



(51) International Patent Classification:

C10G 1/04 (2006.01) *C02F 1/56* (2006.01)

(21) International Application Number:

PCT/FI2017/050866

(22) International Filing Date:

07 December 2017 (07.12.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/431,630 08 December 2016 (08.12.2016) US
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FI-20521 Turku (FI).(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, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(54) Title: METHOD AND COMPOSITION FOR TREATING TAILINGS

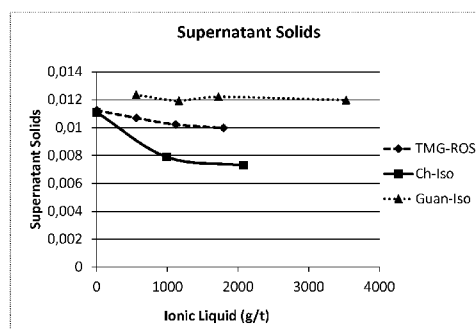


Figure 1 (a)

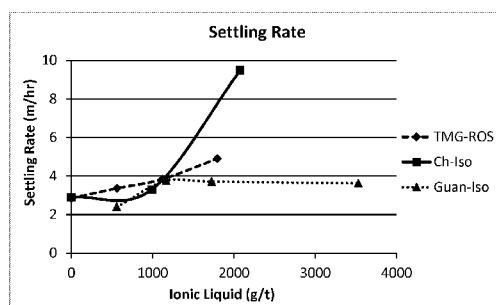


Figure 1 (b)

(57) **Abstract:** The invention relates to method and composition for treating tailings from a separation process, where bitumen is separated from mineral solids. Tailings comprise an aqueous phase with suspended solid particulate material and residual bitumen and have a dry solids content < 25 weight-%. The method comprises addition of a flocculating agent comprising polyacrylamide to the tailings, as well as addition of an auxiliary agent comprising ionic liquid to tailings in conjunction with the flocculating agent. Flocs, which comprise solid particulate material, are formed and the formed flocs are separated from the aqueous phase. The composition comprises a copolymer of (meth)acrylamide and an auxiliary agent comprising ionic liquid.



(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).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

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

METHOD AND COMPOSITION FOR TREATING TAILINGS

The present invention relates to a method and composition for treating tailings according to preambles of enclosed independent claims.

5

Oil sands, which are also known as tar sands, are mixtures of clay, sand, water, and heavy hydrocarbons, such as bitumen. They provide a potential source of hydrocarbons for petrochemical industry. However, the known processes for separating and recovering hydrocarbons from oil sands are expensive,
10 complicated and produce significant environmental damage. The conventional bitumen extraction methods use hot water and caustic soda to separate bitumen from sand and clay in a froth-flotation process. Tailings from the flotation process comprise water, particulate solids, such as clay, residual bitumen and natural surfactants. The result is an aqueous caustic mud-like mixture, which may still
15 contain a significant concentration of toxic hydrocarbons and trace elements, such as arsenic. These hazardous oil sand tailings cannot be piled, especially when the solids content of the tailings is low. In general tailings are difficult to transport, treat or store in a safe and environmentally sustainable manner. Similar problems may also be related to tailings originating from the recovery of oil from oil shale.

20

Polymeric flocculants have been used for chemical treatment of difficult tailings, such as oil sand tailings, in order to dewater the tailings. Even if good results may be obtained by using polymeric flocculants, especially ultrafine solid particles having particle size less than 2 μm are difficult to separate and remain suspended
25 in the water phase. The water phase which contains ultrafine solid particles cannot be recirculated back to previous process stages, because the ultrafine solid particles may start to accumulate in the water phase and disturb the bitumen extraction. Inorganic coagulants, such as gypsum or aluminium sulphate, have been used for improving separation of ultrafine solid particles. However there
30 exists a need for an improved method to treat difficult tailings, as the reduced possibilities for water recycling make the process water intensive and environmentally unfriendly.

An object of this invention is to minimise or even totally eliminate the disadvantages existing in the prior art.

Another object of the present invention is to provide an inexpensive, simple
5 method for treating tailings, especially oil sand tailings, and for separating liquid aqueous phase from solid particulate material.

A further object of the present invention is to provide a method and composition which would be effective and environmentally feasible.
10

A yet further object of the present invention is to provide a method, which is easy to scale up into industrial scale.

The invention is defined in the characterising parts of the enclosed independent
15 claims. Some preferable embodiments of the invention are defined in the dependent claims. All described features apply both for the use as well as the method and composition of the invention, whenever applicable, even if it not necessarily stated so.

20 In typical method according to the present invention for treating tailings from a separation process, where bitumen is separated from mineral solids, the tailings comprising an aqueous phase with suspended solid particulate material and residual bitumen, the tailings having a dry solids content < 25 weight-%, the method comprises

- 25
- adding a flocculating agent comprising polyacrylamide to the tailings,
 - adding an auxiliary agent comprising ionic liquid to tailings in conjunction with the flocculating agent,
 - allowing flocs, which comprise solid particulate material, to form, and
 - allowing the formed flocs to separate from aqueous phase.

30

Typical composition according to the invention for treating tailings comprises a copolymer of (meth)acrylamide and an auxiliary agent comprising ionic liquid.

Typical use of ionic liquid according to the present invention is for treating oil sand tailings together with flocculating agent comprising polyacrylamide.

Now it has been surprisingly found out that use of an auxiliary agent comprising ionic liquid together with polyacrylamide flocculating agent effectively removes solid particulate material from the aqueous phase as well as improves the separation of the formed flocs. When using auxiliary agent, which comprises ionic liquid, it is possible to reduce the amount of used polymer while obtaining the same treatment results.

10

The auxiliary agent comprises ionic liquid and optionally a solvent, for example an organic solvent, such as kerosene or the like.

According to another embodiment the auxiliary agent is free of organic solvents.

15

The term "ionic liquid" is in the present context understood to be an ionic salt-like material, which is liquid at temperature of $< 100\text{ }^{\circ}\text{C}$ at atmospheric pressure of 101.3 kPa. Ionic liquids include two components, namely a cation component and an anion component. The ionic liquids which are especially suitable for use in the present invention have a negligible vapour pressure at room temperature, typically about 10^{-10} Pa , but they can be converted into form, which has vapour pressure $> 0.01\text{ Pa}$, preferably $> 0.1\text{ Pa}$, at $130\text{ }^{\circ}\text{C}$. The ionic liquids are soluble in water and insoluble in non-polar organic solvents. According to one embodiment the auxiliary agent consists of ionic liquid.

25

Ionic liquids are non-flammable and thermally stable, which makes the auxiliary agent safe to handle and transport and minimizes the occupational hazards during its use.

30 The ionic liquid used in the auxiliary agent is also preferably biodegradable. In this context compounds and compositions are referred biodegradable if they reach a biodegradation level higher than 60 %, evaluation being based on the so-called

BOD5 (Biochemical oxygen demand after 5 days) or "Closed Bottle Test" (OECD 301D).

The auxiliary agent comprises preferably at least one ionic liquid prepared from an unsubstituted or substituted primary, secondary or tertiary amine, such as tributylamine; or from an unsubstituted or substituted pyridine, amidine or guanidine, preferably together with a fatty acid or rosin acid. According to one preferable embodiment of the present invention the ionic liquid is prepared from substituted tertiary amine which is choline or from substituted guanidine, which is tetramethylguanidine (TMG). According to one embodiment the substituted guanidine is 1,1,2,3,3-pentamethylguanidine (PMG) or 2-butyl-1,1,3,3-tetramethylguanidine (BTMG).

The auxiliary agent may comprise also at least one fatty and/or resin acid. According to one embodiment of the invention the auxiliary agent comprises a mixture of fatty acids and/or resin acids. Suitable fatty acids may be saturated or unsaturated, and they can be branched or linear. Examples of suitable fatty acids are stearic acid, hexanoic acid and isostearic acid. According to one preferable embodiment of the invention the fatty acid is selected from stearic acid or isostearic acid. By proper selection of fatty and/or resin acids the properties of the auxiliary agent may be tailored to provide optimal interaction with the flocculating agent, which comprises polyacrylamide. According to one preferable embodiment of the invention the resin acid is rosin acid.

According to one preferable embodiment the auxiliary agent comprises ionic liquid, which is selected from choline isostearate or tetramethylguanidine rosinate.

The flocculating agent may be added in such amount that the concentration of polyacrylamide in the tailings is 70 – 90, preferably 80 – 160, more preferably 90 – 120, given as g polymer/ton tailings.

In the present context "polyacrylamide" denotes a copolymer of methacrylamide or acrylamide and cationic, anionic and/or non-ionic monomers, preferably a

copolymer of methacrylamide or acrylamide and cationic or anionic monomers, more preferably a copolymer of acrylamide and cationic or anionic monomers.

According to one embodiment of the invention the flocculating agent comprises a cationic polyacrylamide. Cationic polyacrylamide is a copolymer of (meth)acrylamide and at least one cationic monomer, preferably a copolymer of acrylamide and at least one cationic monomer. The cationic monomer may be selected from 2-(dimethylamino)ethyl acrylate (ADAM), [2-(acryloyloxy)ethyl] trimethylammonium chloride (ADAM-Cl), 2-dimethylaminoethyl methacrylate (MADAM), [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MADAM-Cl), [3-(acryloylamino)propyl] trimethylammonium chloride (APTAC), [3-(methacryloylamino)propyl] trimethylammonium chloride (MAPTAC), or any combinations thereof. According to an embodiment of the invention, the polyacrylamide originates from 15 – 40 mol-%, preferably 20 – 35 mol-% of cationic monomers, calculated from total amount of monomers used in polymerisation.

According to another embodiment of the invention the flocculating agent comprises an anionic polyacrylamide. Anionic polyacrylamide is a copolymer of (meth)acrylamide and at least one anionic monomer. The anionic monomer may be selected from unsaturated mono- or dicarboxylic acids, such as acrylic acid, maleic acid, fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid, crotonic acid, isocrotonic acid, angelic acid or tiglic acid.

In the present method also a flocculating agent comprising polyacrylamide is added to the tailings. The flocculating agent may be added to the tailings simultaneously but separately with the auxiliary agent, which comprises ionic liquid. Alternatively the flocculating agent may be added before or after the auxiliary agent.

30

An auxiliary agent comprising ionic liquid is added to the tailings in conjunction with the flocculating agent. As explained above, this means that the auxiliary agent may be added before or after the addition of the flocculating agent, or it may be

added simultaneously, but separately, with the flocculating agent. According to one preferable embodiment the auxiliary agent is added before the flocculating agent.

- 5 According to one embodiment of the invention the flocculating agent and the auxiliary agent are mixed together to form a composition in liquid form that can be added to the tailings.

10 According to one embodiment the auxiliary agent may be added in such amount that the concentration of ionic liquid in the tailings is 500 – 3000, preferably 1000-2500, more preferably 1200 – 2200, given as g active substance/ton tailings.

The auxiliary agent may also comprise a plurality of, i.e. two or more, different ionic liquids.

15

After addition of the flocculating agent and the auxiliary agent flocs, which comprise solid particulate material, are allowed to form. The synergetic effect produced by the flocculating agent and the auxiliary agent provides effective formation of flocs comprising also fine solid particulate material. Furthermore, the
20 formed flocs settle relatively fast, which makes their separation effective also by using conventional settling arrangements, such as gravity settlers. The aqueous phase, after it is separated from the formed flocs, may comprises less than 2 weight-%, preferably less than 1.5 weight-%, more preferably less than 1 weight-%, of fine solid particulate material having diameter less than 2 μm . Preferably the
25 aqueous phase, after separation of flocs, is free of solid particulate material having diameter $>2 \mu\text{m}$.

The formed flocs may be separated from the aqueous phase by settling, centrifugation, filtration, thin lift dewatering or with any suitable separation
30 technique. According to one preferable embodiment a settled floc phase is obtained, which floc phase has a solids content of at least 30 weight-%, preferably at least 40 weight-%, more preferably at least 45 weight-%. Due to the high solids

content the floc phase is easy to handle, requires less space when stored and is more convenient to pile.

In one embodiment the ionic liquid may be separated from floc phase, if desired,
5 regenerated and recycled back in preceding steps in the treating process.

The separated aqueous phase may be recycled back to the separation process, where bitumen is separated from mineral solids. The invention achieves a clean aqueous phase that can be used in the original separation process from where the
10 tailings originate or it may be used in some other associated process. Alternatively the aqueous phase may be returned to the surroundings, after optional further water treatment steps.

Tailings, which are treated with the present invention, originate from a separation
15 process, where bitumen is separated from mineral solids. Tailings may originate from a separation process involving oil sand, oil shale, oil contaminated sand or oil contaminated earth or sand containing crude oil. Preferable tailings are oil sand tailings. The tailings may have a dry solids content < 25 weight-%, preferably < 20 weight-%, more preferably < 15 weight-%. According to one embodiment the dry
20 solids content of the tailings may be in a range of 5 – 25 weight-%, preferably 7 – 20 weight-%, more preferably 7 – 15 weight-%. Tailings may comprise solid mineral particles, such as clay and/or sand, having particle size < 45 µm, preferably < 30 µm, more preferably < 15 µm, sometimes even < 5 µm.

25 Tailings may comprise also residual bitumen. In the present context the term “bitumen” is understood as a highly viscous mixture of crude oil, comprising hydrocarbons heavier than pentanes, and which mixture has a viscosity above 10 000 cP, and is non-mobile at reservoir conditions. Bitumen may have an API gravity < 12°, preferably < 10°, more preferably < 8°. The API gravity of bitumen
30 may be in the range of 12° – 6°. Bitumen may comprise > 15 weight-%, preferably > 25 weight-%, of asphaltenes. The total amount of asphaltenes and resins in bitumen may be >40 weight-%, preferably >45 weight-%. Tailings may comprise <

5 weight-%, preferably < 2 weight-%, more preferably < 1 weight-%, of bitumen, before addition of the flocculating and/or auxiliary agent.

EXPERIMENTAL

- 5 Some embodiments of the invention are described in the following non-limiting examples.

Following materials were used in experimental studies:

10 Ionic Liquids

Choline Iso sterate (Ch-Iso): active content 51.3 %

Tetramethylguanidine rosin ate (TMG ROS): active content 27.3 %

Guanidinium isostearate (Guan-Iso): active content 10.0 %

15 Polymer Flocculants

Polyacrylamide 1: standard viscosity 3.5 cP, charge 30 %

Polyacrylamide 2: standard viscosity 4.0 cP, charge 30 %

Process samples

- 20 The tailings used for the experiments were thickener feed samples from an industrial process. The tailings contained approximately 11-13% solids and less than 1% bitumen.

- 25 The water used for polymer dilution was industrial gland water, and it was used to prepare polymer solutions at a concentration of 0.4 %. Same water was also used to dilute the polymer solutions to 0.05% directly before their use.

Flocculation Experiment Procedure

- 30 Flocculation experiments were done according to following procedure:
- 1) A bucket of industrial thickener feed tailings was vigorously stirred to homogenize the tailings, and 150 – 170 g aliquots were transferred to 250 ml plastic beakers.

- 2) The tailings aliquots in beakers were stirred with a 4-blade pitched impellers for 60 sec at 400 rpm prior to chemical addition.
- 3) When ionic liquid was used it was added to the tailings aliquot and mixed for an additional 60 sec.
- 5 4) The chosen polymer flocculant, 0.05 % solution in industrial gland water was then added to the tailings aliquot as a single injection.
- 5) The tailings aliquot was stirred for an additional 30 sec at 400 rpm to condition the flocs and then the impeller was stopped.
- 6) The tailings aliquots were transferred to a 250 ml graduated cylinder and the
10 volume height of the settling floc bed was recorded over time.
- 7) After 10 minutes of settling, the final bed height was recorded and the top 60 ml of supernatant was transferred into a separate container.
- 8) The supernatant was stirred to homogenize and then a 25 g sample was taken and measured for solids content by drying the sample in an oven overnight
15 at 110°C.

Comparison of Different Ionic Liquids

In Figures 1(a) and 2(a) the solids content (y-axis) is given in weight-%, and the
20 shown numerical values of the y-axis should be multiplied with 100%. In Figure 3(a)-(d) the y-axis values are given as %-values, and shown numerical values of the y-axis should be multiplied with 100%.

In order to determine the affinity of different ionic liquids to the tailings the results
25 for supernatant solids are shown in Figure 1A and results for settling rate are shown in Figure 1B for three ionic liquids TMG-ROS, Ch-Iso and Guan-Iso. Polymer flocculant used was polymer flocculant 2.

From the figures it can be seen that the addition of Guan-Iso showed very little
30 performance change. There was a slight but noticeable improvement with the addition of TMG-ROS, while Ch-Iso showed significant improvement in both results.

Comparison of Different Dosage Amounts

Ch-Iso was added at dosages of 0 g/t, 1000 g/t, 2000 g/t and 3000 g/t, while the flocculant polymer 1 dosage was between 80 and 190 g/t. The results the supernatant solids are shown in Figure 2A and results for settling rates are shown
5 in Figure 2B at different Ch-Iso dosages. Figures 3A - 3D show settling curves for each flocculant polymer dosage.

It can be observed that at each flocculant polymer dosage the addition of Ch-Iso improved and reduced the supernatant solids content. The settling rate was also
10 improved at all doses other than 84 g/t. The settling curves help to demonstrate that after the ten minute settling period, the increase in settling rate was coupled with an improvement in settling volume, which may result to higher underflow densities in the thickener.

15 As the addition of Ch-Iso improved the thickener results at a given dosage it also means that flocculant polymer dosage could be reduced, while still meeting the desired performance criteria. For example, if a supernatant solids content of 1 % was desired, without addition of Ch-Iso this would occur at an approximate flocculant polymer dosage of 160 g/t. After the addition of 1000 g/t Ch-Iso, 1 %
20 solids content could be achieved at a flocculant polymer dosage of approximately 105 g/t. This means that the reduction in polymer dosage of greater than 30 % is achieved.

Although certain embodiments and examples have been described in detail above,
25 those having ordinary skill in the art will clearly understand that many modifications are possible in the embodiments and examples without departing from the teachings thereof. All such modifications are intended to be encompassed within the below claims of the invention.

CLAIMS

1. Method for treating tailings from a separation process, where bitumen is separated from mineral solids, the tailings comprising an aqueous phase with
5 suspended solid particulate material and residual bitumen, the tailings having a dry solids content < 25 weight-%, the method comprising
- adding a flocculating agent comprising polyacrylamide to the tailings,
 - adding an auxiliary agent comprising ionic liquid to tailings in conjunction with the flocculating agent,
 - 10 - allowing flocs, which comprise solid particulate material, to form, and
 - allowing the formed flocs to separate from the aqueous phase.
2. Method according to claim 1, **characterised** in adding the auxiliary agent in such amount that the concentration of ionic liquid in the tailings is 500 – 3000,
15 preferably 1000- 2500, more preferably 1200 – 2200, given as g active substance/ton tailings.
3. Method according to claim 1 or 2, **characterised** in that ionic liquid is selected from choline isostearate or tetramethylguanidine rosinate.
20
4. Method according to claim 1, 2 or 3, **characterised** in that the flocculating agent comprises a cationic polyacrylamide.
5. Method according to claim 1, 2 or 3, **characterised** in that the flocculating agent
25 comprises an anionic polyacrylamide.
6. Method according to any of preceding claims 1 – 5, **characterised** in adding flocculating agent in such amount that the concentration of polyacrylamide is 70 – 90, preferably 80 – 160, more preferably 90 – 120, given as g/ton tailings.
30
7. Method according to any of preceding claims 1 – 6, **characterised** in that the aqueous phase after separation of formed flocs comprises less than 2 weight-%,

preferably less than 1.5 weight-%, more preferably less than 1 weight-%, of fine solid particulate material having diameter less than 2 μm .

8. Method according to any of preceding claims 1 – 7, **characterised** in obtaining
5 a settled floc phase with solids content of at least 30 weight-%, preferably at least 40 weight-%, more preferably at least 45 weight-%.

9. Method according to any of preceding claims 1 – 8, **characterised** in recycling
the separated aqueous phase to the separation process, where bitumen is
10 separated from mineral solids.

10. Method according to any of preceding claims 1 – 9, **characterised** in that the auxiliary agent is added before the flocculating agent.

15 11. Method according to any of preceding claims 1 – 10, **characterised** in that the formed flocs are separated from the aqueous phase by settling, centrifugation, filtration or thin lift dewatering.

12. Composition for treating tailings comprising a copolymer of (meth)acrylamide
20 and an auxiliary agent comprising ionic liquid.

13. Composition according claim 12, **characterised** in that the auxiliary agent comprises at least one ionic liquid prepared from an unsubstituted or substituted primary, secondary or tertiary amine, such as tributylamine; or from an
25 unsubstituted or substituted pyridine, amidine or guanidine.

14. Composition according claim 12 or 13, **characterised** in that the auxiliary agent further comprises at least one fatty and/or resin acid, such as stearic acid, hexanoic acid and/or isostearic acid.

30

15. Composition according claim 12 – 14, **characterised** in that the ionic liquid is selected from choline isostearate or tetramethylguanidine rosinate.

16. Composition according claim 12 – 15, **characterised** in that the auxiliary agent comprises a plurality of different ionic liquids.

17. Composition according claim 12 – 16, **characterised** in that the copolymer of
5 (meth)acrylamide is a copolymer of (meth)acrylamide and at least one cationic monomer, which is selected from 2-(dimethylamino)ethyl acrylate (ADAM), [2-(acryloyloxy)ethyl] trimethylammonium chloride (ADAM-Cl), 2-dimethylaminoethyl methacrylate (MADAM), [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MADAM-Cl), [3-(acryloylamino)propyl] trimethylammonium chloride (APTAC), [3-
10 (methacryloylamino)propyl] trimethylammonium chloride (MAPTAC), or any combinations thereof.

18. Composition according claim 12 – 16, **characterised** in that the copolymer of (meth)acrylamide is an anionic copolymer of (meth)acrylamide.

15

19. Use of ionic liquid for treating oil sand tailings together with polyacrylamide.

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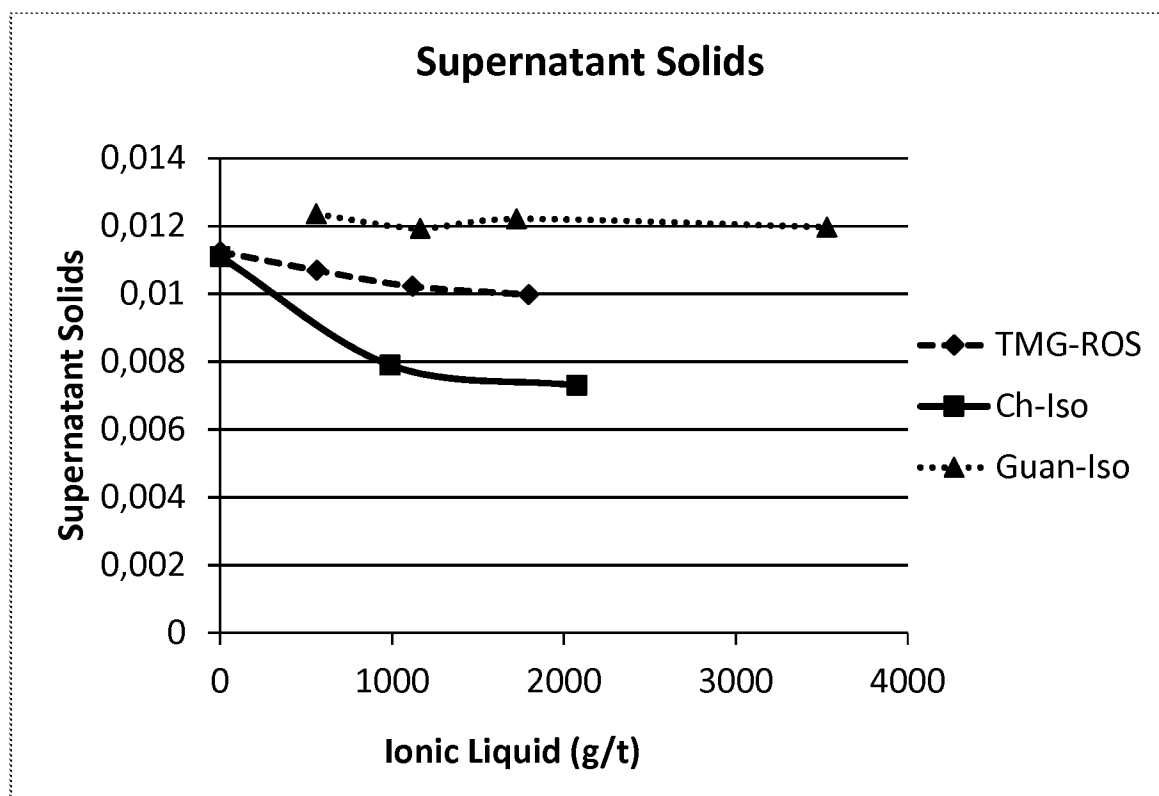


Figure 1 (a)

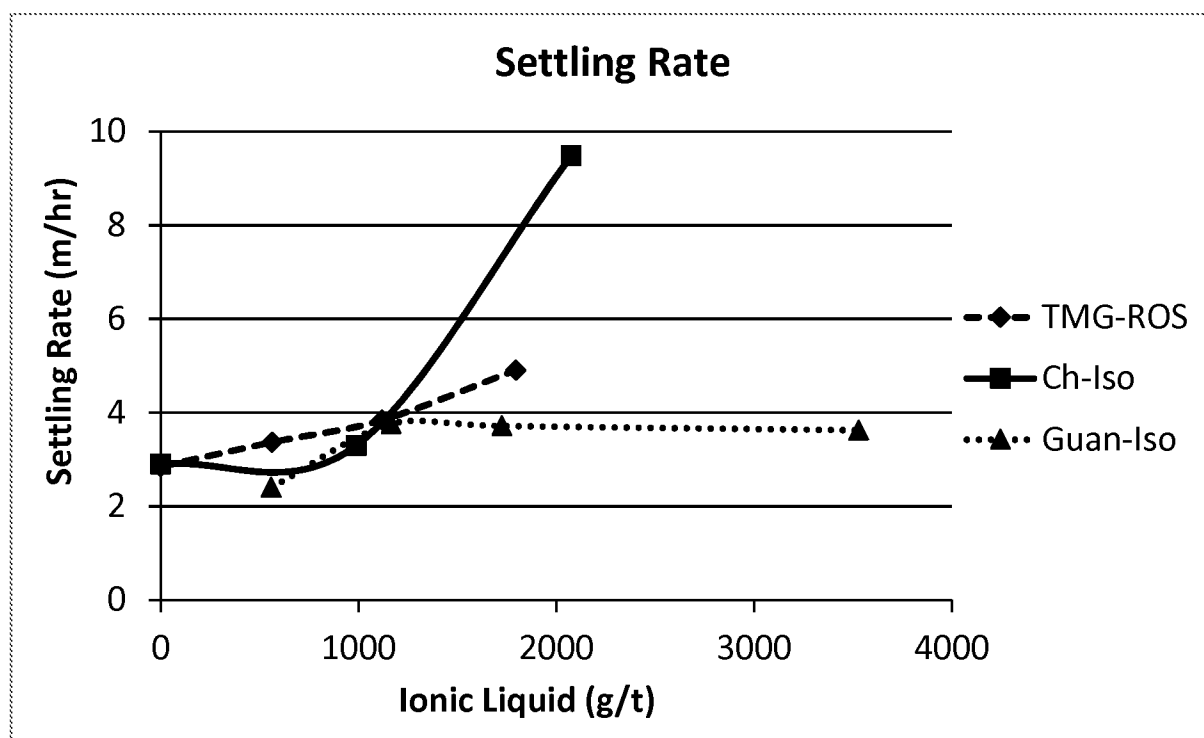


Figure 1 (b)

2/4

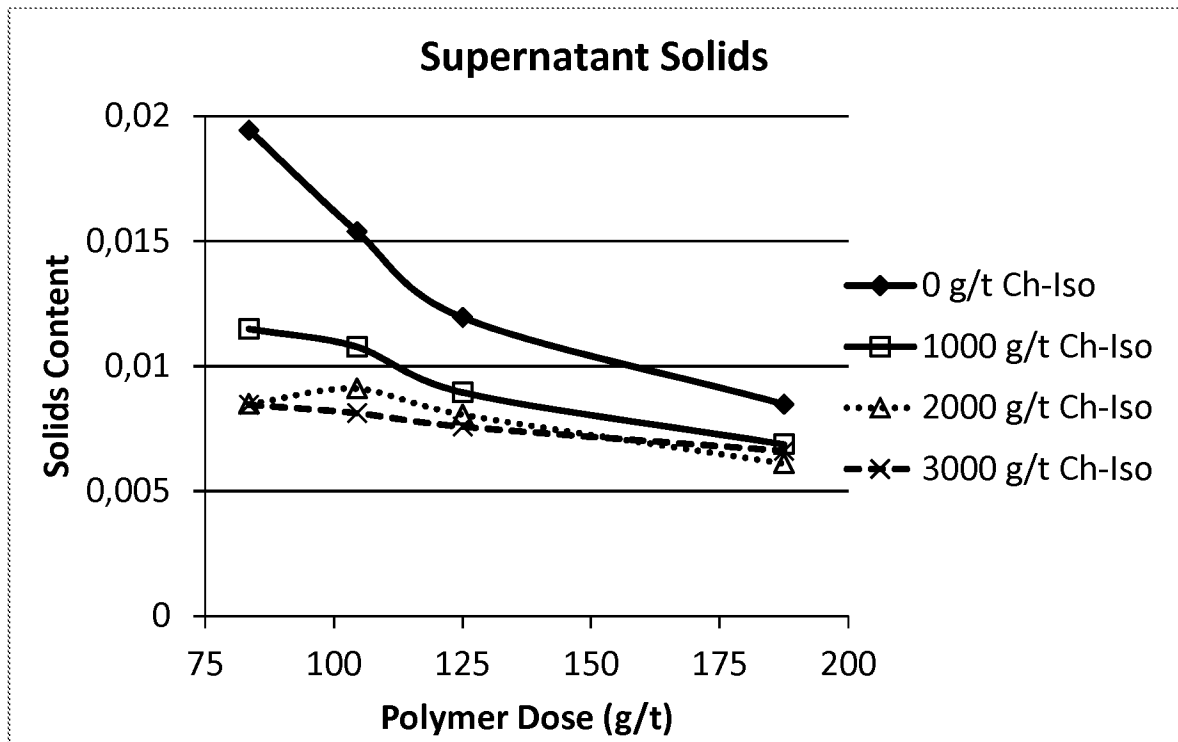


Figure 2 (a)

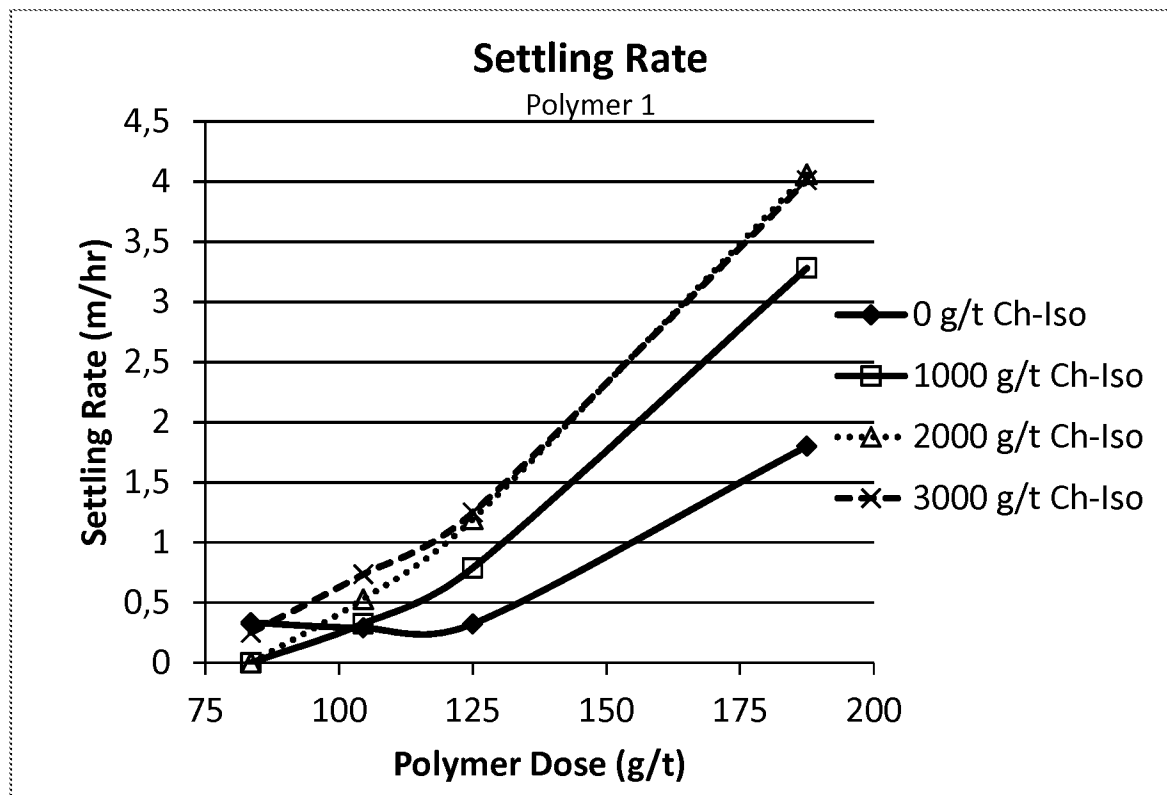


Figure 2 (b)

3/4

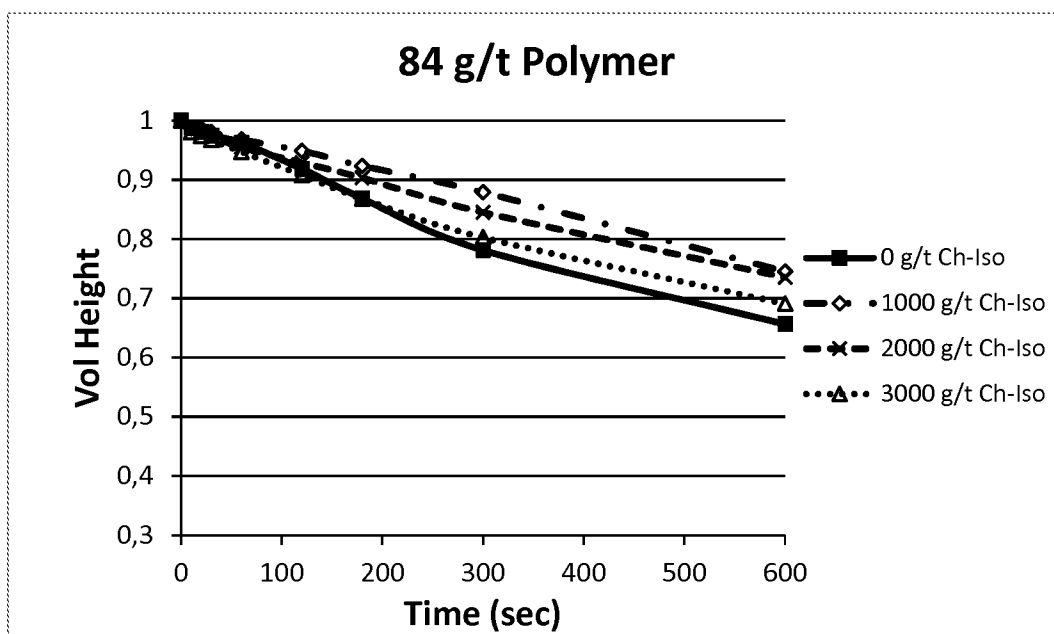


Figure 3 (a)

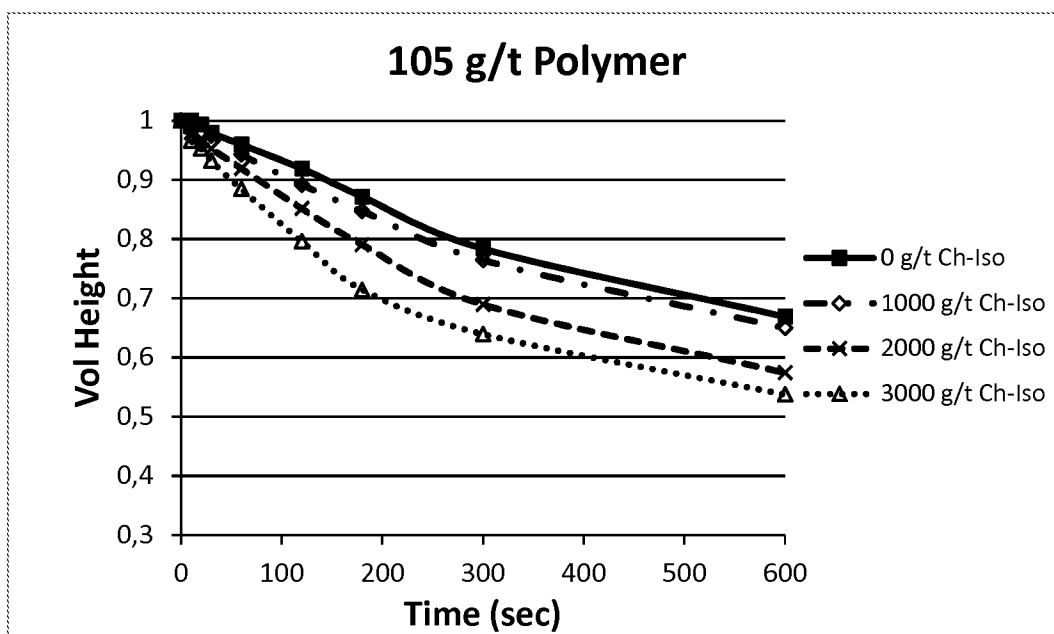


Figure 3 (b)

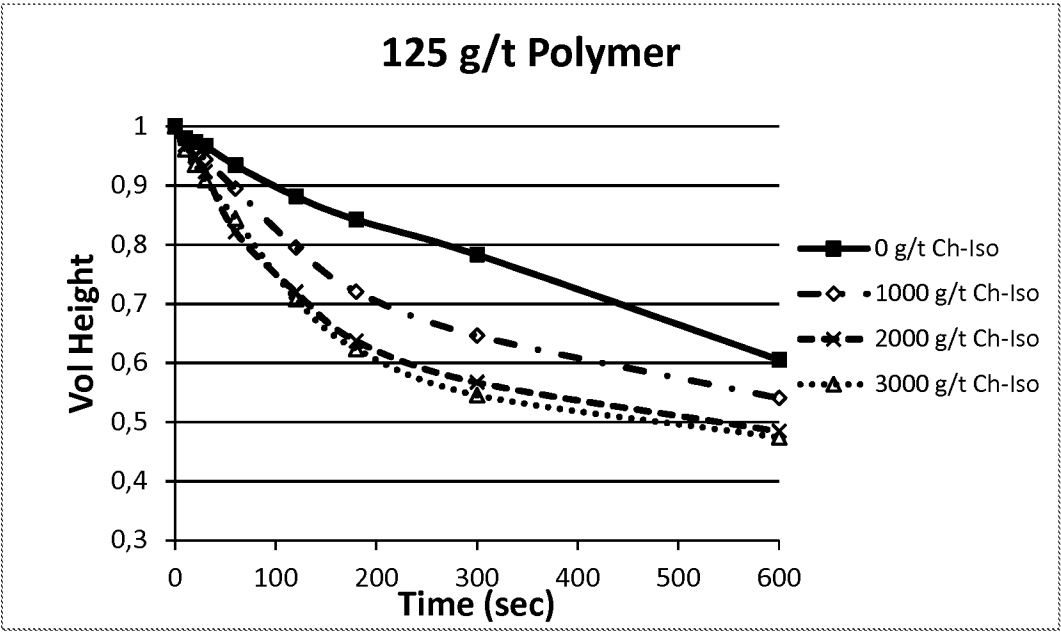


Figure 3 (c)

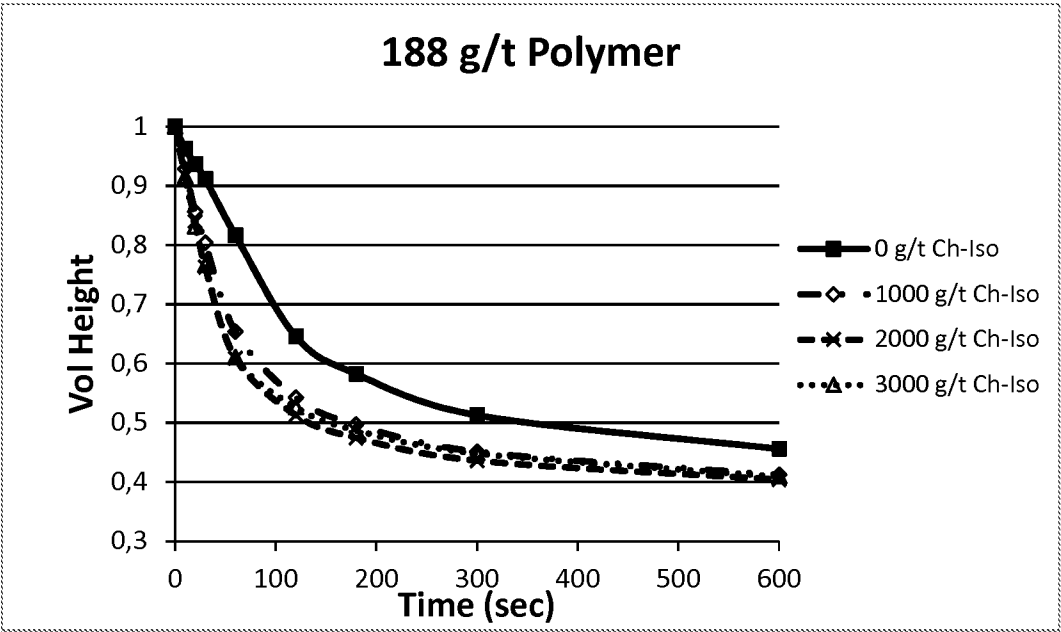


Figure 3 (d)

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2017/050866

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G1/04 C02F1/56
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)
C10G C02F

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 105 176 716 A (ANHUI WANGDONG CHECU AUTOMOBILE CLEANING SERVICE CO LTD) 23 December 2015 (2015-12-23) claim 1	12-18
X	----- US 2011/284428 A1 (ADEYINKA OLUSOLA B [CA] ET AL) 24 November 2011 (2011-11-24) paragraphs [0003], [0098], [0106], [0182], [0183], [0187], [0190]; figure 9	19
A	----- US 2014/054232 A1 (DUTTLINGER JR WILLIAM T [US] ET AL) 27 February 2014 (2014-02-27) paragraphs [0003], [0004], [0005], [0007] ----- -/-	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

1 February 2018

Date of mailing of the international search report

12/02/2018

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

Galleiske, Anke

INTERNATIONAL SEARCH REPORT

International application No

PCT/FI2017/050866

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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