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- (54) Title: A LOW VISCOSITY METAL SILICATE COMPOSITION

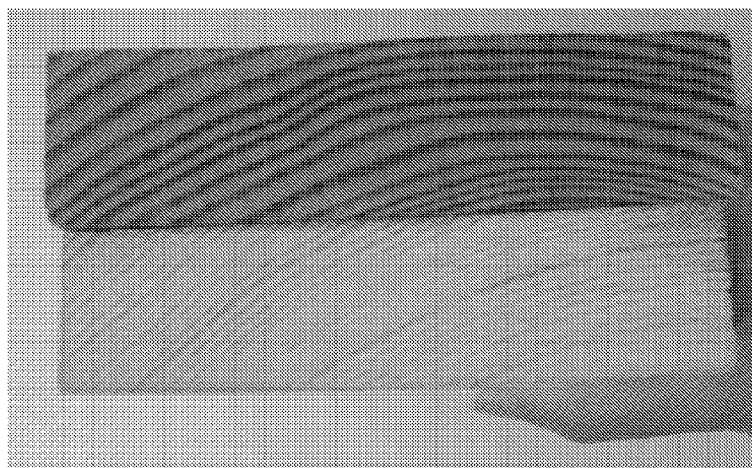


Fig. 1

- (57) Abstract: The present invention
relates to a liquid metal silicate com-
position, having a viscosity of 45 mPa.s
or less measured at 20°C at a solid con-
tent of 39% of said metal silicate, in an
aqueous solution.



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A low viscosity metal silicate composition

Technical field of the invention

The present invention relates to a novel composition comprising a liquid metal
5 silicate composition such as sodium silicate, potassium silicate and/or lithium
silicate having a reduced viscosity relative to the solid content of the composition
and which are reduced relative to corresponding types of liquid metal silicates.

Background of the invention

10 Metal silicates are a group of compounds including sodium silicate, potassium
silicate and lithium silicate. Sodium silicate is the most widely used metal silicate,
and is the common name for sodium metasilicate, Na_2SiO_3 , also known as water
glass or liquid glass. It is available in aqueous solution and in solid form and may
find use in e.g. cements, passive fire protection, refractories, textile and lumber
15 processing, and automobiles.

It has been known for several years that metal silicate and in particular sodium
silicate can be used as e.g. a fire protective agent in wood preservation, such as
in a paint composition or as an "impregnation" agent. However, the uptake of the
20 metal silicate in the cellulosic material is limited, if any uptake happens at all.

WO 94/12289 discloses a method for using silicate compounds to create a surface
protection of e.g. a wood article. The chemical properties of the silicate
compounds are not further defined.

25

US 6,146,766 discloses a method for fire-protecting cellulosic material with
sodium silicate. It is described that the method uses a combination of vacuum and
pressure to penetrate cellular walls. Increased fire protection appears to be
documented, however there are no data showing that the sodium silicate actually
30 penetrates the materials. Furthermore, the chemical properties of the used
sodium silicate are not further defined.

WO 2009/008797 discloses a method for strengthening wood structures comprising the use of a waterglass composition having a pH below 5. This document does not define any further details on the chemical properties of the composition used, besides the pH.

5

In sum, none of the cited prior art addresses any problems with the chemical properties of sodium silicate in relation to the efficiency of penetrating the materials to which they are applied.

Hence, there is a need for an improved metal silicate composition with improved
10 properties which is stable, easy to produce and inexpensive.

Summary of the invention

Though the prior art described above relates to preservation of cellulosic material with sodium silicate, none of WO 94/12289, US 6,146,766 and WO 2009/008797
15 show any actual results demonstrating that the metal silicate is penetrating into cellulosic structures such as wood structures. Penetration efficiency may be influenced by the chemical structures of the metal silicate in the composition, in here represented by the viscosity of the metal silicate. It is generally believed that the main factors influencing the viscosity of metal silicates are the mole ratio
20 between the silicate and metal, the solid content of the metal silicate and the temperature. The present invention relates to a novel liquid metal silicate composition, such as sodium silicate, potassium silicate and/or lithium silicate, having a reduced viscosity relative to a corresponding type of liquid metal silicate, which has not been modified.

25

Thus, an aspect of the present invention relates to a liquid metal silicate composition, having a viscosity of 45 mPa.s or less, measured at 20°C at a solid content of about 39% of said metal silicate, in an aqueous solution. In a more specific embodiment the metal silicate is selected from the group consisting of
30 sodium silicate, potassium silicate and lithium silicate, preferably sodium silicate.

Generally preparation of the various structures of metal silicate depends on the SiO_2 :Metal₂O ratio and each structure provide certain properties to the metal silicate. The present invention discloses a novel process for subjecting the liquid

metal silicate composition to a modification treatment obtaining a new liquid metal silicate composition and new properties.

Thus, another aspect relates to a process for producing a liquid metal silicate composition comprising the steps of:

- a) providing a first liquid metal silicate composition,
- b) subjecting said first liquid metal silicate composition to modification treatment, obtaining a second liquid metal silicate composition,
- c) optionally, subjecting said second liquid metal silicate composition to one or more steps of modification treatment.

Similar, a further aspect relates to a process for producing a liquid metal silicate composition according to the invention comprising

- a) providing a first liquid metal silicate composition,
- b) subjecting said first liquid metal silicate composition to modification treatment, obtaining a second liquid metal silicate composition, having a viscosity of 45 mPa.s or less measured at 20°C at a solid content of about 39%, in an aqueous solution, and
- c) optionally, subjecting said second liquid metal silicate composition to one or more steps of modification treatment.

Yet an aspect of the present invention relates to a liquid metal silicate composition obtainable by a process according to the present invention.

The compositions according to the present invention may find use in different applications. Thus a further aspect relates to the use of a composition according to the invention for preserving cellulosic material.

In particular, it is an object of the present invention to provide a liquid metal silicate composition and/or a process for preserving cellulosic material that solves the above mentioned problems of the prior art with respect to uptake of liquid metal silicate into cellulosic material e.g. a wood structure.

The present invention also discloses a process for providing a cellulosic material comprising a liquid metal silicate composition.

Thus, in an aspect the present invention relates to a process for providing a cellulosic material comprising a liquid metal silicate composition, the process comprises the steps of:

- providing a liquid metal silicate composition according to the invention,
- 5 - optionally diluting or concentrating said sodium silicate composition,
- positioning said liquid metal silicate composition into and/or onto said cellulosic material.

Yet an aspect of the present invention relates to a process for providing a
10 cellulosic material comprising metal silicate, the process comprising the steps of:

- providing a liquid metal silicate composition according to the invention,
- optionally diluting or concentrating said liquid metal silicate composition,
- positioning said liquid metal silicate composition into and/or onto said cellulosic material, providing a cellulosic material comprising metal silicate.

15

Still another aspect relates to a cellulosic material obtainable by a process according to the invention.

The present invention will now be described in more detail in the following.

20

Figure legends

Figure 1

Figure 1 shows wood impregnated with modified low viscosity sodium silicate (top) and with non-modified low viscosity sodium silicate (bottom). It can be seen
25 that only the modified sodium silicate penetrates into the wood board (darker coloring). For the non-modified sodium silicate very thin dark coloring at the surface of the board is visible. The board has the dimensions 2.54 cm X 10,16 cm (1 X 4 inches).

30 Figures 2-4

Figures 2-4 show state-of-the-art graphs in relation to sodium silicate dependency on solid content, ratio and temperature (textbook by J.G. Vail, Soluble Silicates Vol. 1, Reinhold, New York, 1952).

Figure 5

Figure 5 shows state-of-the-art knowledge in relation to the change in types of silicates present in a sodium silicate composition when changing the Na:Si ratio.

X-axis Na:Si ratio; Y-axis relative change in intensity of each type.

- 5 Each line indicate a different type of silicate. For further information see: Zur Abhängigkeit der Struktur der Silicatanionen in wässrigen Natriumsilicatlösungen vom Na:Si-Verhältnis. Z. anorg. allg. Chem. 418, 17-28 (1975).

Detailed description of the invention

10 Composition

The present invention relates to a novel composition comprising a liquid metal silicate composition, such as sodium silicate, potassium silicate and/or lithium silicate having a lower viscosity than a corresponding type of liquid metal silicate.

- 15 Thus, in a first aspect the invention relates to a liquid metal silicate composition, having a viscosity of 45 mPa.s or less measured at 20°C at a solid content of 39% or about 39% of said metal silicate, in an aqueous solution.

In the present context the term "about" refers to a deviation of the solid content

- 20 in the percentages of +/- 2%, such as +/- 1.5%, such as +/- 1%, such as +/- 0.5%.

When determining the viscosity different factors may influence on the viscosity of e.g. a liquid metal silicate. The main factors have been considered being e.g. the

- 25 mole ratio, solid content and temperature. Thus, if a change in viscosity is needed, at least one of the mole ratio, solid content or temperature could be adjusted. However in many scenarios it is not favourable to make adjustments of these parameters, or it is simply not possible.

- 30 It is to be understood that compositions according to the present invention also covers compositions with a solid content different from 39%, compositions with temperatures different from 20°C and compositions which are not in an aqueous solution. The 39% solid content, the 20°C temperature and the aqueous solution simply relate to the condition under which the viscosity should be measured. The

person skilled in the art would know how to change these conditions to match these criteria. Thus, the compositions according to the invention may have different solid contents, different temperatures and be solubilised in different solutions, which may result in a lower or higher viscosity, however when adjusted
5 to the conditions defined herein, the skilled person be capable of evaluating if the viscosity falls within the scope of the present invention, having a viscosity of 45 mPa.s or less.

In an embodiment the metal silicate composition according to the present invention
10 has a solid content of the metal silicate in the range 5-60%, such as 10-60%, such as 15-60%, such as 20-60%, such as 30-60%, such as 10-50%, such as 10-40%, such as 10-30%, or such as 10-20% metal silicate. Again it is to be understood that the viscosity of such compositions may still be measured at 20°C at a solid content of about 39% of said metal silicate, in an aqueous solution.

15

The viscosity of the liquid metal silicate according to the invention may vary depending on the specific purpose. Thus, in an embodiment the viscosity at 20°C at a solid content of about 39% of said metal silicate, in an aqueous solution is in the range 1-45 mPa.s, such as 1-43 mPa.s, such as 1-41 mPa.s, such as 1-39
20 mPa.s, such as 1-35 mPa.s, such as 1-30 mPa.s, such as in the range 1-25 mPa.s, such as 1-20 mPa.s, such as 1-15 mPa.s, such as 1-10 mPa.s. In another embodiment the viscosity at 20°C at a solid content of about 39% of said metal silicate, in an aqueous solution is in the range 5-45 mPa.s, such as 10-45 mPa.s, such as 15-45 mPa.s, such as 15-43 mPa.s, such as 15-41 mPa.s, such as 15-39
25 mPa.s, such as in the range 20-39 mPa.s, such as 25-39 mPa.s, or such as 28-39 mPa.s. In yet an embodiment the viscosity at 20°C at a solid content of about 39% of said metal silicate, in an aqueous solution is in the range 5-15 mPa.s, in the range 10-20 mPa.s, in the range 15-25 mPa.s, in the range 20-30 mPa.s, in the range 25-35 mPa.s, in the range 30-40 mPa.s, or in the range 35-45 mPa.s.

30

In the present context viscosity is measured by a Brookfield viscosimeter at 20°C. Said viscosity is measured at average sea-level pressure, such as 101.325 kPa, e.g. using a Brookfield viscosimeter model LVT-DVII, serienr. 017141.

Different types of metal silicates exist and in the table below some types of metal silicates are listed.

The table shows examples of different types of sodium silicate and potassium silicate and their properties. These metal silicates may be used as starting materials for preparing the metal silicate composition of the present invention, as the first liquid metal silicate.

Type of metal silicate	°Be	visc. mPa.s	Solid content %	GV%	pH
Sodium Type 37/40	38.3	48.3	36	3.2-3.4	12
Sodium Type 44	44.3	52.8	38.4	2	14
Sodium Type 46	46.3	72.3	40.3	2	14
Sodium Type 50	50,3	200	44,3	2	14
Potassium Type 4009	40	46.6	39.4	2	13

°Be=Baume, GV=weight/weight ratio between SiO₂ and Na₂O or between SiO₂

10 and K₂O.

In an embodiment of the present invention the metal silicate may be selected from the group consisting of sodium silicate, potassium silicate and lithium silicate. Preferably, the metal silicate may be selected from the group consisting of sodium silicate and potassium silicate, more preferably the metal silicate is sodium silicate.

Sodium silicate (water glass) is a member of the family of soluble sodium silicates and is considered the simplest form of glass. Water glass is derived by fusing sand and soda ash; it is non-combustible with low toxicity. It may be used as catalysts and silica gels; soaps and detergents; adhesives; water treatment; bleaching and sizing of textiles and paper pulp; ore treatment; soil solidification; glass foam; pigments; drilling muds; binder for foundry cores and molds; waterproofing mortars and cements; and surface impregnating wood.

25

The liquid metal silicate composition according to the invention may have different pHs depending on the purpose, however preferably the pH is alkaline. Thus, in another embodiment the liquid metal silicate composition has a pH in the range 8.5-14, such as 9-14, such as 11-14 or such as 12-14. At such elevated pHs the composition is stable for long periods of time.

It is known from the prior art that e.g. sodium silicate polymerizes when the pH drops to below 7. However, in protection of cellulosic material this may be an advantage, since polymerization after preservation may limit leaching of the metal silicate from the material. WO 2009/008797 discloses such method where the pH of sodium silicate is rapidly dropped to below 5 to avoid fast polymerization. Thus, in a further embodiment of the present invention the liquid metal silicate composition has a pH in the range 1-5, such as 1-4.5, such as 1-4, such as 2-4, such as 2.5-4, or such as 3.5-4.

15

Since the viscosity may depend on the solid content of the liquid metal silicate the liquid metal composition according to the invention may be defined by the ratio between the viscosity and the solid content of the metal silicate. Thus, in a specific aspect, the invention relates to a liquid metal silicate composition characterized in that said composition has a ratio between the viscosity and the solid content of said metal silicate of less than 1.150, such as less than 1, such as less than 0.8, or such as less than 0.6. In the present context the viscosity is measured as mPa.s and the solid content is measured as (w/w) on dry matter % of the metal silicate. Dry matter is a measurement of the mass percentage of the matter when completely dried relative to the un-dried matter.

SiO₂ to Na₂O ratio and SiO₂ to K₂O ratio

It is known in the art that the viscosity of metal silicates also depend on the weight/weight ratio between the metal and the silicate, such as the SiO₂ to Na₂O ratio and SiO₂ to K₂O ratio.

Thus, in an embodiment the weight/weight ratio between the silicate and the metal, such as the SiO₂ to Na₂O ratio, is above 0.50, e.g. above 0.75, such as above 1, e.g. above 1.25, such as above 1.50, e.g. above 1.70, e.g. above 2, such as above 2.25, e.g. above 2.50, such as above 2.75, e.g. above 3, e.g. in

the range of 20 to 1, such as 6 to 1, such as 5 to 1, such as 4 to 1 or such as 3.30 to 1.58.

A composition according to the invention may find use in many applications.

- 5 However one particular application may be in preservation of cellulosic material. Thus, in an embodiment said composition is an agent for preserving cellulosic material, such as wood.

- In the present context the terms "preservation", "preserved" or "preservation agent" relates to an improvement of cellulosic material compared to a control material without metal silicate. An enhancement may be in relation to fire protection, attacks from insects such as termites, and attacks from micro-organisms, such as fungus and bacteria. Thus, in an embodiment the cellulosic material according to the invention is preserved with metal silicate. In a
- 10
- 15 corresponding embodiment the process according to the invention relates to a process for providing a cellulosic material preserved with a metal silicate.

- A further benefit of providing enhancement according to the present invention is the benefit on the environmental safety due to non-toxicity of the composition
- 20 relative to other known fungicides and fire retardant components.

- The composition according to the invention is capable of maintaining a reduced viscosity over a long period of time, preferably, without having to take special precautions. Thus, in an embodiment said viscosity is stable for at least 2 hours,
- 25 at least 10 hours, at least 1 day, at least 2 days, at least 5 days, at least 20 days, at least 40 days, such as at least 60 days, or such as at least 90 days.

Process for producing a liquid metal silicate composition

- The improved properties of the liquid metal silicate composition of the present
- 30 invention may be provided by the process of producing the composition.

Thus, another aspect relates to a process for producing a liquid metal silicate composition comprising the steps of:

- a) providing a first liquid metal silicate composition,

- b) subjecting said first liquid metal silicate composition to modification treatment, obtaining a second liquid metal silicate composition,
- c) optionally, subjecting said second liquid metal silicate composition to one or more steps of modification treatment.

5

Preferably the modification treatment is mechanical treatment.

Thus, in a preferred embodiment of the present invention relates to a process for producing a liquid metal silicate composition according to the invention comprising

- 10 a) providing a first liquid metal silicate composition,
- b) subjecting said first liquid metal silicate composition to a modification treatment, obtaining a second liquid metal silicate composition, having a viscosity of 45 mPa.s or less measured at 20°C at a solid content of about 39%, in an aqueous solution, and
- 15 c) optionally, subjecting said second liquid metal silicate composition to one or more steps of modification treatment.

In the present context the term "first metal silicate composition" relates to any metal silicate composition, whereas the second metal silicate composition relates
20 to a metal silicate composition which has been subjected to a process according to the invention. As described under c) such process may be repeated to further modify the composition.

It has surprisingly been found that by modifying the metal silicate structures in a
25 solution the viscosity may be significantly reduced compared to an unmodified solution with identical content (see e.g. Example 1). As previously mentioned, it is to be understood that compositions according to the present invention also cover compositions with a solid content different from 39%, compositions with temperatures different from 20°C and compositions which are in a liquid solution
30 different from an aqueous solution. The 39% solid content, the 20°C temperature and the aqueous solution simply relate to the condition under which the viscosity should be measured.

The modification treatment according to the invention may be performed by
35 different means or combination of different means. Thus, in yet an embodiment

the modification treatment may be selected from the group consisting of mechanical treatment, chemical treatment, enzymatic treatment, temperature treatment and pressure treatment.

- 5 Different types of mechanical treatment may be applied. Thus, in a more specific embodiment said mechanical treatment is provided by beading, milling, comminuting or grinding. The means for making these mechanical treatments may also vary. Thus, in another embodiment said beading, milling, comminuting or grinding is performed by a bead mill.

10

The period of performing the modification treatment may vary depending on the specific type of modification treatment at the desired viscosity to reach. Thus, in an embodiment said modification treatment, such as mechanical treatment, may be repeated for at least 2 minutes such as at least 5 minutes, such as at least 10

- 15 minutes, such as at least 20 minutes, such as at least 30 minutes, such as at least 60 minutes, such as at least 60 minutes such as at least 4 hours, or such as at least 8 hours. In yet an embodiment the modification treatment, such as mechanical treatment is repeated for a period of 2 minutes to 8 hours, such as 2 minutes to 4 hours, such as 2 minutes to 60 minutes, such as 15 minutes to 60
20 minutes. The time may be adjusted also by e.g. the force applied during mechanical treatment.

In the case of the use of a bead mill as also illustrated in the example section, the force may also be adjusted by the size of the beads. The optimal size of beads
25 may be determined by determining the size of the particles which are to be used in the bead mill.

- The Particle size distribution in a sodium silicate composition was determined by using a Malvern Mastersizer 2000 instrument with a Hydro S dispersion unit with
30 demineralised water as dispersant.

The measurement was performed by means of laser diffraction and particles in the size interval from 0,02-2000 μm were measured.

- The sample (unmodified waterglass type 44) was measured twice. The particle size distribution was calculated based on the assumption that the particles are
35 spherical.

The Waterglass was found to contain two particle sizes. One size visualised as a small peak at 4µm and one size visualised as a significant, larger peak at 45µm.

5 Bead size.

The optimal bead size may be calculated as follows:

Particle size = x; Optimal bead size = $x * 10$; Max grinding result = $x/100$

10 In this case $x = 45 \mu\text{m}$

Optimal bead size = $450 \mu\text{m}$

Max grinding result = $0.45 \mu\text{m}$.

Though the theoretical optimal bead size may be around $450 \mu\text{m}$, other beads
15 sizes may be used to adjust the final viscosity. Similarly, for other types of metal silicates other bead sizes may be preferred depending on the specific particles present in the composition in question.

Thus, in an embodiment the beads have an average diameter in the range 20-
20 $1300 \mu\text{m}$, such as in the range $100\text{-}1300 \mu\text{m}$, such as in the range $200\text{-}1300 \mu\text{m}$, such as in the range $300\text{-}1300 \mu\text{m}$, such as in the range $400\text{-}1300 \mu\text{m}$, such as in the range $500\text{-}1300 \mu\text{m}$, such as in the range $20\text{-}1000 \mu\text{m}$, such as in the range $20\text{-}800 \mu\text{m}$, such as in the range $20\text{-}600 \mu\text{m}$, such as in the range $20\text{-}400 \mu\text{m}$, such as in the range $20\text{-}300 \mu\text{m}$, such as in the range $20\text{-}200 \mu\text{m}$, such as in the
25 range $100\text{-}700 \mu\text{m}$, such as in the range $200\text{-}600 \mu\text{m}$, such as in the range $300\text{-}500 \mu\text{m}$. A glass bead may e.g. be made of glass (such as microglass beads) or titanium. Suitable glass beads are commercially available from Sigmund Lindner.

Thus, it will be within the capacity of the skilled person to adjust several
30 parameters of e.g. mechanical treatment to obtain a desired viscosity level.

In a preferred embodiment of the present invention:

- the second metal silicate composition has a reduced viscosity relative to the first metal silicate composition, and/or

- the second metal silicate composition has a reduced ratio between the viscosity and the solid content relative to the first metal silicate composition.
- In another embodiment the second metal silicate composition has a viscosity which is reduced relative to the first metal silicate composition, with at least 10%, such as at least 20%, such as at least 30%, such as 10-70%, such as 20-70% or such as 30-70% reduced relative to the first metal silicate composition.

10 Product by process

In the art of metal silicates, it is generally believed that the viscosity of metal silicates depends on the solid content, the ratio between the metal and the silicate, the density and the temperature (see e.g. figures 2-4). For example WO2009/087262 describes the problem of high viscosity sodium silicate when impregnating wood. In WO2009/087262 the problem of high viscosity is solved by using a low concentration of sodium silicate (15%), which has a lower viscosity. This of course has the disadvantage that less sodium silicate is positioned inside the wood than if a higher concentration were used with a similar viscosity.

It is generally believed in the art of metal silicates that a metal silicate composition comprises an equilibrium of different forms of the metal silicate as also illustrated in figure 5, which is considered to represent state of the art (figure from 5 is obtained from "Zur Abhängigkeit der Struktur der Silicatanionen in wässrigen Natriumsilicatlösungen vom Na:Si-Verhältnis. Z. anorg. allg. Chem. 418, 17-28 (1975)"). Without being bound by theory it is the hypothesis that the equilibrium is shifted towards ring structures (and away from branched structures) when the composition is treated according to the present invention, such as by mechanical treatment. Thus, since it may be difficult to define the composition by its components the viscosity of the composition may be used as a reliable measure of a very specific feature for such composition and a good indicator that the components of a composition has been modified.

As described above, the present inventors have identified a new parameter which may influence the viscosity of metal silicate compositions, independent of the

concentration of the metal silicate, by changing the equilibrium of the components of the metal silicates in the composition and thus providing a novel composition.

Thus, an aspect of the present invention relates to a liquid metal silicate
5 composition obtainable by a process according to the present invention.

Thus, in an embodiment the viscosity is reduced without changing the concentration of metal silicate in the composition. In yet an embodiment the solid content of metal silicates in the second composition is the same as the solid
10 content in the first composition. In a further embodiment the viscosity is reduced independent of the solid content. In another embodiment the viscosity is reduced without changing the ratio between the metal component and the silicate component. In yet an embodiment the viscosity is reduced without changing the temperature of the metal silicate in the composition or the overall temperature of
15 the composition.

Use of a composition for preserving cellulosic material

Liquid metal silicate compositions according to the present invention, may find use in different applications. It is well known in the art that e.g. sodium silicate may
20 improve preservation of cellulosic materials, such as wood. However, it is also known that sodium silicate cannot penetrate into wood. Thus, sodium silicate preservation may only result in surface preservation, which of course is less efficient, e.g. if preserved wood is subsequently cleaved into smaller units or wear which would result in surfaces starts appearing which are not preserved. Thus, in
25 yet an aspect the invention relates to the use of a composition according to the invention for preserving cellulosic material. Examples 5 and 6 shows that the modified metal silicate is able to penetrate into the wood structures, which is not the case for unmodified metal silicates as illustrated in figure 1.

30 It is to be understood that the composition according to the present invention may be part of e.g. a liquid paint formulation.

In the present context the term "cellulosic material" refers to materials comprising cellulose, such as plywood, fibreboard and wood. In a preferred embodiment the cellulosic material according to the invention is wood.

- 5 In the present context the term "wood" refers to fibrous tissue found in many plants. It is an organic material, a natural composite of cellulose fibers (which are strong in tension) embedded in a matrix of lignin which resists compression. It is common to classify wood as either softwood or hardwood. The wood from conifers (e.g. pine) is called softwood, and the wood from dicotyledons (usually
10 broad-leaved trees, e.g. oak) is called hardwood.

Wood may be further divided into heartwood and sapwood.

- Heartwood is wood that as a result of a naturally occurring chemical
15 transformation has become more resistant to decay. Heartwood may (or may not) be much darker than living wood. It may (or may not) be sharply distinct from the sapwood. However, other processes, such as decay, can discolour wood, even in woody plants that do not form heartwood, with a similar colour difference, which may lead to confusion.

20

- Sapwood is the younger, outermost wood; in the growing tree it is living wood, and its principal functions are to transport water from the roots to the leaves and to store up and give back according to the season the reserves prepared in the leaves. However, by the time it become incompetent to conduct water, all xylem
25 tracheids and vessels have lost their cytoplasm and the cells are therefore functionally dead. All wood in a tree is first formed as sapwood.

- In an embodiment said wood is hardwood or softwood or a combination thereof. In another embodiment said wood comprises heartwood and/or sapwood. In a
30 preferred embodiment said wood is sapwood, e.g. from pine.

Further examples of wood materials according to the present invention are timber and lumber (boards) of different sizes and shapes.

A fire retardant material is one having properties that provide comparatively low flammability or flame spread properties. There are a number of materials that have been used to treat wood for fire retardancy including ammonium phosphate, ammonium sulfate, zinc chloride, dicyandiamide-phosphoric acid and sodium
5 borate.

Process for preserving cellulosic material

As mentioned the liquid metal silicate composition of the present invention may preferably be applied to a cellulosic material. Thus, a preferred embodiment of the present invention relates to a process for providing a cellulosic material
10 comprising metal silicate, the method comprises the steps of:

- providing a liquid metal silicate composition according to the invention,
- optionally diluting or concentrating said liquid metal silicate composition,
- positioning said liquid metal silicate composition into and/or onto said
cellulosic material, providing a cellulosic material comprising metal silicate.

15

The liquid metal compositions according to the present invention show improved penetration of metal silicate into the cellulosic material, such as wood, compared to unmodified liquid metal silicate compositions (see also example 2).

20 In the present context the term "into said cellulosic material" refers to the situation where the metal silicate according to the present invention is detectable inside the wood structure. In an embodiment of the present invention the metal silicate according to the present invention is detectable more than 1 mm into said cellulosic material, such as more than 2 mm, such as more than 3 mm, such as
25 more than 4 mm, or such as more than 5 mm.

In the present context the term "onto said cellulosic material" refers to the situation where the metal silicate according to the present invention is only detectable on the surface of the cellulosic material. In an embodiment of the
30 present invention the metal silicate according to the present invention is only detectable for at most 1 mm into said cellulosic material, such as at most 0.5 mm into said cellulosic material, e.g. at most 0.25 mm into said cellulosic material. It is to be understood by the mentioned distance, that it relates to the distance from any surface of said cellulosic material, wherein said surface is a surface visible to

the human eye. Thus, a "surface" is not a microscopic surface present inside e.g. a wood structure, but relates to what would normally be considered the surface of e.g. a standard wood board. Thus, in an embodiment said surface is a visible surface.

5

The inventors of the present invention surprisingly found that the modified liquid metal silicate composition (second metal silicate composition) of the present invention were able to penetrate the cellulosic material (the sapwood) and enter into the cellulosic material. Whereas the unmodified liquid metal silicate
10 composition (a first metal silicate composition) was not able to enter into the cellulosic material but stayed onto the surface of the cellulosic material.

Though the viscosity of the liquid metal silicate composition of the present invention is relatively lower than an unmodified metal silicate composition, there
15 may still be a high solid content. Thus, in an embodiment the liquid metal silicate composition according to the invention has a solid content of the metal silicate in the range 0.5% - 80%, such as in the range 0.5% - 70%, such as in the range, 0.5% - 60%, such as in the range, 0.5% - 50%, such as in the range, 0.5% - 40%, such as in the range, 0.5% - 30%, such as in the range, 0.5% - 20%, such
20 as in the range 0.5% - 10%, such as in the range 0.5% - 5%, such as in the range 0.5% - 3%. Since this may also depend on the specific type of cellulosic material the user has to consider whether it is appropriate to dilute or concentrate the composition before use.

25 Without being bound by theory, since heart wood is denser in structure than sapwood it is more difficult to get the liquid metal silicate composition into heartwood compared to sapwood. On the other hand sapwood has a more open structure which may allow the metal silicate composition to penetrate more deeply into the structure. Some cellulosic material, such as boards may comprise both
30 heartwood and sapwood and they may not be equally modified with the liquid metal silicate composition. However since heartwood is much more resistant to e.g. moisture and therefore also microorganisms such difference may not affect the overall preservation of the material.

The cellulosic material may preferably have a volume of at least about 0.5 cm³, such as at least 1 cm³, such as at least 2 cm³, such as at least 5 cm³, such as at least 50 cm³, such as at least 500 cm³, such as at least 1000 cm³, such as at least 10000 cm³. It is to be understood that timber or boards may have a much larger
5 volume.

In an embodiment the material is not biologically pre-treated, such as with blue-stain fungus. Such procedure is e.g. described in WO2009/087262. Biological pre-treatment may weaken the cellulosic material, e.g. the wood structure and
10 may therefore be undesirable in order to provide a cellulosic material of high quality. Furthermore, such pre-treatment is a slow, inhomogeneous, and un-reproducible process which would result in an increased price.

The metal silicate composition may be positioned into or onto the cellulosic
15 material by different means. Thus, in an embodiment said positioning is performed by at least one of the methods selected from the group consisting of reduced pressure, e.g. vacuum, added pressure, dipping, brushing, spraying, and sap-, microwaving, high-frequency, and introduction of the sodium silicate composition in a supercritical state. Such processes are known to the person
20 skilled in the art and will not be discussed in further detail.

Though it is known that liquid metal silicates cannot penetrate deeply into the cellulosic material, e.g. wood structures several attempts have been performed. One of the typical obstacles which has turned up is that the metal silicate will
25 leach from the cellulosic material, e.g. wood, since it is located on the surface of the cellulosic material and because it is water soluble. Several different solution to the problem has been found all of which include hardening the metal silicate composition after it has been applied onto e.g. a wood board. Thus, in an embodiment the process further comprises hardening said liquid metal silicate
30 composition after the liquid metal silicate composition has been positioned into and/or onto said cellulosic material.

In yet an embodiment said hardening is provided by
- exposing said liquid metal silicate preserved material to energy, such as
35 heat or radiation, and/or

- adding a coagulant, and/or
 - adding a hardener to said material such as an acid, CO₂, bicarbonate, or one or more metal salt such as calcium chloride and/or zinc chloride,
- 5 The principle behind these types of hardening is that the metal silicate will polymerize thus become water insoluble and subsequently be unable to leach from the material or perform a reduced leaching. The problem with leaching may be less pronounced if the liquid metal silicate is positioned inside a cellulosic material such as a wood structure, opposed to standard positioning of the metal
- 10 silicate where it will only be positioned on the surface of the cellulosic material, e.g. wood structure due to lack of penetration. In the present context the term "leaching" refers to the loss of a part of the metal silicate composition from the cellulosic material over a period of time. Leaching may be due to rain or high moisture content in the surrounding environment. In the present context the term
- 15 "hardening" refers to the situation where the metal silicate composition or part of the metal silicate composition is stabilized. Hardening may be by polymerization of the metal silicate which reduces the water solubility and makes it difficult for the metal silicate to leach from the cellulosic material.
- 20 Another possible process to avoid or reduce leaching may be to combine heating and reduced pressure, e.g. vacuum. Thus, in another embodiment said hardening process is performed under reduced pressure, e.g. vacuum, at a temperature in the range 45-85°C. Thus, in a further embodiment, said temperature is in the range 55-85°C, such as 65-85°C, or such as 75-85°C. In a further embodiment
- 25 said temperature is in the range 45-75°C, such as 45-65°C, or such as 45-55°C. The advantage of the reduced pressure, e.g. vacuum, is that the effect of heating at standard pressure may be obtained at a lower temperature. This is an advantage for cellulosic material, e.g. wood, where too high a temperature may affect the strength of the cellulosic material, e.g. wood, and may result in bending
- 30 of the cellulosic material, e.g. wood boards. In a further embodiment said reduced pressure or vacuum is in the range 0.1-0.9 bar, such as 0.20-0.90 bar, such as 0.30-0.90 bar, such as 0.40-0.90 bar, such as 0.50-0.90 bar, such as 0.60-0.90 bar, such as 0.70-0.90 bar, or such as 0.80-0.90 bar. In yet an embodiment said reduced pressure or vacuum is in the range 0.1-0.8 bar, such as 0.10-0.70 bar,
- 35 such as 0.10-0.60 bar, such as 0.10-0.50 bar, such as 0.10-0.40 bar, such as

0.10-0.30 bar, or such as 0.10-0.20 bar. In another embodiment said hardening process takes place for 10 minutes to 24 hours, such as 1-24 hours, such as 3-24 hours, such as 5-24 hours, such as 8-24 hours, such as 12-24 hours, such as 16-24 hours, or such as 20-24 hours. In another embodiment said hardening process
5 takes place for 10 minutes to 20 hours, such as 1-16 hours, such as 1-12 hours, such as 1-8 hours, or such as 1-4.

In an embodiment said reduced pressure, e.g. vacuum, is in the range 1-90% vacuum and said temperature is in the range 45-85°C. In a further embodiment
10 said hardening process is performed for 30 minutes to 24 hours, such as 0-24 hours.

When the composition according to the invention is used for wood preservation it may be advantageously to have other components added to the composition.
15

Thus, in yet an embodiment the liquid metal silicate composition further comprises one or more colouring agents. In yet a further embodiment the liquid metal silicate composition further comprises one or more stability enhancing agents. Colouring agent may be beneficial if there is a need to change the
20 appearance of the cellulosic material e.g. wood boards.

Cellulosic material obtainable by a process according to the invention

In a preferred embodiment the invention relates to a cellulosic material obtainable by a process according to the invention.
25

In another aspect the invention relates to a cellulosic material comprising metal silicate

- comprising detectable metal silicate more than 1 mm from any surface of said material, such as more than 2 mm, such as more than 3 mm, such as
30 more than 4 mm, such as more than 5 mm, such as more than 6 mm, such as more than 8 mm, such as more than 10 mm, such as more than 20 mm such as more than 30 mm, and/or

- wherein at least 10%, such as at least 20%, such as at least 30%, such as at least 40%, such as at least 50%, such as at least 60% such as at least 70%, such as at least 80%, such as at least 90% or such as at least 95% of said cellulosic material is preserved with metal silicate, and/or
- 5 - having a weight/weight ratio between the cellulosic material and metal silicate of at most 100:1, such as 10:1, such as at most 8:1, such as at most 5:1, such as at most 3:1, or such as at most 1:1.
- 10 - comprising at least 50 kg metal silicate / m³ of cellulosic material, such as at least 100 kg metal silicate / m³, such as at least 150 kg metal silicate / m³, such as at least 200 kg metal silicate / m³, such as at least 250 kg metal silicate / m³, such as at least 300 kg metal silicate / m³, such as at least 350 kg metal silicate / m³, such as at least 400 kg metal silicate / m³, such as at least 500 kg metal silicate / m³, such as at least 600 kg metal silicate / m³, such as at least 700 kg metal silicate / m³, such as at least 800 kg metal silicate / m³, such as at least 900 kg metal silicate / m³, such as in the range 50 kg to 2000 kg metal silicate / m³, such as, in the range 50 kg to 1800 kg metal silicate / m³, such as in the range 50 kg to 1500 kg metal silicate / m³, such as in the range 50 kg to 1300 kg metal silicate / m³, or such as in the range 50 kg to 1000 kg metal silicate / m³.

The presented aspect solves the problem of pre-treatment of the cellulosic material as previously described. The above features describing the presence of the metal silicate in the cellulosic material all relates to the presence of metal silicate throughout a large proportion of the cellulosic material. The amount of metal silicate present inside the cellulosic material may be determined by different methods:

- 30 - Measurements of the distribution of metal silicate in the cellulosic material may be determined by electron microscopy.
- The percentage of preserved cellulosic material may be determined as the amount of material wherein metal silicate can be determined.
- The weight/weight ratio may be determined by measuring the dry weight of the cellulosic material before and after the preservation treatment, or by comparison to a reference level.

Cellulosic materials as described above, may be obtained by a process according to the present invention. In a more specific embodiment said cellulosic material has not been pre-treated with blue-stain fungus. In yet a specific embodiment
5 said cellulosic material does not comprise viable or non-viable blue-stain fungus or tracers thereof. It may be determined by the eye if a cellulosic material has been pre-treated/infected with the blue stain fungus, since there is a visible change in the colour. However, molecular analysis may also be performed. It is noted that without pre-treatment of the cellulosic material the metal silicate will not enter
10 into the wood structures (see example 2).

It should be noted that embodiments and features described in the context of one of the aspects of the present invention also apply to the other aspects of the invention.

15

All patent and non-patent references cited in the present application, are hereby incorporated by reference in their entirety.

The invention will now be described in further details in the following non-limiting
20 examples.

Examples

Example 1

The present example illustrates how the viscosity of different types of sodium
25 silicate composition can be lowered.

Methods

Different types of sodium silicate (sodium silicate type 37/40 and sodium silicate type 44) were processed in a bead mill for different periods of time ranging from
30 0-40 minutes. The viscosity of the compositions was subsequently measured using a Brookfield viscosimeter model LVT-DVII, serienr. 017141.

Unmodified liquid sodium silicate is generally produced by fusing sand and soda ash and may be provided by different suppliers.

Results

A sodium silicate type 37/40 and a sodium silicate type 44 were modified as described earlier in the specification.

5

Irrespective of the type of sodium silicate used, it was observed that the viscosity dropped significantly with increasing time of treatment/modification of the specific type of sodium silicate. After approximately 30 minutes it seemed like the viscosity could not go further down, however test exceeding 40 minutes were not

10 conducted.

In a second experiment the viscosities were measured using a Brookfield viscosimeter at 20°C.

15 The table below shows a comparison of the viscosities of modified and unmodified type 37/40 and a type 44 sodium silicate. The samples were modified for 40 minutes.

Type of sodium silicate	Not modified	Modified
Type 37/40	48.3 mPa.s	31 mPa.s
Type 44	52.8 mPa.s	28.9 mPa.s

20 The lowered viscosity is stable for at least three month when stored at ambient temperature.

Conclusion

These results clearly indicate that it is possible to lower the viscosity of sodium

25 silicate while maintaining the solid content and/or the $\text{SiO}_2:\text{Na}_2\text{O}$ ratio by the use of a bead mill and the results clearly show that a reduced viscosity is obtained.

Example 2

The present example illustrates how cellulosic materials (exemplified by wood

30 boards) may be preserved using sodium silicate with a lowered viscosity compared to a standard (un-modified) sodium silicate.

Methods

Wood boards (Pine size from 19x100mm to 50x125mm) were preserved with sodium silicate modified according to the present invention using the following
5 process.

Modified (by a bead mill as described above) or un-modified sodium silicate Type
44 were diluted in water to a solid content of approximately 3.9% and 7.8%.

- 10 1) A reduced pressure of 0.9 bar were applied for a period of 20 minutes,
- 2) The pressure was increased by the addition of liquid sodium silicate,
- 3) A pressure of 13 bar was maintained for a period of 45 minutes,
- 4) The pressure was reduced to 0.9 bars for a period of 10 minutes.

15 The results are shown in the following tables:

3.9% sodium silicate

Timber no.	weight increase before drying in %
3	94.19
(Blue stained) 16	70.52
22	86.05

7.8% sodium silicate

Timber no.	weight increase before drying in %
(blue-stained) 34	104.54
35	107.53
36	105.23

20

Preservation with unmodified sodium silicate resulted in practically no penetration and thus, only 1-4% increased weight of the boards (data not shown).

From samples number 16 and 34 it can be seen that a good uptake is achieved
25 when the sample wood has previously been exposed to the blue-stain fungus.
However, this is normally not desirable since blue-stain results in degradation of the wood. The overall variance between the boards may be due the distribution between hardwood and sapwood in the individual boards.

Conclusion

It can clearly be seen that an increase in weight after preservation is obtained, indicating that the processed sodium silicate is being obtained in the boards.

5

Furthermore, it can be seen that a good uptake is obtained both with a solid content of sodium silicate of 7.8 % and 3.9% and that the higher the solid content of the metal silicate composition the higher the uptake of the cellulosic material.

10 Example 3

This example illustrates how leaching of sodium silicate may be avoided after preservation of the cellulosic material.

Following preservation of the cellulosic material, such as wood boards with
15 modified sodium silicate, an after-treatment protocol (hardening protocol) may be performed comprising drying said preserved wood, wherein said drying is performed under reduced pressure, e.g. vacuum, at a temperature in the range 45-85°C.

20 Different ranges of reduced pressure may be applied such as 1-90% vacuum. Similar the temperature may be in the range 45-85°C. The time of drying may depend on the type and size of the cellulosic material, thus the time of drying could be in the range 1-3 weeks.

25 An advantage of this procedure compared to standard heating processes is that due to the vacuum the same effect may be obtained at a lower temperature. This is more cost effective. However another important feature is that the cellulosic material is not exposed to high temperatures which may result in e.g. bending of wood materials.

30

It is believed that by the above treatment, sodium silicate polymerizes and becomes insoluble and therefore do not leach from the timber. Thus, a long term preservation effect is obtained.

As also described in this application, leaching of sodium silicate may also be avoided or reduced by chemical means, however due to environmental and economical reasons this is preferably avoided.

Example 4

- 5 Wood boards impregnated with low viscosity modified sodium silicate.

Materials

Wood: sapwood of scots pine (*Pinus sylvestris*) of a length of 1.2 meters and a thickness of 2 cm.

10

Sodium silicate: Modified sodium silicate type 44 as described in example 1 heated to 60°C.

Results

- 15 Concentrated type 44 sodium silicate

Label	Uptake			
	m (before)	m (after)	(g)	kg/m ³
1	1854,05	3718,35	1864,30	621,43
2	1829,00	3554,00	1725,00	575,00
3	1732,97	3757,60	2024,63	674,88
4	1747,95	3796,50	2048,55	682,85
5	1773,23	3120,26	1347,03	449,01
6	2048,72	4619,22	2570,5	856,83
Mean				643,3

Sodium silicate type 44 diluted 6 times with water.

Label	m (before)	m (after)	(g)	kg/m ³
7	1754,96	2409,78	654,82	218,27
8	2128,39	2591,21	462,82	154,27
9	2064,65	2507,84	443,19	147,73
10	1777,68	2432,03	654,35	218,12
11	1777,14	2369,14	592,00	197,33
12	1572,32	2566,27	993,95	331,32
Mean				211,2

Conclusion

By using the concentrated form of modified sodium silicate the highest uptake of sodium silicate is obtained.

5 Example 5

Wood boards impregnated with low viscosity modified sodium silicate type 44.

Materials

Wood: Sapwood of scots pine (*Pinus sylvestris*) of a length of 0.5 m, width of 0.1 m, and a height of 0.025 m. Volume 0.00125 m³ The boards were sealed at the ends before impregnation to avoid uptake through the ends.

Sodium silicate: Modified sodium silicate type 44 as described in example 1 heated to 60°C.

15

#	m(before)	m (after)	Uptake (g)	Uptake (kg/m ³)
107	692,17	1160,66	468,49	374,79
108	728,19	1256,80	528,61	422,89
109	671,43	1036,06	364,63	291,70
110	747,14	1180,54	433,40	346,72
111	690,53	1005,12	314,59	251,67
112	753,85	1320,61	566,76	453,41
Mean				356,86

Conclusion

Since these boards were sealed at the ends, it can be concluded that the uptake is not due to uptake through the ends. Thus, the method is clearly also applicable to larger boards.

Example 6

Figure 1 shows two boards impregnated with sodium silicate. Top: modified low viscosity sodium silicate according to the present invention. Bottom: Un-modified sodium silicate. Dark coloring indicate impregnated parts of the wood.

Conclusion

It can be seen that low viscosity modified sodium silicate can penetrate into the center of a standard board. Importantly it can also be seen that un-modified
5 sodium silicate is unable to penetrate the wood and therefore stays at the surface of the wood.

Example 7

Experiments have been performed showing that wood impregnated with modified
10 sodium silicate show excellent capabilities in relation to fire protection (fire tube test) and protection against fungus attacks (data not shown).

Claims

1. A liquid metal silicate composition, having a viscosity of 45 mPa.s or less measured at 20°C at a solid content of 39% of said metal silicate, in an aqueous solution.
- 5 2. The liquid metal silicate composition according to claim 1, wherein said metal silicate is selected from the group consisting of sodium silicate, potassium silicate and lithium silicate.
- 10 3. The liquid metal silicate composition according to any of the preceding claims, wherein the viscosity at 20°C at a solid content of 39% of said metal silicate, in an aqueous solution is in the range 5-45 mPa.s.
4. The liquid metal composition according to any of the preceding claims, wherein
15 said composition is an agent for preserving cellulosic material.
5. The liquid metal composition according to any of the preceding claims, wherein the weight/weight ratio between the silicate and the metal is above 0.50.
- 20 6. A process for producing a liquid metal silicate composition comprising
 - a) providing a first liquid metal silicate composition,
 - b) subjecting said first liquid metal silicate composition to mechanical modification treatment, obtaining a second liquid metal silicate composition, wherein the second metal silicate composition has a reduced
25 viscosity relative to the first metal silicate composition, and
 - c) optionally, subjecting said second liquid metal silicate composition to one or more steps of modification treatment.
7. The process according to claim 6, wherein the viscosity reduced relative to the
30 first metal silicate composition, with at least 10%, such as at least 20%, such as at least 30%, such as 10-70%, such as 20-70 or such as 30-70% reduced relative to the first metal silicate composition.

8. The process according to claim 6 or 7, wherein the second metal silicate composition has a viscosity of 45 mPa.s or less measured at 20°C at a solid content of about 39% of said metal silicate, in an aqueous solution.

5

9. A liquid metal silicate composition obtainable by a process according to any of claims 6-8.

10. Use of a composition according to any of claims 1-5 or claim 9 for preserving
10 cellulosic material.

11. A process for providing a cellulosic material comprising metal silicate, said method comprising the steps of:

- 15
- providing a liquid metal silicate composition according to any of claims 1-5 or claim 9,
 - optionally diluting or concentrating said liquid metal silicate composition,
 - positioning said liquid metal silicate composition into and/or onto said cellulosic material, providing a cellulosic material comprising metal silicate.

20 12. A cellulosic material obtainable by a process according to claim 11.

1/5

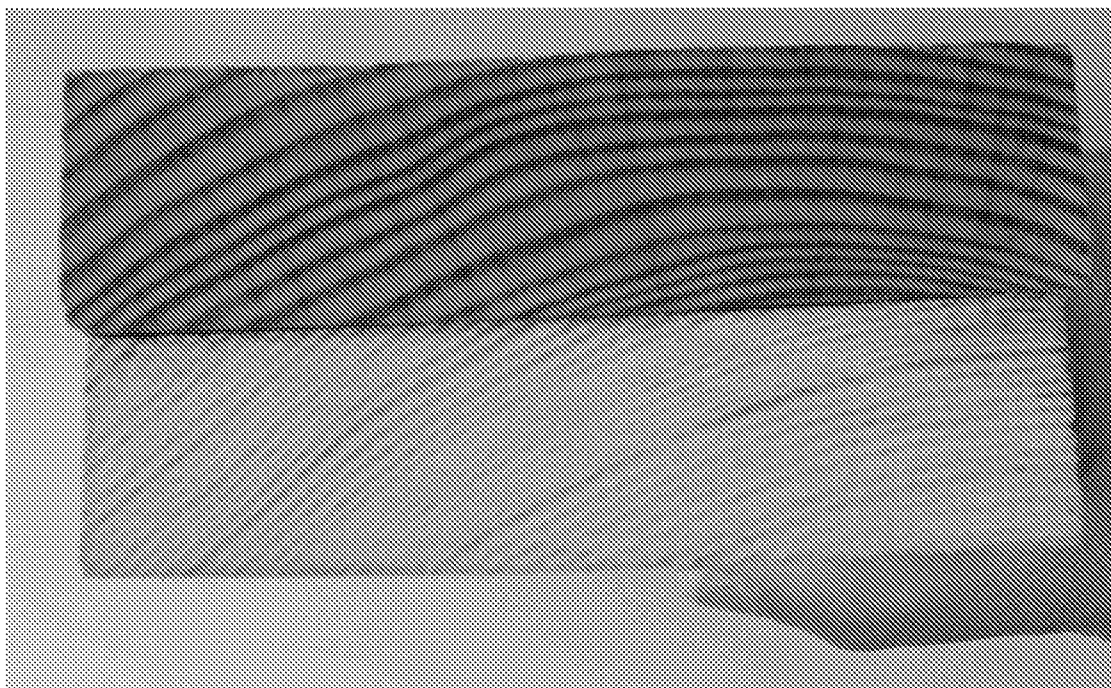


Fig. 1

2/5

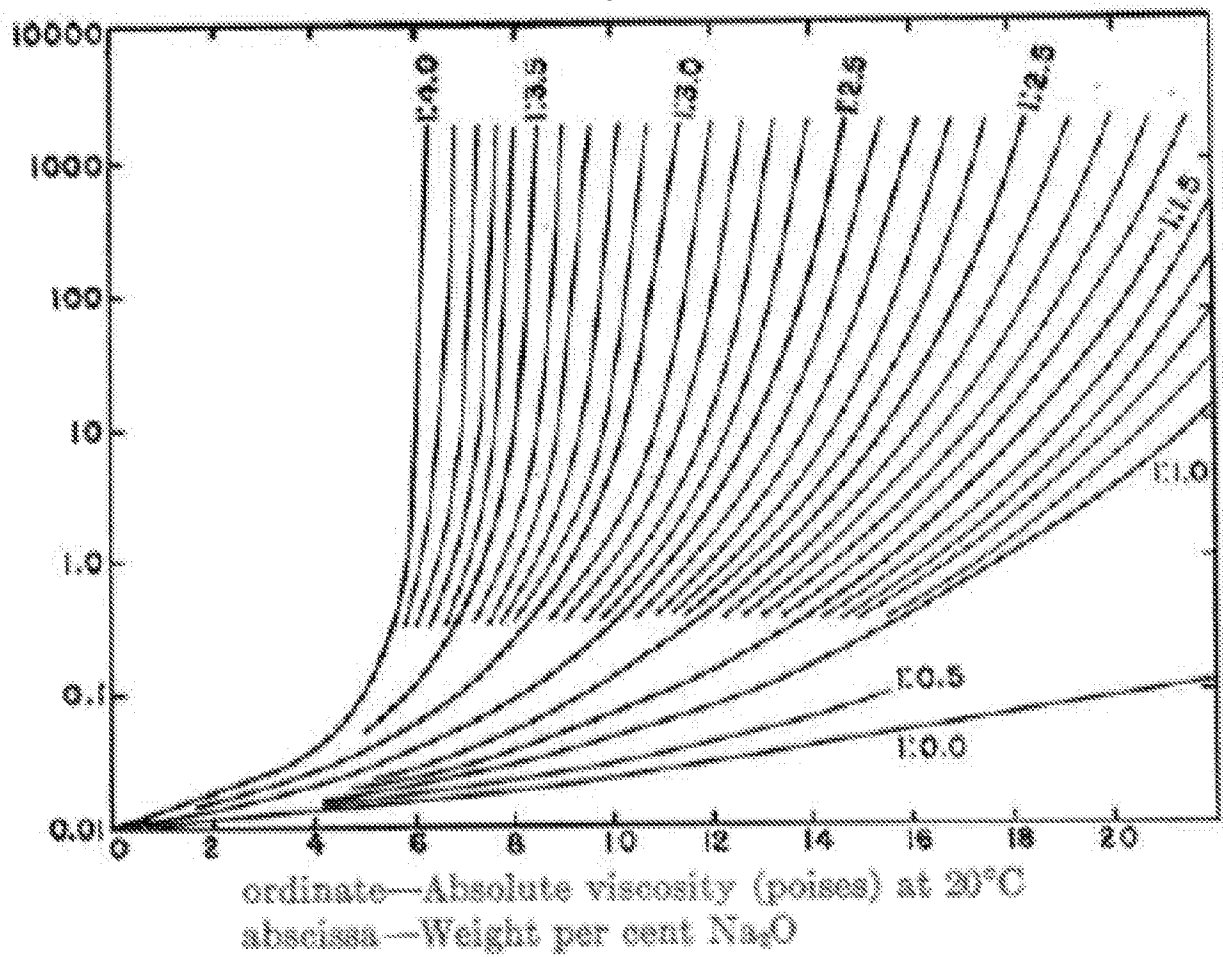


Fig. 2

3/5

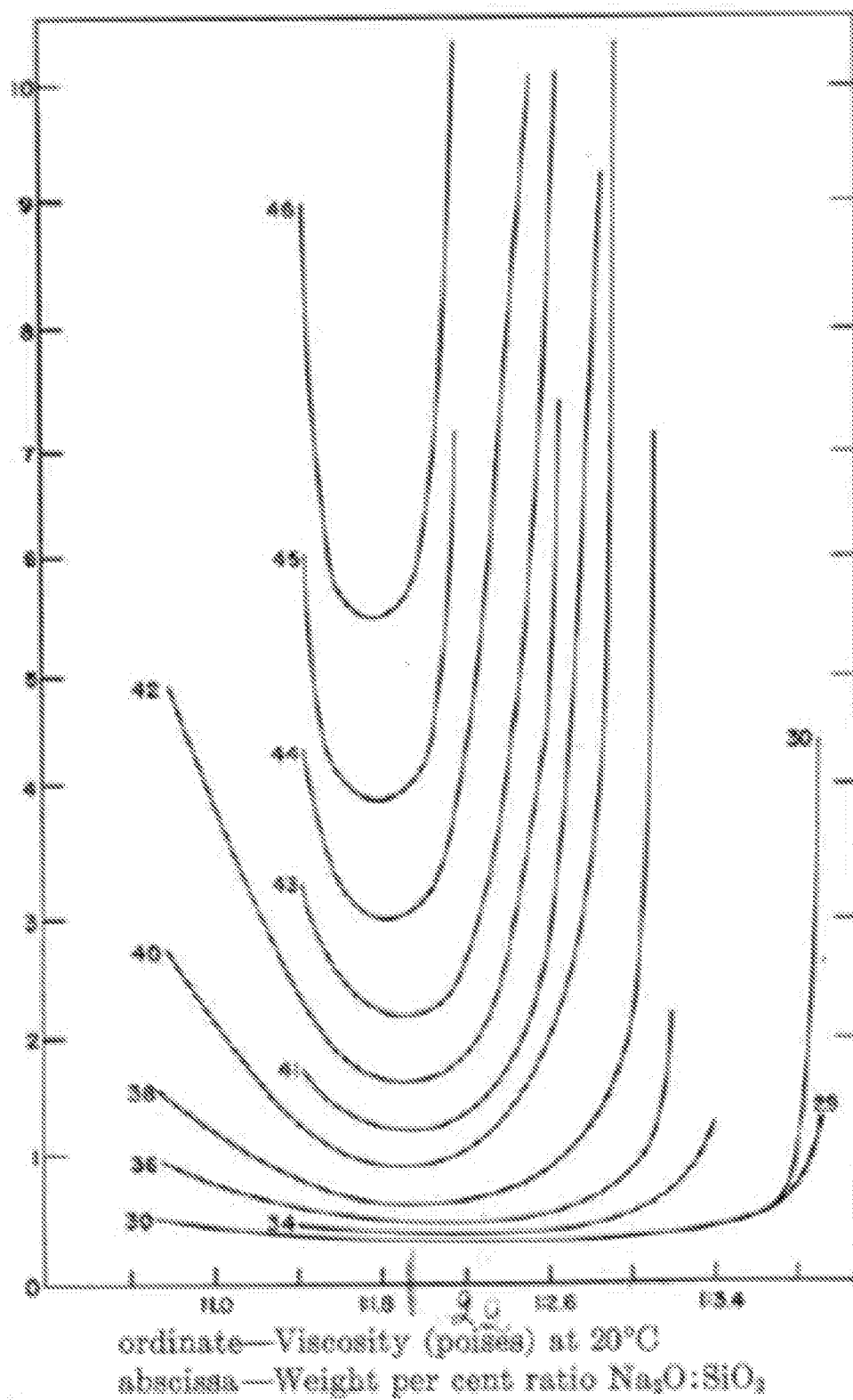


Fig. 3

4/5

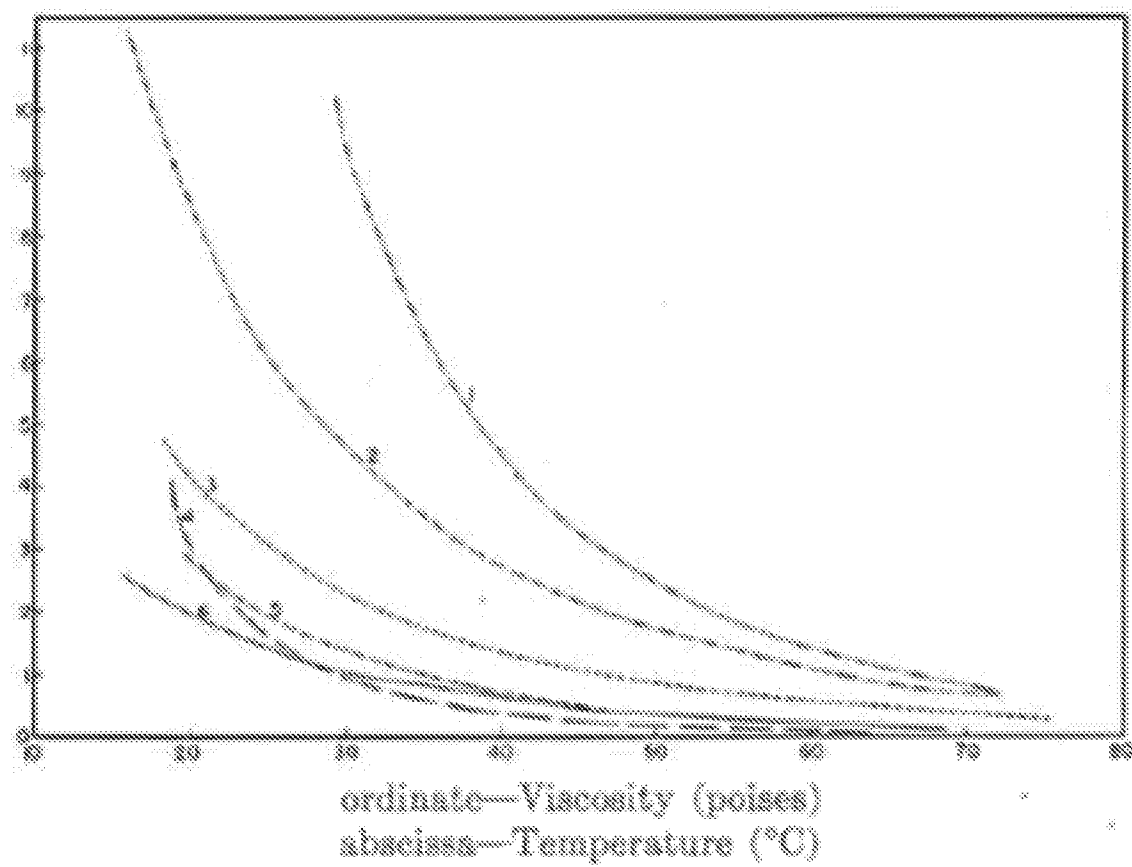


Fig. 4

5/5

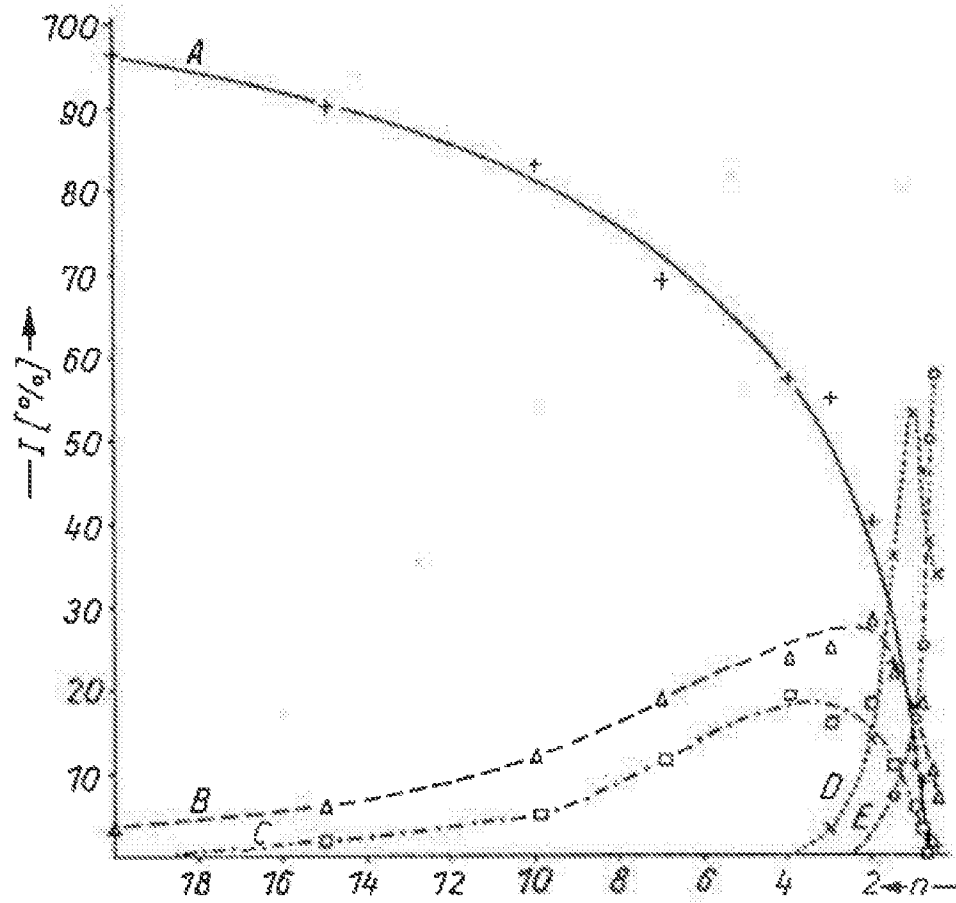


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No

PCT/DK2012/050285

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B33/32 B27K3/15
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)

C01B B27N B27K C09K

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 366 767 A (HOWARD RICHARD [US]) 22 November 1994 (1994-11-22) column 1, lines 6-12 column 2, line 27 - column 6, line 26 -----	1-12
X	US 3 180 746 A (PATTON ROBERT H ET AL) 27 April 1965 (1965-04-27) column 1, lines 10-17 column 1, line 29 - column 2, line 58 claims; examples -----	1-12
X	US 2003/116054 A1 (JOHN ANTHONY JACOB [AU] ET AL) 26 June 2003 (2003-06-26) examples 1,2,4,5,7,8,11,12,14,15 paragraphs [0001], [0002], [0004], [0015] - [0045] ----- -/-	1-12

☒ 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

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"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

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Date of the actual completion of the international search

16 November 2012

Date of mailing of the international search report

26/11/2012

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INTERNATIONAL SEARCH REPORT

International application No

PCT/DK2012/050285

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/130475 A1 (CASTILLO DONALD [US] ET AL) 21 May 2009 (2009-05-21) paragraphs [0001], [0005], [0007] - [0014] claims; example -----	1-12
X	GB 1 576 843 A (DEGUSSA; HENKEL KGAA) 15 October 1980 (1980-10-15) page 1, line 9 - page 5, line 2 -----	1-4,6-9
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