The second portion of the sodium coagulation salt 31 is then recycled to be treated, together with the aqueous composition 10, in the cooler 110. What is left after precipitation and separation of the second portion of the sodium coagulation salt 31 in the second separator 140, such as a centrifuge, is a recovered aqueous sodium hydroxide solution 20.

With reference to Fig. 2, the separate recovery of sodium hydroxide and the sodium coagulation salt is incorporated into a flow chart of the various process steps in an embodiment of a process for cellulose fiber spinning and/or film forming.

In short, the flow chart in Fig. 2 describes a process for forming cellulose fibers or film from dissolved cellulose. The process comprises the steps of:

- dissolving cellulose 40 in an aqueous sodium hydroxide (NaOH) solution in dissolving vessel 210 to provide a cellulose spin dope 41;
- extruding the cellulose spin dope 41 into an aqueous coagulation bath liquid 60 comprising a dissolved sodium coagulation salt and having a pH of more than 7, the aqueous coagulation bath liquid 60 being present in a coagulation vessel 220, to provide cellulose fibers or film 42;
- withdrawing the cellulose fibers or film 42 from the coagulation vessel;
- washing the withdrawn cellulose fibers or film 42 with an aqueous washing liquid 50 in a washer 230 to extract sodium hydroxide (NaOH) and sodium coagulation salt therefrom;
- recovering an aqueous sodium hydroxide (NaOH) solution 20 and the sodium coagulation salt, respectively, from spent aqueous washing liquid 51 resulting from the

step of washing the fibers, or the film 42, and/or from the aqueous coagulation bath liquid 60 used in the step of extruding the cellulose spin dope 41 into an aqueous coagulation bath liquid, as described in relation to Fig. 1;

- using the recovered sodium hydroxide (NaOH) solution 20 in the step of dissolving cellulose 40, in the dissolving vessel 210; and

- using recovered sodium coagulation salt 30 as make up in the aqueous coagulation bath liquid 60, in the coagulation vessel 220.

Fig. 2 will now be explained in more detail. Cellulose 40 is dissolved in an alkali solution in dissolving vessel 210 to provide a cellulose spin dope 41. The alkali solution is an aqueous sodium hydroxide (NaOH) solution which may comprise 6 to 18 wt.%, such as 7.5 to 12 wt.% NaOH, and less than 1.0 wt.%, such as less than 0.5 wt.% sodium coagulation salt, preferably even less than 0.3 wt.% sodium coagulation salt. The NaOH solution may optionally further comprise up to 2.7 wt.% zinc oxide (ZnO).

The formed cellulose spin dope 41 may comprise 4 to 12 wt.%, preferably 5 to 8 wt.% cellulose, and/or the cellulose in the cellulose spin dope may have a DP of 140 to 600, such as 180 to 600, 200 to 400, 160 to 400, or 180 to 300. In addition, the cellulose in the cellulose spin dope may have an intrinsic viscosity according to ISO5351:2010(E) of 115 to 450, such as 150 to 450 ml/g, 190 to 300 ml/g, 130 to 300 ml/g, or 140 to 230 ml/g, and/or the cellulose spin dope may have a viscosity at $1s^{-1}$ of 1 to 500 Pas, preferably 5 to 100 Pas. Furthermore, the cellulose in the cellulose spin dope may have a degree of substitution DS of not more than 0.1, preferably not more than 0.05. The cellulose spin dope may further comprise 5 to 10 wt.% NaOH, preferably 6.5 to 8.5 wt.% NaOH.

In the next step shown in Fig. 2, the spin dope 41 is fed through spinnerets and extruded into an aqueous coagulation bath liquid 60 in a coagulation vessel 220. The aqueous coagulation bath liquid 60 may comprise for instance 14 to 32 wt.%, preferably 16 to 24 wt.% sodium coagulation salt. The temperature of the cellulose spin dope 41 upon extruding it into the coagulation bath liquid may be 5°C to 30°C. Furthermore, the temperature of the coagulation bath may be 20°C to 50°C, preferably 20°C to 30°C. The sodium coagulation salt may be sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4) or a combination thereof.

The regenerated cellulose fibers or film 42 precipitated in the coagulation bath, are pulled out of the coagulation bath and washed with an aqueous washing liquid 50 in a washer 230 to provide washed cellulose fibers or films 43. The washing may comprise one or more washing steps. The spent washing liquid 51 is fed into the aqueous

composition 10 of the recycling process shown in Fig. 1 such that the NaOH and the sodium coagulation salt may be separately recovered and re-cycled to a process for cellulose fiber spinning and film forming.

As shown in Fig. 2, the precipitated first portion of the sodium coagulation salt 30 is fed back into the aqueous coagulation bath liquid 60 of the coagulation vessel 220. Furthermore, water may be evaporated from the precipitated first portion of the sodium coagulation salt 30 (indicated by the dashed box “Drier” in Fig. 2) to affect the water balance in the aqueous coagulation bath liquid. The recovered aqueous sodium hydroxide solution 20 is fed back into the solution comprising the cellulose spin dope 41. As explained also with reference to Fig. 1, the ingoing material in the aqueous composition 10 may hence optionally be an overflow of the aqueous coagulation bath liquid 60 from the coagulation vessel 220 (indicated by the dashed arrow in Fig. 2) and the generated waste stream 51 of the aqueous wash liquid 50.

Without further elaboration, it is believed that one skilled in the art may, using the preceding description, utilize the present invention to its fullest extent. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative and not limitative of the disclosure in any way whatsoever.

Although the present invention has been described above with reference to specific embodiments, it is not intended to be limited to the specific form set forth herein. Rather, the invention is limited only by the accompanying claims and other embodiments than the specific embodiments described above are equally possible within the scope of these appended claims.

In the claims, the term "comprises/comprising" does not exclude the presence of other elements or steps. Additionally, although individual features may be included in different claims, these may possibly advantageously be combined, and the inclusion in different claims does not imply that a combination of features is not feasible and/or advantageous.

In addition, singular references do not exclude a plurality. The terms "a", "an", “first”, “second” etc. do not preclude a plurality.

Examples

The following examples are mere examples and should by no means be interpreted to limit the scope of the invention, as the invention is limited only by the accompanying claims.

Example 1 – Cooling crystallization – separation efficiency

A number of cooling crystallization experiments have been performed in which the starting aqueous composition was cooled to -5°C to induce a first precipitation of Na_2CO_3 x $10H_2O$. Table 1 shows the compositions of the wash liquids that were used in the experiments and the achieved distribution of NaOH and Na_2CO_3 between the supernatant and the precipitate.

Table 1

Experiment		1:1	2:1	3:1	4:1	5:1	6:1
Aqueous composition	NaOH [wt%]	3.7	3.7	3.9	3.9	5.8	6.4
	Na_2CO_3 [wt%]	10.4	10.4	10.8	11.,4	12.7	11.7
NaOH-separation [%]: Liquid phase[1]/Solid phase[2]		93/2	87/5	95/3	95/6	96/5	102/4
Na_2CO_3-separation [%]: Liquid phase[1]/Solid phase[2]		34/56	18/73	19/80	23/71	12/80	26/69
NaOH - concentration in Solid phase[1] [wt%]		0.5	0.7	0.5	0.9	0.9	1.1

[1]Liquid phase = supernatant solution, [2]Solid phase = decahydrate salt slurry

For example, in experiment 1:1, 34% of the Na_2CO_3 ended up in the supernatant solution and 56% in the decahydrate slurry, whereas the corresponding distribution of NaOH was 93% and 2%. With only 56% of the Na_2CO_3 ending up in the decahydrate salt slurry, this particular experiment (i.e. no. 1:1) resulted in the lowest separation efficiency for Na_2CO_3. The reason for this is that the decahydrate salt slurry was washed once with cold water (1˚C) in an attempt to wash out NaOH from the crystals. The washing seems to have worked in terms of removing NaOH, but some Na_2CO_3 was also washed out and added to the supernatant instead. In the other experiments (i.e. no. 2:1 to 6:1), the cooling crystallization step has successfully removed about 70-80% of the Na_2CO_3 from the aqueous composition. Overall, the concentration of NaOH in the decahydrate salt slurry is low.

This is a clear evidence that lowering the temperature of the aqueous composition is a successful method to facilitate the precipitation of the first portion of Na_2CO_3. Further, the amount of NaOH in the precipitated first portion of Na_2CO_3 is very low and does not need to be washed away.

Example 2 – Evaporation experiments – separation efficiency

A series of experiments have been performed in which the evaporation approach has been tested to separate Na_2CO_3 from NaOH solutions. An overview of these experiments is given in Table 2.

Table 2

Experiment		1:2	2:2	3:2	4:2	5:2	6:2	7:2	8:2	9:2	10:2
Aqueous composition [wt%]	NaOH	3.5	4.4	5.1	5.1	5.1	5.1	5.1	5.0	8.1	8.8
	Na_2CO_3	3.6	2.6	2.8	2.8	2.8	2.8	2.8	3.6	2.2	4.1
NaOH-separation [%]: Liq. phase[1]/Sol. phase[2]		31/42	83/10	60/28	39/53	32/62	47/48	46/52	35/65	41/53	64/32
Na_2CO_3-separation [%]: Liq.phase[1]/Sol. phase[2]		5/59	16/86	1/97	4/102	1/103	0/100	0/96	0/106	6/112	1/83

[1]*Liquid phase = supernatant solution;* [2]*Solid phase = monohydrate salt paste.*

The second row of Table 2 shows the concentrations of Na_2CO_3 in each solution that has been used in the evaporation experiments. The concentrations are on the same level or below the NaOH concentrations since most of the Na_2CO_3 has been removed in the cooling crystallization (as described in Example 1). As already described, the evaporation is efficient in terms of forcing the dissolved Na_2CO_3 out of solution as a precipitate (as is also evident from the experimental data), but the separation of the precipitate from the solution is difficult. This can be seen by the separation data in Table 2.

As an example, in the second experiment (2:2) the precipitate was removed from the remaining liquid phase using centrifugation followed by decantation (filtration was not possible) resulting in 83% of the NaOH in the liquid phase and 10% in the solid phase. The corresponding distribution of Na_2CO_3 was 16% in the liquid phase and 86% in the solid phase. Obviously, the percentages should add up to 100% for both compounds, but material losses in the lab-scale experiments and some uncertainties in the titration data etc. causes the mass balance calculations to be slightly inexact.

It is obvious that there is a considerable fraction of the ingoing NaOH found in both the liquid phase and the solid phase. For Na_2CO_3, the separation is somewhat better. In experiments 3:2-9:2, close to 100% of the Na_2CO_3 is found in the solid phase. However, even low percentages of Na_2CO_3 in the NaOH solutions can be a problem

considering the ratio limit of 0.04. The concentrations of the different phases are shown in **Error! Reference source not found.** 3 below.

Table 3

Experiment	1:3	2:3	3:3	4:3	5:3	6:3	7:3	8:3	9:3	10:3
NaOH conc. liq. phase[1] [wt%]	25.0	26.4	34.3	29.6	33.8	30.8	31.4	32.2	31.1	34.7
Theoretical[3] Na_2CO_3 conc. liq. phase[1] [wt%]	3.2	2.4	0.4	1.1	0.4	0.8	0.7	0.6	0.8	0.3
Actual Na_2CO_3 conc. liq. phase[1] [wt%]	4.3	3.1	0.4	1.6	0.6	0.0	0.0	0.2	1.2	0.2
Ratio Na_2CO_3/NaOH	0.170	0.116	0.012	0.054	0.019	0.001	0.001	0.006	0.038	0.005
NaOH conc. in sol. phase[2] [wt%]	18.7	10.9	20.9	23.5	25.8	21. 6	23.0	22.6	23.8	20.9

[1]Liquid phase = supernatant solution; [2]Solid phase = monohydrate salt paste; [3]Based on curve fitting for solubility data at 25°C.

It is known from the solubility data at 25°C (cf. Figs 3 and 4) that a NaOH concentration of about 30% is needed to get the solubility of Na_2CO_3 to go below the ratio limit line corresponding to a ratio of Na_2CO_3 to NaOH of 0.04:1. The first row of **Error! Reference source not found.** shows that not enough water was evaporated in experiments 1:3, 2:3, and 4:3 to reach this concentration, if precipitating at a temperature of about 25°C. Precipitation of Na_2CO_3 at a lower temperature would have resulted in a lower relative amount of Na_2CO_3. These three experiments also ended up with a too high ratio of Na_2CO_3 :NaOH. The second and third rows show the theoretical solubility and actual concentrations of Na_2CO_3 in the liquid phases generated in the experiments. The actual concentrations of Na_2CO_3 in some experiments are higher than the theoretical solubility limit. Without being bond to any theory, this is believed to be an effect of incomplete separation in the centrifugation/decantation step. Fine undissolved particles of Na_2CO_3 seems to be present in the liquid phase even if the solutions appear transparent and clear. Still, most of the experiments resulted in liquid

phases with low enough Na_2CO_3 :NaOH ratios to be suitable for recycling and reuse as solvents for cellulose when forming a spinning dope.

The final row of Table 3**Error! Reference source not found.** shows the NaOH concentrations in the solid phase. As can be seen, the concentrations are high in all experiments.

Example 3 – Dissolution tests using recycled NaOH/Zn supernatant from evaporation

Several wash liquid solutions have been subjected to the separation steps of cooling crystallization, followed by centrifugation/filtration, continued with evaporation and subsequent centrifugation and decantation. Some of the solutions were chosen as solvents for cellulose in dissolution tests. The easiest way to compare the quality of a series of dissolutions is to measure the clogging values. The lower the clogging value, the better the solution. The solution compositions and the resulting clogging values (CV) are shown in Table 4 below**Error! Reference source not found.**.

Table 4

#	Sample origin	NaOH [wt%]	Na_2CO_3 [wt%]	Zn [wt%]	TOC [wt%]	CV
-	Reference	7.50	0.00	0.76	0.00	254
1:4	Wash liquid, evap. @40°C	7.50	0.01	0.80	0.11	282
2:4	Wash liquid, evap. @100°C	7.50	0.14	0.89	0.14	265
3:4	Wash liquid, evap. @100°C (IBZ)	7.50	0.19	0.87	0.28	319

The data in Table 4 shows that samples 1:4 and 2:4 had clogging values reasonably close to the reference It is not surprising that sample 3:4 should have a high clogging value, since this wash liquid was evaporated in several steps at high temperature and with insufficient stirring (high viscosity due to Na_2CO_3 precipitation). None of the clogging values are too high, and all solutions would be expected to work perfectly in a fiber spinning experiment.

Another qualitative measure of the solutions is the behavior during the dissolution process. The lab procedure involves keeping the solution at -4°C for 15 minutes with the highest possible rate of high shear mixing in a small vessel. A circulating flow of cooling liquid through the jacket of the dissolution vessel keeps the solution cold. If the temperature goes higher than -4°C, the rate of high shear mixing is reduced. Thus, by looking at the rate of high shear mixing it is possible to get an

indirect measure of the solution viscosity. The higher the mixing rate, the lower the viscosity. During the dissolution of the four samples in **Error! Reference source not found.**, the reference showed the normal behavior whereas sample 3:4 had a much higher viscosity (lower shear rate needed) than the other samples. Samples 1:4 and 2:4, were both in between the reference sample and sample 3:4. Again, none of the samples show too high apparent viscosity and would thus be expected to be usable in a fiber spinning experiment.

Example 4 – Loop test – repeated (3 times) cooling crystallization and evaporation

The experimental process for the loop test involved the following steps:

1) Fresh wash liquid of known composition is cooled to -5°C. Na_2CO_3 x $10{\cdot}H_2O$ precipitates.
2) The precipitate is separated from the supernatant NaOH solution by centrifugation/filtration.
3) Water is evaporated from the supernatant NaOH solution. Na_2CO_3 x $1{\cdot}H_2O$ precipitates.
4) The precipitate is separated from the supernatant NaOH solution by centrifugation and decantation.
5) The isolated precipitate is added to a new portion of fresh wash liquid.

Steps 1-5 are repeated twice (i.e. 3 cycles in total)

The concentrations of NaOH and Na_2CO_3 in each fraction were determined by titration. Some fractions were also analyzed with respect to total organic carbon (TOC), Zn, and other metals. The experiment verifies that the concentrations of NaOH and Na_2CO_3 stay within expected ranges and that recycling of the paste-like sediment comprising NaOH and Na_2CO_3 x $1{\cdot}H_2O$, will not cause practical problems in the dissolution and/or evaporation step.

The distribution of NaOH and Na_2CO_3 between supernatant and sediment after centrifugation and decantation for each cycle of the loop test (evaporations 8:2, 9:2 and 10:2) is shown in Table 2**Error! Reference source not found.**. The same data are presented graphically in Fig. 5**Error! Reference source not found.**.

With reference to Fig. 5, the results indicates that the recovery of NaOH increases for every loop, starting with 35%, increasing to 41%, and ending up at 64% in the supernatant in the third loop. Further, it is clear that the supernatant fraction is almost completely free of Na_2CO_3. Basically, all Na_2CO_3 ends up in the sediment. The fact that the percentages do not sum up to 100 is an indication of the error that is associated with the test. The lower diagram in Fig. 5 also shows the fraction of NaOH that could not be separated from the sediment.

The effect of the sediment composition as it is recycled to the cooling crystallization step on the composition of the wash liquid in each loop cycle is shown in Fig. 6**Error! Reference source not found.**.

The data points in the diagram in Fig. 6 are measured values from the loop test, whereas the curves are calculated based on the following assumptions:

- Separation efficiency of 95% for NaOH in the cooling crystallization
- Separation efficiency of 75% for Na_2CO_3 in the cooling crystallization
- Evaporation performed until 32% NaOH concentration
- Separation efficiency of 50% for NaOH in the evaporation
- Separation efficiency of 100% for Na_2CO_3 in the evaporation
- Starting wash liquid composition (cycle 0) is 3.9% NaOH and 11.4% Na_2CO_3.

All assumptions are based on the experimental results from the loop test. Calculations based on these assumptions stabilize at a NaOH concentration of 6.1% and a Na_2CO_3 concentration of 12.4%. The actual data from the loop test roughly follows the predicted composition. The return percentage will also depend on the composition of the ingoing wash liquid.

The conclusion from the loop test and the calculations above is that returning a certain amount of sediment containing $Na_2CO_3 \times 1{\cdot}H_2O$ and NaOH to the cooling crystallization step will alter the composition going into the separation step slightly – but a steady state composition will soon be reached. Furthermore, improving the separation efficiency in the evaporation step will reduce the amount of material that has to be looped back to the cooling crystallization.

CLAIMS

1. A process for separately recovering sodium hydroxide (NaOH) and a sodium coagulation salt, respectively, from an aqueous composition (10) comprising a dissolved sodium coagulation salt, having been used in an aqueous coagulation bath liquid (60) for alkaline fiber or film spinning, and dissolved sodium hydroxide (NaOH), having been used in dissolving cellulose (40) to provide a cellulose spin dope (41) for fiber or film spinning in an aqueous coagulation bath liquid (60) for alkaline fiber or film spinning, the aqueous coagulation bath liquid (60) comprising a dissolved sodium coagulation salt, the aqueous composition (10) having a pH of more than 7, wherein the process comprises the steps of:

- cooling the aqueous composition (10) to precipitate a first portion of the sodium coagulation salt (30), to provide a sodium coagulation salt reduced aqueous composition (11) comprising dissolved sodium hydroxide (NaOH);
- separating the precipitated, first portion of the sodium coagulation salt (30) from the sodium coagulation salt reduced aqueous composition (11) to provide recovered sodium coagulation salt (30) for subsequent use as make up in an aqueous coagulation bath liquid (60) comprising a sodium coagulation salt, wherein the aqueous coagulation bath liquid is for use in alkaline fiber or film spinning;
- evaporating water from the sodium coagulation salt reduced aqueous composition (11), thereby increasing the concentration of sodium hydroxide (NaOH) and remaining sodium coagulation salt to form a concentrated aqueous composition (12);
- precipitating and separating a second portion of the sodium coagulation salt (31) from the concentrated aqueous composition (12), thereby providing a recovered aqueous sodium hydroxide solution (20) comprising dissolved sodium hydroxide (NaOH) for use in dissolving cellulose (40) to provide a cellulose spin dope (41) for fiber or film spinning.

2. The process according to claim 1, wherein the removed second portion of sodium coagulation salt (31) comprises sodium hydroxide (NaOH), said second portion of the sodium coagulation salt (31) being recirculated to be treated, together with the aqueous composition (10), in said step of cooling the aqueous composition (10) to precipitate a first portion of the sodium coagulation salt (30).

3. The process according to claim 1 or 2, wherein the aqueous composition (10) comprises spent aqueous washing liquid (51) resulting from washing a fiber, or a film, (42) spun from a cellulose spin dope (41), comprising dissolved cellulose (40), sodium hydroxide (NaOH), and optionally zinc oxide (ZnO), in an aqueous coagulation bath liquid (60) comprising a sodium coagulation salt.

4. The process according to any one of claims 1 to 3, wherein the aqueous composition (10) comprises an aqueous coagulation bath liquid (60), comprising a sodium coagulation salt, used in alkaline fiber or film spinning of a cellulose spin dope (41) comprising dissolved cellulose, sodium hydroxide (NaOH), and optionally zinc oxide (ZnO).

5. The process according to any one of claims 1 to 4, wherein the temperature of the aqueous composition (10), in said step of cooling it to precipitate the first portion of the sodium coagulation salt (30), remains above the freezing point of the aqueous composition (10), whereby essentially no water is frozen to ice; preferably the separated, precipitated first portion of the sodium coagulation salt (30) comprises less than 1.5 wt.%, such as less than 1.0 wt.% sodium hydroxide (NaOH).

6. The process according to any one of claims 1 or 5, wherein the aqueous composition (10) to recover sodium hydroxide (NaOH) and the sodium coagulation salt, respectively, from comprises:

- 2 to 10 wt.% sodium hydroxide (NaOH), such as 3 to 6 wt.% sodium hydroxide (NaOH);
- 8 to 22 wt.% sodium coagulation salt, e.g. sodium carbonate (Na_2CO_3) and/or sodium sulfate (Na_2SO_4), such as 9 to 15 wt.% sodium coagulation salt, e.g. sodium carbonate (Na_2CO_3) and/or sodium sulfate (Na_2SO_4); and
- optionally zinc oxide (ZnO), the zinc oxide (ZnO) being recovered with the sodium hydroxide (NaOH).

7. The process according to any one of claims 1 to 6, wherein the precipitated, first portion of sodium coagulation salt (30) is separated from the sodium coagulation salt reduced aqueous composition (11) by means of separation technique selected from the group consisting of centrifugation, decantation, and filtration, such as by a filter press or a filter belt, or combinations thereof.

8. The process according to any one of claims 1 to 7, wherein the sodium coagulation salt reduced aqueous composition (11) is heated in the step of evaporating water, optionally sub-atmospheric pressure being applied in the step of evaporating water; and/or wherein said step of evaporating water is continued until the concentration of sodium hydroxide (NaOH) in the concentrated aqueous composition (12) is at least 25 wt.%, such as at least 26 wt.%, 27 wt.%, 28 wt.%, 29 wt.%, or 30 wt.%; preferably at least 28 wt.%, 29 wt.%, or 30 wt.%; more preferably at least 30 wt.%.

9. The process according to any one of claims 1 to 8, wherein the step of precipitating a second portion of sodium coagulation salt (31) from the concentrated aqueous composition (12) comprises lowering the temperature of the concentrated aqueous composition (12); and/or wherein the mass ratio of sodium coagulation salt:sodium hydroxide (NaOH) in the recovered aqueous sodium hydroxide solution (20) is 0.05:1 or less, such as 0.04:1 or less, or 0.03:1 or less.

10. The process according to any one of claims 1 to 9, wherein the separated second portion of sodium coagulation salt (31) comprises sodium hydroxide (NaOH), the separated second portion of sodium coagulation salt (31) comprising sodium hydroxide (NaOH) being added to an aqueous composition (10) comprising dissolved sodium hydroxide (NaOH), having been used in dissolving cellulose to provide a cellulose spin dope for fiber or film spinning in an aqueous coagulation bath liquid (60) for alkaline fiber or film spinning, and dissolved sodium coagulation salt, having been used in an aqueous coagulation bath liquid for alkaline fiber or film spinning, wherein sodium hydroxide (NaOH) and sodium coagulation salt, respectively, subsequently is recovered, in accordance with any one of claims 1 to 9, from the aqueous composition (10) to which the separated second portion of sodium coagulation salt (31) comprising sodium hydroxide (NaOH) has been added.

11. The process according to any one of claims 1 to 10, wherein the sodium coagulation salt is sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4) or a combination thereof.

12. The process according to claim 11, wherein the sodium coagulation salt is sodium carbonate (Na_2CO_3), and wherein the first portion of sodium coagulation salt is

precipitated as sodium carbonate decahydrate ($Na_2CO_3 \times 10 \cdot H_2O$); optionally the process further comprising the step of drying the precipitated sodium carbonate decahydrate ($Na_2CO_3 \times 10 \cdot H_2O$) in order to reduce its water content.

13. A process for forming cellulose fibers or film (43) from dissolved cellulose (40), said process comprising the steps of:

- dissolving cellulose (40) in an aqueous sodium hydroxide (NaOH) solution to provide a cellulose spin dope (41);
- extruding the cellulose spin dope (41) into an aqueous coagulation bath liquid (60) comprising a dissolved sodium coagulation salt and having a pH of more than 7, the aqueous coagulation bath liquid (60) being present in a coagulation vessel, to provide cellulose fibers or film (42);
- withdrawing the cellulose fibers or film (42) from the coagulation vessel;
- washing the withdrawn cellulose fibers or film (42) with an aqueous washing liquid (50) to extract sodium hydroxide (NaOH) and sodium coagulation salt therefrom;
- separately recovering an aqueous sodium hydroxide (NaOH) solution (20) and the sodium coagulation salt, respectively, from spent aqueous washing liquid (51) resulting from the step of washing the fibers, or the film, (42) and/or from the aqueous coagulation bath liquid (60) used in the step of extruding the cellulose spin dope (41) into an aqueous coagulation bath liquid (60), in accordance with any of claims 1 to 12;
- using the recovered aqueous sodium hydroxide (NaOH) solution (20) in the step of dissolving cellulose (40); and
- using recovered sodium coagulation salt as make up in the aqueous coagulation bath liquid (60).

14. The process according to claim 13, wherein:

- the cellulose spin dope (41) comprises 4 to 12 wt.%, preferably 5 to 8 wt.% cellulose; and/or
- the cellulose (40) in the cellulose spin dope (41) has a DP of 140 to 600, such as 180 to 600, 200 to 400, 160 to 400, or 180 to 300; and/or
- the cellulose (40) in the cellulose spin dope (41) has an intrinsic viscosity according to ISO5351:2010(E) of 115 to 450, such as 150 to 450ml/g, 190 to 300ml/g, 130 to 300 ml/g, or 140 to 230 ml/g; and/or
- the cellulose spin dope (41) has a viscosity at $1s^{-1}$ of 1 to 500 Pas, preferably 5 to 100 Pas; and/or

- the cellulose (40) in the cellulose spin dope (41) has a degree of substitution DS of not more than 0.1, preferably not more than 0.05; and/or;

- the cellulose spin dope (41) comprises 5 to 10 wt.% NaOH, preferably 6.5 to 8.5 wt.% NaOH.

15. The process according to any one of claims 13 or 14, wherein the aqueous sodium hydroxide (NaOH) solution used in said step of dissolving the cellulose (40) comprises:

- 6 to 18 wt.% NaOH, such as 7.5 to 12 wt.% NaOH; and

- less than 1.0 wt.% sodium coagulation salt, such as less than 0.5 wt.% sodium coagulation salt, preferably even less than 0.3 wt.%; and

- optionally up to 2.7 wt.% zinc oxide (ZnO).

16. The process according to any one of claims 13 to 15, wherein:

- the aqueous coagulation bath liquid (60) comprises 14 to 32 wt.% sodium coagulation salt, preferably 16 to 24 wt.% sodium coagulation salt; and/or

- the temperature of the cellulose spin dope (41) upon extruding it into the aqueous coagulation bath liquid (60) is 5°C to 30°C; and/or

- the temperature of the aqueous coagulation bath liquid (60) is 20°C to 50°C, preferably 20°C to 30°C; and/or

- the sodium coagulation salt is sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), or a combination thereof.

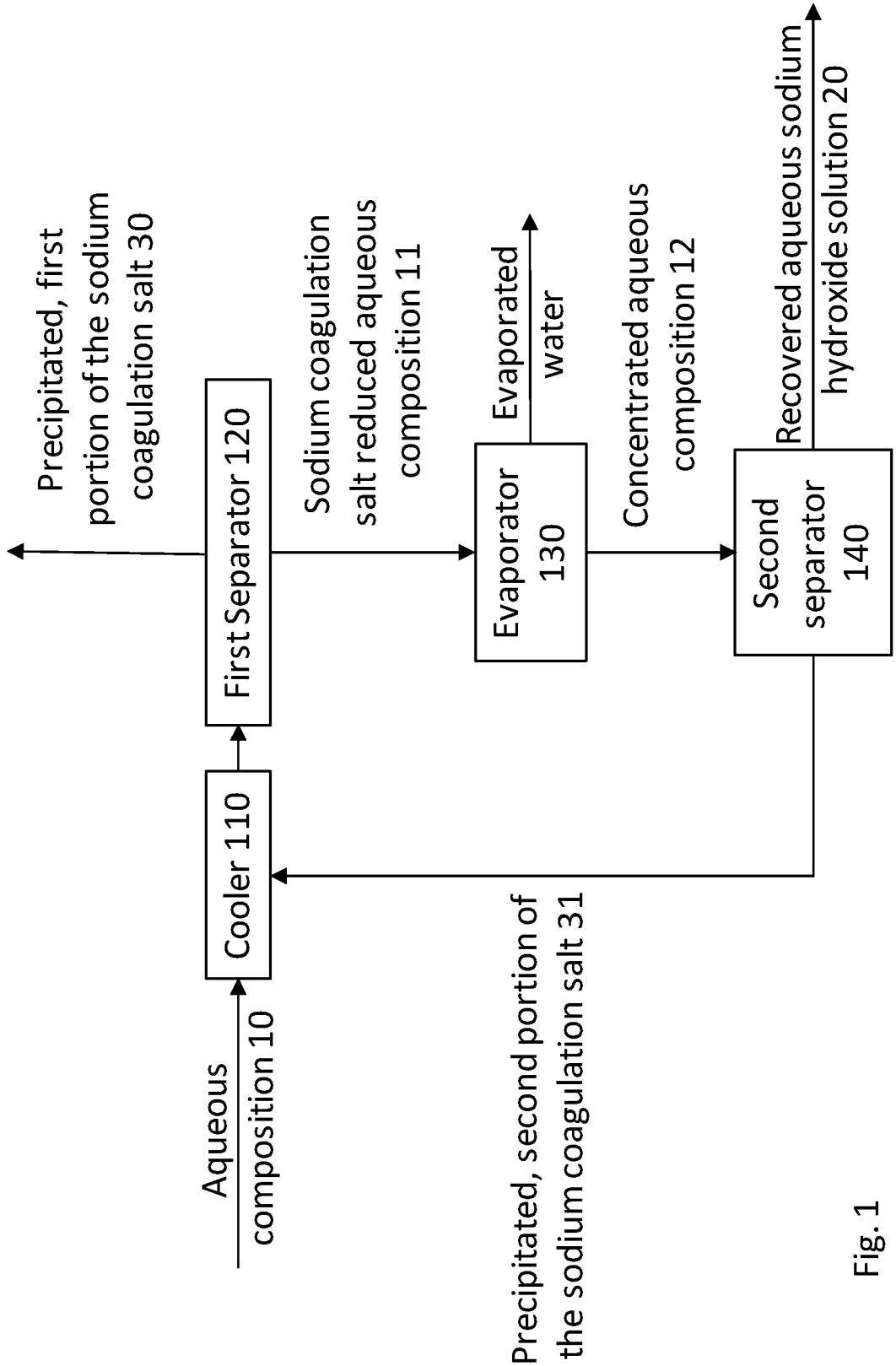
Aqueous composition 10
Cooler 110
First Separator 120
Precipitated, first portion of the sodium coagulation salt 30
Sodium coagulation salt reduced aqueous composition 11
Evaporator 130
Evaporated water
Concentrated aqueous composition 12
Second separator 140
Recovered aqueous sodium hydroxide solution 20
Precipitated, second portion of the sodium coagulation salt 31

Fig. 1

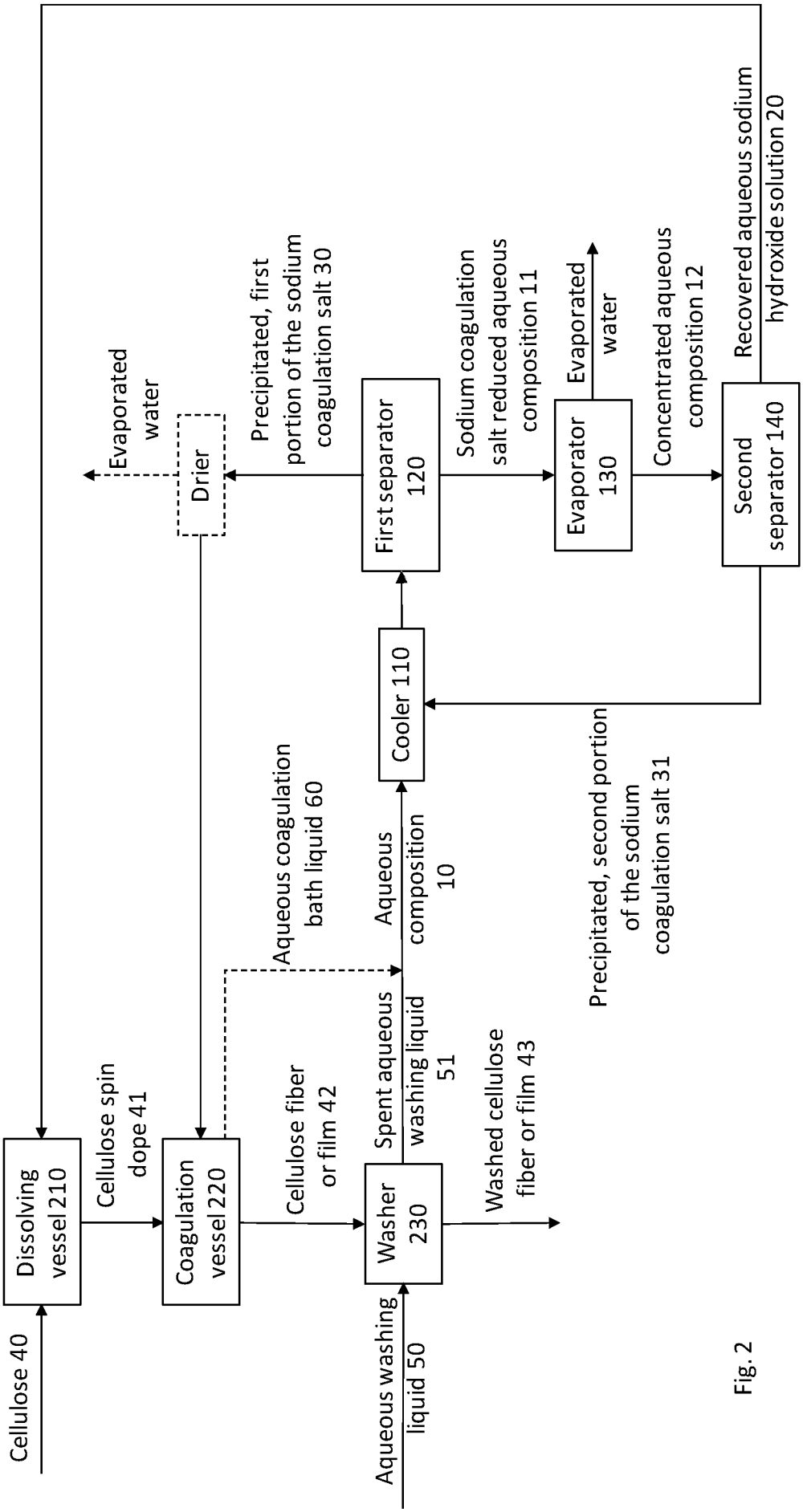
Cellulose 40
Dissolving vessel 210
Cellulose spin dope 41
Coagulation vessel 220
Cellulose fiber or film 42
Washer 230
Aqueous washing liquid 50
Spent aqueous washing liquid 51
Washed cellulose fiber or film 43
Aqueous coagulation bath liquid 60
Aqueous composition 10
Cooler 110
Drier
Evaporated water
Precipitated, first portion of the sodium coagulation salt 30
First separator 120
Sodium coagulation salt reduced aqueous composition 11
Evaporator 130
Evaporated water
Concentrated aqueous composition 12
Second separator 140
Recovered aqueous sodium hydroxide solution 20
Precipitated, second portion of the sodium coagulation salt 31

Fig. 2

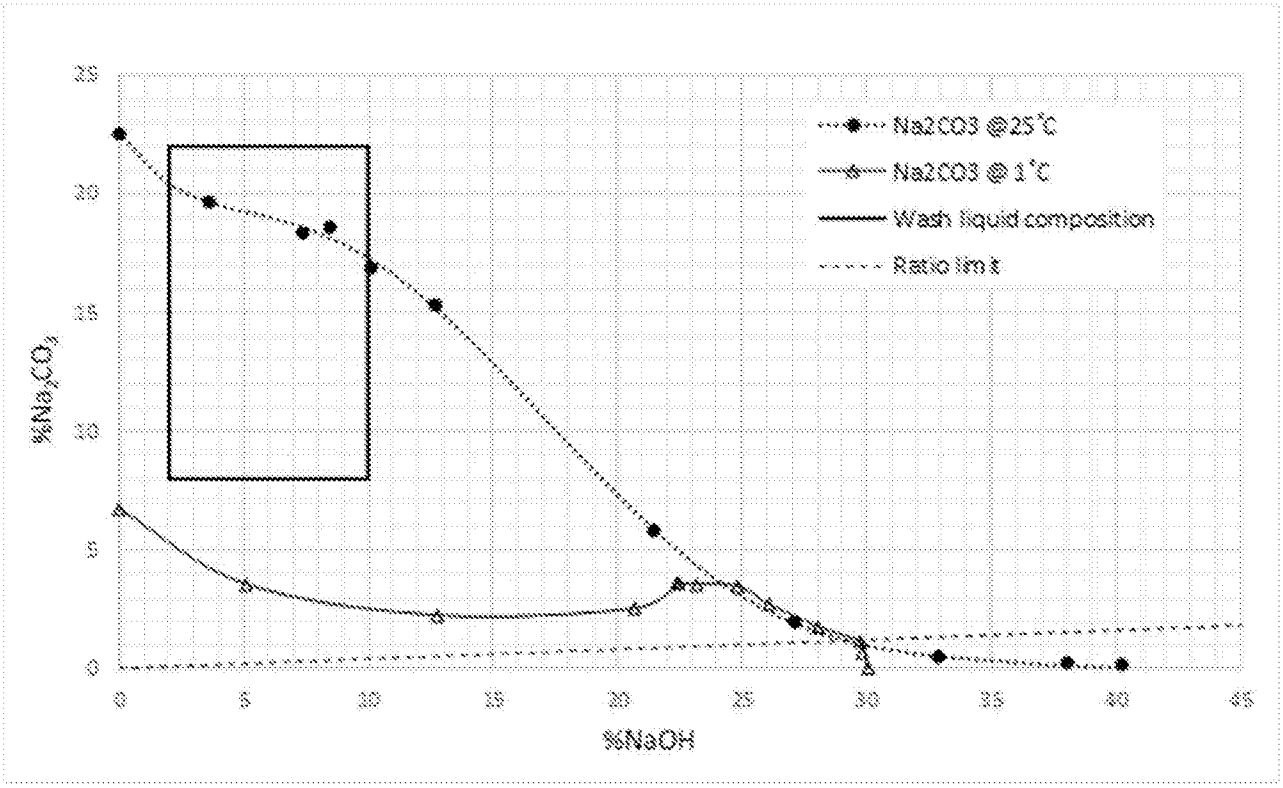
Na2CO3 @25°C
Na2CO3 @ 1°C
Wash liquid composition
Ratio limit
%Na2CO3
%NaOH
0
5
10
15
20
25
30
35
40
45

Fig. 3

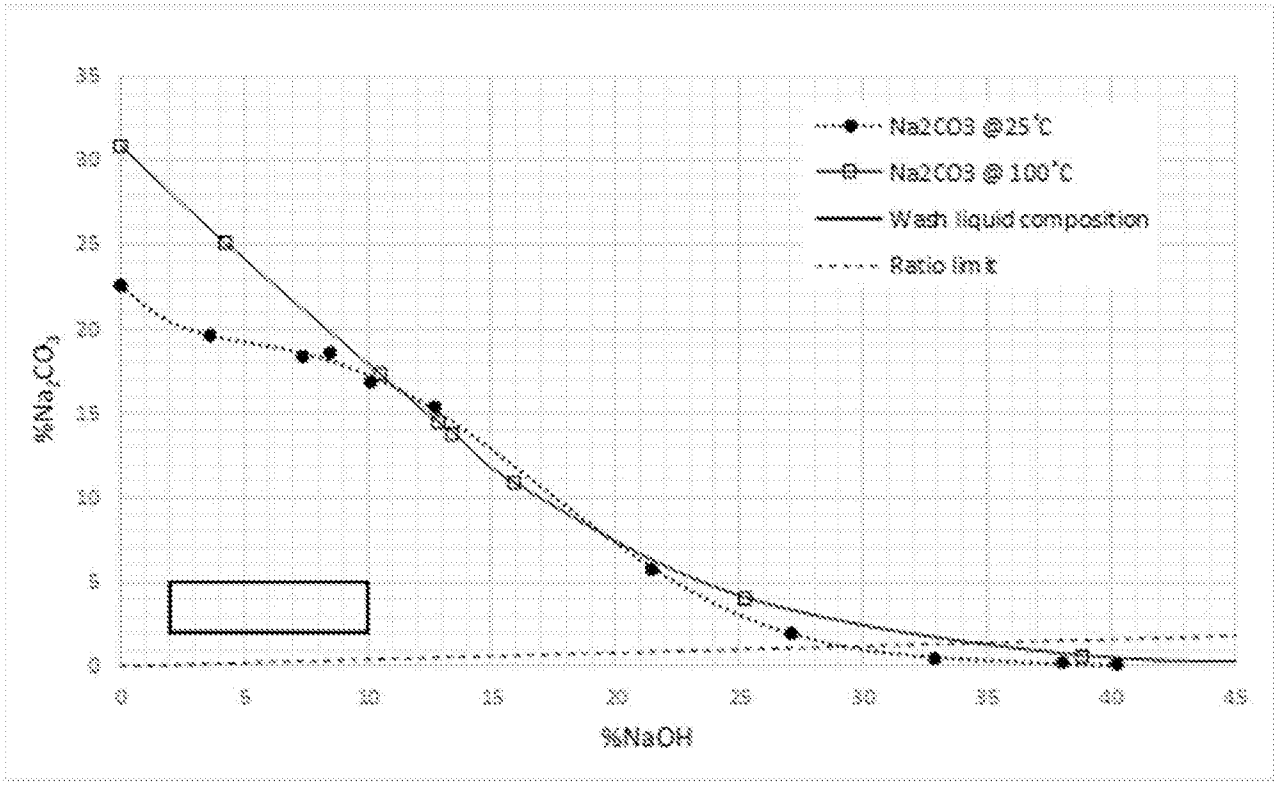
Na2CO3 @25°C
Na2CO3 @ 100°C
Wash liquid composition
Ratio limit
%Na2CO3
%NaOH
0
5
10
15
20
25
30
35
40
45

Fig. 4

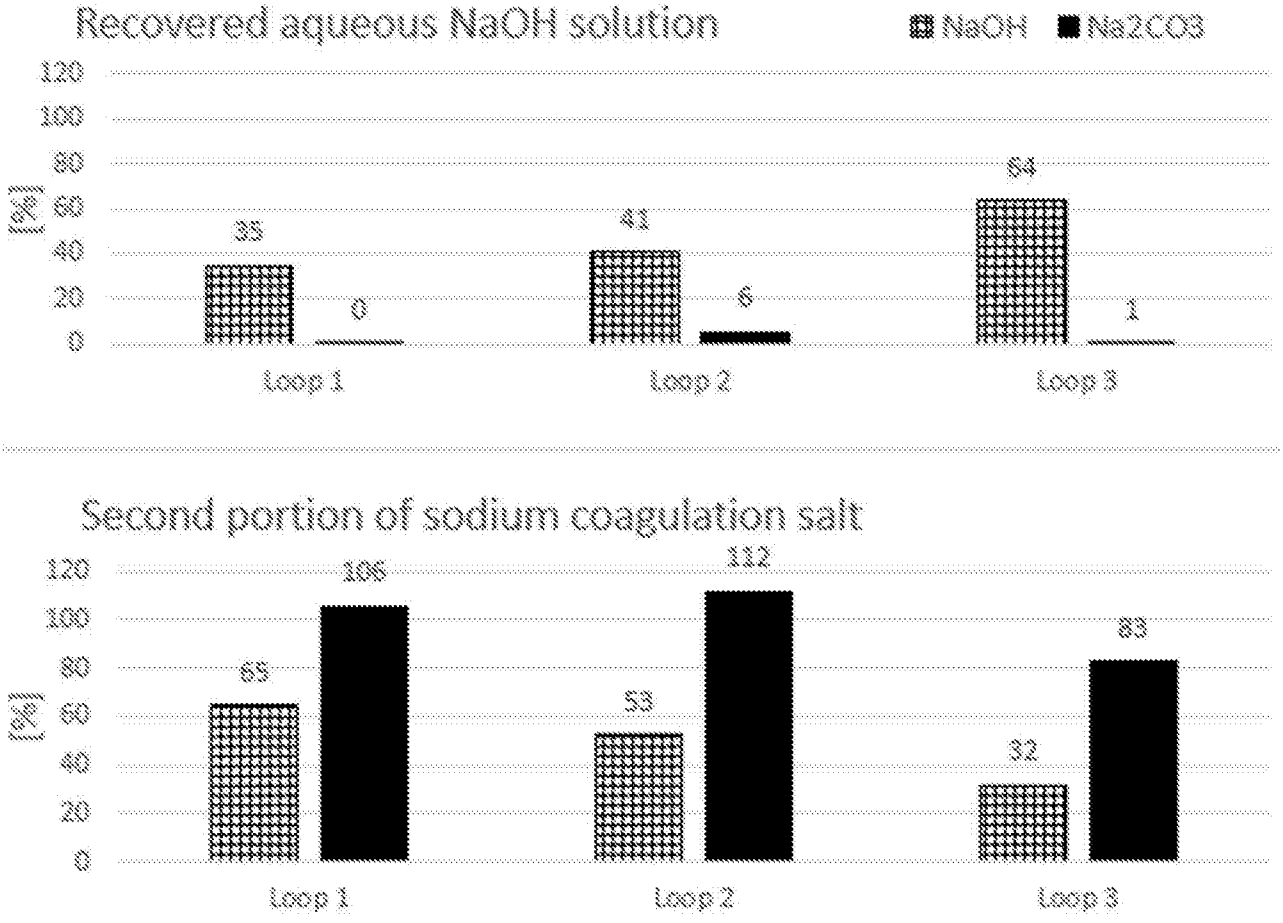
Recovered aqueous NaOH solution
NaOH
Na2CO3
[%]
120
100
80
60
40
20
0
35
0
41
6
84
1
Loop 1
Loop 2
Loop 3
Second portion of sodium coagulation salt
[%]
120
100
80
60
40
20
0
65
106
53
112
32
83
Loop 1
Loop 2
Loop 3

Fig. 5

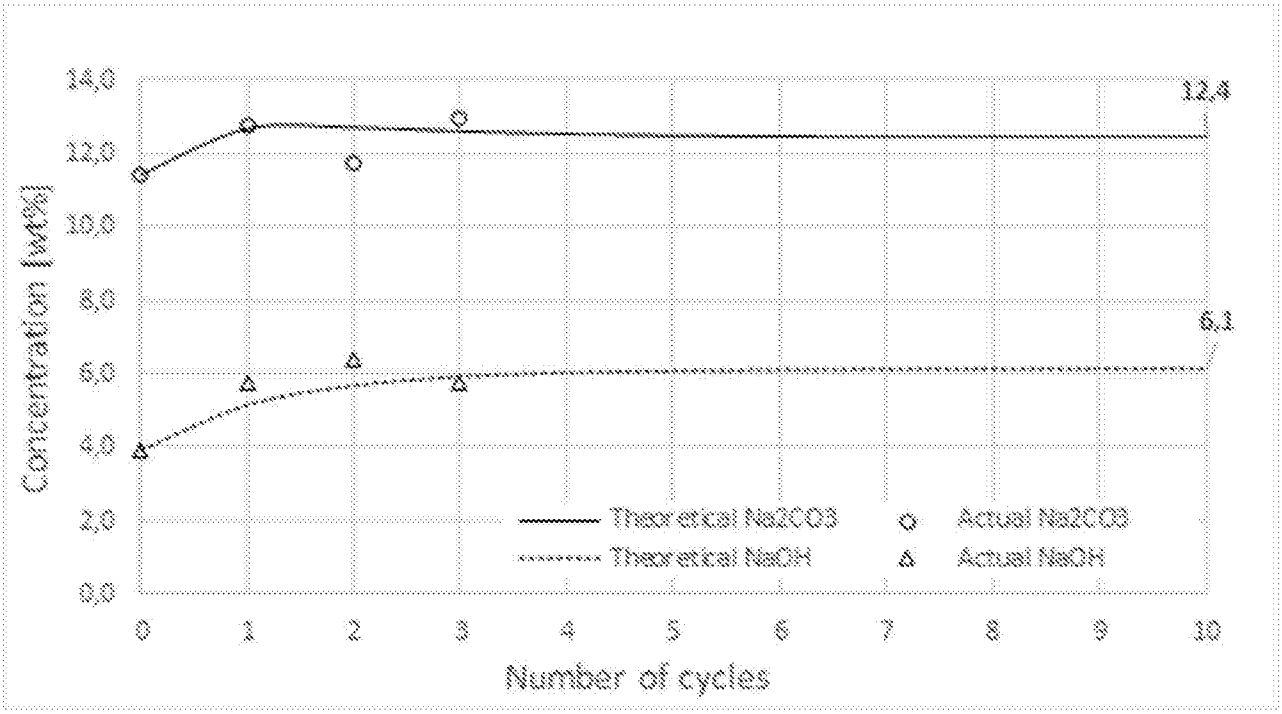
Concentration [wt%]
14,0
12,0
10,0
8,0
6,0
4,0
2,0
0,0
12,4
6,1
Theoretical Na2CO3
Actual Na2CO3
Theoretical NaOH
Actual NaOH
0
1
2
3
4
5
6
7
8
9
10
Number of cycles

Fig. 6

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference		**FOR FURTHER ACTION**
PC-21115591		see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/SE2020/050475	08-05-2020	15-05-2019
Applicant		
TREETOTEXTILE AB		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 6 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of:

☒ the international application in the language in which it was filed.

☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).

c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (See Box No. II).

3. ☐ **Unity of invention is lacking** (See Box No. III).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings**,

a. the figure of the **drawings** to be published with the abstract is Figure No. 2

☒ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

b. ☐ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2020/050475

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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: C08B, C08L, D01D, D01F

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

SE, DK, FI, NO classes as above

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

EPO-Internal, PAJ, WPI data, COMPENDEX, PIRA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2164943 A (NESTE OY), 3 April 1986 (1986-04-03); page 1, line 57 - page 1, line 63; page 2, line 14 - page 2, line 25; page 2, line 32 - page 2, line 39; page 2, line 61 - page 2, line 62; page 3, line 5 - page 3, line 22; figure 1	1-16
Y	--	1-16
D, Y	WO 2015000820 A1 (KIRAM AB), 8 January 2015 (2015-01-08); abstract; figure 1	1-16
	--	
D, Y	WO 2017178532 A1 (TREETOTEXTILE AB), 19 October 2017 (2017-10-19); abstract; figure 1	1-16
	--	

☒ 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

"D" document cited by the applicant in the international application

"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	Date of mailing of the international search report
29-06-2020	29-06-2020

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2020/050475

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2164942 A (NESTE OY), 3 April 1986 (1986-04-03); whole document -- --------	1-16

International application No.
PCT/SE2020/050475

Continuation of: second sheet

International Patent Classification (IPC)

D01F 13/02 (2006.01)
C08B 16/00 (2006.01)
D01F 2/02 (2006.01)
D01D 5/06 (2006.01)

GB	2164943	A	03/04/1986	AT	389327	B	27/11/1989
				AT	A280785	A	15/04/1989
				BR	8504752	A	22/07/1986
				CA	1236095	A	03/05/1988
				CS	673185	A2	13/12/1990
				DD	238982	A5	10/09/1986
				DE	3534357	C2	01/12/1988
				FI	69853	C	26/05/1986
				FI	843814	A0	27/09/1984
				FR	2570707	A1	28/03/1986
				IN	164447	B	18/03/1989
				IT	1201468	B	02/02/1989
				JP	0455622	B2	03/09/1992
				JP	6185452	A	01/05/1986
				NO	163229	C	25/04/1990
				NO	853794	L	01/04/1986
				RO	92931	A	30/11/1987
				SE	8504457	L	28/03/1986
				SE	461099	B	08/01/1990
				US	4639515	A	27/01/1987
				ZA	8507170	B	28/05/1986
WO	2015000820	A1	08/01/2015	CA	2915765	A1	08/01/2015
				CN	105517955	A	20/04/2016
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				EP	3521248	A1	07/08/2019
				US	10138578	B2	27/11/2018
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				EP	3231901	A1	18/10/2017
				US	20190062950	A1	28/02/2019

GB	2164942 A	03/04/1986	AT	389328	B	27/11/1989
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			US	4639514	A	27/01/1987
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