

## FILTER METAL PLATES COATED WITH MULTIFUNCTIONAL NANOCOATINGS

**FIELD OF THE INVENTION**

This invention refers to the field of filter plates.

In particular, it refers to filter metal plates coated with functionalized nanocoatings.

**5 BACKGROUND OF THE INVENTION**

Vee-wire (or V-wire) filter metal plates, marketed for example by Aqseptence Group Srl, are known in the field of filter metal plates.

Vee-wire filter screens possess substantial application benefits due to their versatility, ease of production, and mechanical strength.

- 10 However, in certain applications, such as filter pressing, water filtration in very cold environments, oil/water separation, the plates are not capable of performing well on their own.

In the field of filter pressing, the use of steel plates as a replacement for the polymeric fabrics currently used could offer tremendous process advantages in terms of resistance to wear,  
15 thus avoiding frequent maintenance cycles at facilities. However, metal surfaces are the source of substantial, irreversible adhesion phenomena of the filtrate on the screen, thus rendering the filter pressing process ineffective.

The problem of ice adhering to the metal plates used in water intake processes, that is, taking water from water basins or waterways, and submerged in waterways affected by the frazil ice  
20 phenomenon, although limited to northern countries, particularly the United States and Canada, entails a noteworthy use of energy to heat the plates.

The frazil ice phenomenon and the critical conditions that it causes are known and documented in the literature (1, 2); likewise, the literature reports on processes for obtaining nanostructured anti-ice coatings (3-5), however there currently are no reported solutions  
25 calling for application to filter plates nor the ability to limit the adhesion of ice under submerged conditions.

The problem of oil-water separation by means of nonmetric coatings on permeable substrates, such as metal screens, sponges, and fabrics, is described in the literature (6-11),

however extremely complex multistep processes that are difficult to apply and scale up to large surfaces, are often reported.

There is consequently the need to solve certain problems related to the used of filter metal plates, particularly Vee-wire plates, in certain major applications.

## 5 SUMMARY OF THE INVENTION

It has been found that the coating of filter metal plates with appropriately functionalized nanocoatings has the following advantages:

- 10 i) it insures the detachment of solids from the surface of the plates, providing a substantial benefit during the filter pressing process, in which the solid filtrate (cake) does not completely separate from the filter plates, requiring continuous machine stoppages;
- ii) during water intake operations in cold areas, it limits ice adhesion, which would otherwise prevent the water from passing through;
- 15 iii) in waste treatment processes, it makes it possible to separate oil from water and recover water from emulsion mixtures.

One subject matter of the invention is the use of:

- a) metal oxide nanoparticles coupled with one or more fluoroalkylsilanes and/or one or more organosilanes and/or one or more polymers functionalized with fluoroalkylsilanes and/or with organosilanes; and/or
- 20 b) metal oxide nanoparticles coupled with a polymeric matrix functionalized with fluorinated molecules or groups,

for coating a metal filter plate.

The subject matter of the invention is also a filter metal plate coated with at least one of the following coatings:

- 25 a) metal oxide nanoparticles coupled with one or more fluoroalkylsilanes and/or one or more organosilanes and/or one or more polymers functionalized with fluoroalkylsilanes and/or with organosilanes;
- b) metal oxide nanoparticles coupled with a polymeric matrix functionalized with fluorinated molecules or groups.

In a preferred embodiment, said filter metal plate is made of stainless steel.

In a preferred embodiment, said filter metal plate is a Vee-wire plate.

In a preferred embodiment, said metal oxide is silicon dioxide (SiO<sub>2</sub>).

In a preferred embodiment, said nanoparticles a) are metal oxide nanoparticles coupled with one or more fluoroalkylsilanes.

In a preferred embodiment, said nanoparticles a) are metal oxide nanoparticles coupled with one or more organosilanes.

In another preferred embodiment, said nanoparticles a) are metal oxide nanoparticles coupled with one or more organosilane polymers.

10 In a preferred embodiment, said nanoparticles b) are obtained by precipitation of a suspension of metal oxide nanoparticles in poly(diallyldimethylammonium chloride) (PDMA) and perfluorooctanoic acid or in poly (diallyldimethylammonium chloride) (PDMA) and at least one anionic fluorosurfactant, and subsequent dispersion in an alcoholic solvent.

The plate according to the invention is coated with inorganic metal oxide nanoparticles, for example SiO<sub>2</sub>, coupled with fluorinated or organosilane polymers; the synergy between the two components makes it possible to achieve the technologically attractive functionalities important to the field of filter plate application: detachment of mud and ice and water-oil separation.

20 The materials can be found among commercially available products and are easy to apply for the purpose of future scalability.

Regarding the functionality of mud detachment, the implementation of Vee-wire screens with developed nanometric coatings has made it possible to achieve perfect detachment of solids from surfaces, thus paving the way for the use of metal plates as a substitute for conventional polymer fabrics.

25 Vee-wire plates coated with nanocoatings show very promising results, including in repeated cyclical tests applied in pilot filter pressing plants (Figure 2).

The advantage of the developed treatment lies not only in the achieved functionality, but also in the ease of application; indeed, large surfaces can be coated with the claimed coatings by simply painting or spraying.

30 Readily available and applicable materials are likewise used for the preparation of nanometric coatings capable of limiting the adhesion of ice, both in the air and when submerged in

supercooled water, a condition simulating the frazil ice phenomenon typical of waterways in northern countries. Samples of Vee-wire screens coated according to the invention have been characterized with regard to wettability, and particularly in terms of their ability to avoid the accumulation of an ice layer when submerged in supercooled water. Compared to the as-is sample, the sample developed according to the invention has shown an optimum ability to avoid the accumulation of ice on the surface, thus maintaining optimum performance even when undergoing several submersion cycles (Figure 3).

Compared to untreated surfaces, the Vee-wire screens coated according to the invention and tested for oil-water separation have shown decreased contact angles with respect to water (more hydrophilic) and increased contact angles with respect to biodiesel (more oleophobic). Lastly, the separation tests conducted for filtration have shown a heightened separation effectiveness in 90/10 mixtures of water/biodiesel (Figure 6), making these screens potential candidates for successful use in the treatment of waste from industrial plants.

Another subject matter of the invention is the use of the filter metal plate coated as described above for filtering liquids, such as water.

A preferred use is for filter pressing, particularly for the removal of mud.

Another preferred use is for water filtration in very cold environments, for example in which the temperature is below 0°. A particular application is in water intake processes, in which water is taken from very cold water basins or waterways.

Another preferred use is for liquid/liquid separation, in particular for the separation of oil/water emulsions, which therefore consist of an aqueous phase and an oil phase.

Another subject matter of the invention is the use of the coated filter metal plate for the treatment of waste water, such as industrial waste water.

Embodiments and experiments illustrating the principles of the invention in reference to the following Figures will now be discussed.

#### Short description of the Figures

Figure 1. Vee-wire screens after adhesion test with mining mud heated to 50°C for 1 hour: sx) untreated sample; dx) sample treated with coating according to the invention.

Figure 2. Vee-wire screens after pilot filter pressing test with mining mud: sx) untreated sample; dx) sample treated with coating according to the invention.

Figure 3. Vee-wire screens after ice adhesion test under submerged conditions: a) untreated sample; b) sample treated with coating based solely on SiO<sub>2</sub>. c) sample treated with coating according to the invention.

Figure 4. Detachment effectiveness in anti-icing application.

5 Figure 5. Schematic illustration of oil-water separation through the filtering septum.

Figure 6. Separation test on a mixture with the following composition: water 90 ml and biodiesel 10 ml.

Figure 7. Contact angle measurements with water and n-hexadecane.

#### DETAILED DESCRIPTION OF THE INVENTION

10 A filter metal plate is understood as a plate of any dimensions and any metal capable of filtering liquids, such as water.

For the purpose of this invention, the term "metal" also includes metal alloys. Said metal may be steel, aluminum, titanium, copper, zinc, noble metals, and their alloys.

For purpose of this invention, a metal plate is understood as a plate of various shapes, for example flat or cylindrical. For purpose of this invention, a "screen" is synonymous with a  
15 plate. A non-continuous surface, such as a screen or metal grid, also falls within the definition of a metal plate according to the invention.

In a preferred embodiment, said filter metal plate is made of stainless steel, for example type A ISI 316.

20 In a preferred embodiment, said filter metal plate is a Vee-wire or V-wire plate. A Vee-wire plate is understood in particular as a plate, also referred to as a screen, having a flat or cylindrical shape, typically comprising a series of support rods around which is wound a continuous length of wire. An example of a Vee-wire plate is the one described in WO2018191611. Vee-wire plates are marketed by Aqseptence Srl.

25 A nanoparticle is understood as a particle having a diameter of between 1 and 500 nm.

The nanoparticles used in the invention are made of metal oxide. The metal oxide may be an oxide of silicon, aluminum, titanium, zinc, zirconium, yttrium, and cerium.

These nanoparticles may be synthesized according to known methods in the field or may be commercially available.

The SiO<sub>2</sub> nanoparticles may be synthesized according to known methods in the field; refer, for example, to references 12 and 13, or they may be commercially available. They may be used  
5 in the form of a suspension or a powder.

“Nanoparticles coupled with” means that there is a bond or an interaction, generally a non-covalent one, between the nanoparticles and the coupled component. In particular, the nanoparticles may be dispersed in a polymer matrix comprising the coupled component, optionally appropriately functionalized. Or the coating may consist of a first layer comprising  
10 the metal oxide nanoparticles and a second layer in contact with said first layer comprising the coupled component, for example the polymer.

The coating may comprise additional elements, for example elements that a person skilled in the art considers suitable for the specific application based on general knowledge in the field.

For the purpose of this invention, a “coating” is understood as a composition intended to fully  
15 or partially cover a surface, particularly a metal plate according to the invention. Coating and nanocoating are used here as synonyms.

In a first embodiment, the coating is composed of nanoparticles made of a metal oxide, such as SiO<sub>2</sub>, coupled with one or more fluoroalkylsilanes.

A fluoroalkylsilane is understood as a compound having the formula (RO-)<sub>3</sub>Si-R<sub>T</sub>, where R is  
20 hydrogen or an alkyl, for example a C<sub>1</sub>-C<sub>4</sub> alkyl, and R<sub>T</sub> is an organic compound that ends with a perfluoroalkyl group. For example, R<sub>T</sub> can be a C<sub>1</sub>-C<sub>12</sub> alkyl.

Examples of fluoroalkylsilanes are 1H,1H,2H,2H-perfluorodecyltriethoxysilane and 1H,1H,2H,2H-perfluorooctyl trimethoxysilane.

In a preferred embodiment the fluoroalkylsilane is the commercial compound SIVO, marketed  
25 for example by Evonik, under the name Dynasylan® SIVO. Various types of SIVO may also be used in this invention; for example, Dynasylan® SIVO 160, Dynasylan® SIVO 113, and/or Dynasylan® SIVO 110 may be used.

The coating may be obtained by applying an inorganic nanometric layer made by dispersing a suspension of metal oxide nanoparticles in water and subsequently an organic layer based on fluoroalkylsilane, dispersed for instance in alcohol.

5 The suspension of metal oxide nanoparticles, for example nano-SiO<sub>2</sub>, is preferably dispersed in water before application at a concentration of between 1% and 10% by weight, preferably between 2% and 6% by weight, and preferably 4% by weight.

The coating may be applied to the metal plate by means of dip-coating, i.e. dipping and removing at a controlled rate, by spraying or percolation with homogeneous contact with the surface being treated. All these methods are known in the field.

10 After the inorganic phase has been applied, the process may comprise a heat treatment, for example at 200°C for 1 hour; a heat treatment may also be applied after the organic phase has been applied, for example at 150°C for 30 minutes.

As an alternative to the heat treatment, the coating may be dried with a hot air stream.

15 In a preferred embodiment, the metal plate is subjected to a sandblasting treatment before the nanocoating is applied. Indeed, this treatment makes it possible to achieve better mud detachment results. The sandblasting treatment is understood as a mechanical process by which a spray of abrasive material particles, such as sand, is directed at a solid surface in order to modify the surface finish or shape, or to remove contaminants.

20 In a second embodiment, the invention calls for a coating of particles made of metal oxide, for example SiO<sub>2</sub>, coupled with one or more organosilane polymers.

An organosilane or organosilane polymer is understood as a polymer composed of one or more molecules containing silicon bound to carbon chains.

25 Examples of organosilane polymers are polysilanes, polysiloxanes, polysilazanes, polyalkylsilanes, polyarylsilanes, or their mixtures. The polymers may be of variable length, for example comprising 1 to 50 repeated units. The polymer may be appropriately functionalized according to known knowledge and methods in the field.

In a preferred embodiment, the metal oxide nanoparticles are coupled with organosilanes.

For example, in addition to the metal oxide nanoparticles, the coating may comprise a commercial product called Metalcoat marketed by Chem Spec Srl. (trade name TECNADIS

METALCOAT BASE), that comprises ceramic nanoparticles and organosilanes in an alcohol suspension.

The coating may comprise additional components, for example components that improve the effectiveness of the coating.

- 5 In a preferred embodiment, said coating comprises an additional component, called an enhancer, comprising a diluted solution of acetic acid in ethanol, which acts as an acid catalyst. An example of an enhancer is known by the trade name TECNADIS METALCOAT ENHANCER, marketed by Chem Spec Srl.

- 10 In a preferred embodiment, the coating of the filter metal plate is composed of SiO<sub>2</sub> nanoparticles, Metalcoat, and enhancer.

The coating may be obtained by first applying an inorganic nanometric layer made by dispersing a suspension of metal oxide nanoparticles, for example SiO<sub>2</sub>, in water, and subsequently a layer comprising the organosilane, for instance dispersed in alcohol, optionally together with an enhancer.

- 15 In one embodiment, the layer comprising the organosilane also comprises additional metal oxide nanoparticles, for example SiO<sub>2</sub> nanoparticles.

The suspension of nano-SiO<sub>2</sub> is preferably dispersed in water at a concentration of between 1% and 10% by weight, preferably between 2% and 6% by weight, and preferably 4% by weight.

- 20 The coating may be applied to the metal plate by means of dip-coating, i.e. dipping and removing at a controlled rate, by spraying or percolation with homogeneous contact with the surface being treated.

After the first layer comprising nano-SiO<sub>2</sub> has been applied, the process may comprise a heat treatment, for example at 200°C for 1 hour; a heat treatment may also be applied after

- 25 application of the layer comprising the organosilane, such as Metalcoat, for example at 170°C for 30 minutes.

As an alternative to the heat treatment, the coating may be dried with a hot hair stream.

In a third embodiment, the invention calls for a coating comprising nanoparticles made of metal oxide, for example  $\text{SiO}_2$ , coupled with a polymer matrix functionalized with fluorinated molecules or groups.

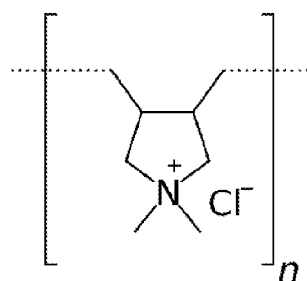
The polymer matrix may be made of a polymer selected from polydiallyldimethyl ammonium chloride, polydimethylsiloxane, for example Sylgard 184 silicone, methyltrimethoxysilane, methyltriacetoxysilane, perfluoropolyether, and chitosan-polyvinyl alcohol.

These fluorinated molecules or groups may be, for example, perfluorooctanoic acid, anionic fluorosurfactant, 1H,1H,2H,2H-perfluorooctyltriethoxysilane, or derivatives thereof.

In one embodiment, this coating is obtained by precipitation of a suspension of metal oxide nanoparticles in poly(diallyldimethylammonium chloride) (PDMA) and perfluorooctanoic acid, and subsequent dispersion in an alcoholic solvent.

In another embodiment, this coating is obtained by precipitation of a suspension of metal oxide nanoparticles in poly(diallyldimethylammonium chloride) (PDMA) and an anionic fluorosurfactant, and subsequent dispersion in an alcoholic solvent.

The poly(diallyldimethylammonium chloride) (PDMA) is composed of repeated units having the formula shown in the following Diagram 1:



**Diagram 1** – Repetitive unit of poly(diallyldimethylammonium chloride)

The anionic fluorosurfactant preferably has the formula  $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{O}(\text{PO}_2)\text{O}(\text{CH}_2)_3\text{OH}$ .

Suitable anionic fluorosurfactants are commercially available, for example Capstone FS-63 sold by DuPont. Other fluorosurfactants in the Capstone series marketed by DuPont may also be used.

The perfluorooctanoic acid has the formula  $\text{CF}_3(\text{CF}_2)_6\text{COOH}$ .

In one embodiment, the invention calls for a filter metal plate coated with a composition obtained by precipitating a suspension of SiO<sub>2</sub> nanoparticles in poly(diallyldimethylammonium chloride) (PDDA) and perfluorooctanoic acid, and subsequent dispersion in an alcoholic solvent. More specifically, this composition may be obtained as described below:

in an aqueous medium, SiO<sub>2</sub> nanoparticles are dispersed in diluted PDDA and subsequently treated with ultrasound for 30 minutes, then a perfluorooctanoic acid solution is added drop by drop; the precipitate is separated and washed with water, and then dried. In order to obtain the powder, the product may be ground, for example manually with a mortar and pestle, to obtain a fine and readily-dispersible solid.

At the time of deposition on the plate, the precipitate obtained as described above is dispersed in an alcoholic solvent, preferably ethanol at a concentration of 1% w/v, for example, and preferably treated with ultrasound.

In another embodiment, the invention calls for a filter metal plate coated with a composition obtained by precipitating a suspension of SiO<sub>2</sub> nanoparticles in poly(diallyldimethylammonium chloride) (PDDA) and an anionic fluorosurfactant, and subsequent dispersion in an alcoholic solvent. More specifically, this composition may be obtained as described below:

in an aqueous medium, the anionic fluorosurfactant and the SiO<sub>2</sub> nanoparticle powder are added to a diluted suspension of poly(diallyldimethylammonium chloride) (PDDA). The suspension is treated with ultrasound for 1 hour and the precipitate is washed and dried. The resulting powder may be ground, for example manually with a mortar and pestle, to obtain a fine and readily-dispersible solid.

At the time of deposition on the plate, the precipitate obtained as described above is dispersed in an alcoholic solvent, preferably ethanol at a concentration of 1% w/v, for example, and preferably treated with ultrasound.

The coating may be applied to the metal plate by means of dip-coating, i.e. dipping and removing at a controlled rate, by spraying or percolation with homogeneous contact with the surface being treated.

Preferably, the coated surface is subjected to a heat treatment to consolidate the adhesion of the coating, for example at a temperature of 150°C for 30 minutes.

After dip-coating, it is preferable to wait at least 10 minutes at room temperature to allow the solvent to slowly evaporate, thus reducing the stress and tensions on the coating during the evaporation of a large volume of solvent when heated.

Preferably, the coating may be reapplied, for instance two or three times. Indeed, multiple  
5 applications make it possible to achieve better and more homogeneous properties on the surface, leading to improved performance.

Simple synthesis processes and the use of off-the-shelf products as raw materials make these coatings simple and easily scalable to larger facilities.

The plates of the invention may be used advantageously for filtering liquids, such as water,  
10 particularly for solid/liquid separation.

A preferred embodiment is filter pressing. Filter pressing is understood as reducing the volume of liquid substances that contain suspended solids within them, particularly mud.

The plates may also be used advantageously for filtering water in very cold environments, for example in which the temperature is below 0°C.

15 In addition, they may be used advantageously for separating oil/water emulsions, i.e. consisting of an aqueous phase and an oil phase. In particular, they may be used in waste water treatment, for example waste from industrial plants.

The invention also relates to a kit for preparing the coatings described herein.

The kit may comprise, for example:

- 20     a) metal oxide nanoparticles as defined earlier; and  
       b) a composition comprising at least one fluoroalkylsilane or organosilane or one or more polymers functionalized with fluoroalkylsilanes and/or organosilanes; or  
       b') at least one polymer and at least one compound containing fluorinated molecules or groups.

25 Preferably, said polymer in b') is a polymer selected from poly (diallyldimethylammonium chloride), polydimethylsiloxane, for example Sylgard 184 silicone, methyltrimethoxysilane, methyltriacetoxysilane, perfluoropolyether and chitosan-polyvinyl alcohol and/or said fluorinated molecules or groups are selected from perfluorooctanoic acid, anionic

fluorosurfactant, 1H,1H,2H,2H-perfluorooctyltriethoxysilane, or molecules or groups derived therefrom.

The kit may further comprise instructions for obtaining the coating and for applying the coating to a filter metal plate.

- 5 The following examples further illustrate the invention.

## EXAMPLES

### Example 1

#### Effect of coatings on Vee-wire screens for filter pressing with respect to mud detachment

##### Materials and methods

- 10 a) *Preparation of type a coatings ( $\text{SiO}_2$  + fluoroalkylsilane)*

The Vee-wire screens made of stainless steel (AISI 316) may be modified (improved condition, but not necessary for achieving good detachment) in their microstructural texture by sandblasting treatment and subsequent coating with the coating based on inorganic nanoparticles coupled with fluoroalkylsilane.

- 15 Inorganic nanoparticles of  $\text{SiO}_2$  dispersed in an aqueous solvent (commercial product LUDOX HS 40) at a dilution of 4% wt are applied to the Vee-wire screens.

- To compare the effect of the microstructural texture, comparisons are made between non-sandblasted Vee-wire plates with a surface roughness of  $\text{Sa} = 0.16 \mu\text{m}$  labeled TQ, sandblasted plates with a surface roughness of  $\text{Sa} = 0.83 \mu\text{m}$  labeled R1, and sandblasted plates with a  
20 surface roughness of  $\text{Sa} = 1.74 \mu\text{m}$  labeled R3.

Then comes application of the polymer phase, a commercial product based on fluoroalkylsilane (SIVO, Evonik) dispersed in isopropyl alcohol.

- $\text{SiO}_2$  and fluoroalkylsilane are deposited on the Vee-wire plates by dip-coating (dipping and removal at a controlled rate of 2 mm/s, with a hold time of 5 seconds for the inorganic  
25 suspensions and 120 seconds for the polymers). Application can also be done by spraying or percolation, which requires homogeneous contact with the surfaces.

Once the inorganic phase has been applied, the process calls for a heat treatment at  $200^\circ\text{C}$  for 1 hour, whereas in the case of the polymers it is  $150^\circ\text{C}$  for 30 minutes. In the case of hybrid coatings combining an inorganic phase with polymers ( $\text{SiO}_2$ /fluoroalkylsilane), both heat

treatments follow the two applications. The resulting samples with different roughnesses are called: SiO<sub>2</sub>\_SIVO, SiO<sub>2</sub>\_SIVO\_R1, SiO<sub>2</sub>\_SIVO\_R3.

*b) Preparation of type b coatings (SiO<sub>2</sub> + fluoroalkylsilane without heat treatment)*

This preparation is conducted according to the same method as example 1a) on non-sandblasted substrates, but without heat treatment, once the SiO<sub>2</sub> and SIVO have been applied; the surfaces are dried with a hot air stream. The resulting sample is called TQ-SiS-1T-1.

*c) Preparation of type c coatings (comparison polymers)*

This preparation is conducted according to the same method as example 1a) but with only the polymer coating being applied to the surface of the screen. Various types of polymer are compared: fluoroalkylsilane called SIVO (Evonik), water-based fluorinated acrylic resin called AFW (Dupont), two methylsilicone resins in isopropyl alcohol called DIS1 and DIS2 (Chem Spec). The samples thus produced on non-sandblasted Vee-wire screens are called: TQ SIVO, TQ AFW, TQ DIS1, TQ DIS2.

*d) Preparation of type d coatings (SiO<sub>2</sub>)*

This preparation is conducted according to the same method as example 1a) on a non-sandblasted surface, but without application of fluoroalkylsilane. The resulting sample is called SiO<sub>2</sub>\_Hydrophilic.

*e) Preparation of type e coatings (fluoroalkylsilane on surfaces with different surface roughnesses)*

Non-sandblasted and sandblasted Vee-wire screens with different roughnesses were treated with fluoroalkylsilane (SIVO) according to the method of example 1a). The resulting samples are called: TQ\_SIVO, SIVO\_R1, SIVO\_R2.

*f) Preparation of type f coatings (Al<sub>2</sub>O<sub>3</sub> + fluoroalkylsilane)*

Al<sub>2</sub>O<sub>3</sub> nanoparticles were obtained by means of sol/gel synthesis in isopropyl alcohol according to the procedure described in WO2013190587, then subsequently applied to the metal screens and treated with the fluoroalkylsilane polymer SIVO (Evonik) according to the same method as example 1a) as example 1a).

*g) Preparation of type g coatings (TiO<sub>2</sub> + fluoroalkylsilane)*

TiO<sub>2</sub> nanoparticles are in a 4% wt aqueous suspension corresponding to PARNASOS PH000026 commercial product (Colorobbia group); they are applied to the metal screens and are treated

with the fluoroalkylsilane polymer SIVO (Evonik) according to the same method as example 1a. The resulting sample is called TN\_SIVO.

Table 1 shows a list of samples prepared to study the detachment of the metal screens.

**Table 1** – Samples prepared as described above.

|                                              | Label                                | Surface finish | Nanoparticles                  | Polymer   |
|----------------------------------------------|--------------------------------------|----------------|--------------------------------|-----------|
| Various roughnesses,<br>no coating           | NT (not treated)                     | TQ (as is)     | -                              | -         |
|                                              | NT_R1                                | Roughness 1    | -                              | -         |
|                                              | NT_R3                                | Roughness 3    | -                              | -         |
| Various polymers                             | TQ SIVO                              | TQ             | -                              | SIVO      |
|                                              | TQ AFW                               | TQ             | -                              | AFW       |
|                                              | TQ DIS1                              | TQ             | -                              | Distacc_1 |
|                                              | TQ DIS2                              | TQ             | -                              | Distacc_2 |
| SIVO on various<br>roughnesses               | TQ SIVO                              | TQ             | -                              | -         |
|                                              | SIVO_R1                              | Roughness 1    | -                              | SIVO      |
|                                              | SIVO_R2                              | Roughness 3    | -                              | SIVO      |
| Hydrophilic                                  | Hydrophilic SiO <sub>2</sub>         | TQ             | SiO <sub>2</sub>               |           |
| SiO <sub>2</sub> SIVO<br>Various roughnesses | SiO <sub>2</sub> _Sivo               | TQ             | SiO <sub>2</sub>               | SIVO      |
|                                              | SiO <sub>2</sub> Sivo_R1             | Roughness 1    | SiO <sub>2</sub>               | SIVO      |
|                                              | SiO <sub>2</sub> Sivo_R3             | Roughness 3    | SiO <sub>2</sub>               | SIVO      |
| Al <sub>2</sub> O <sub>3</sub>               | Al <sub>2</sub> O <sub>3</sub> _SIVO | TQ             | Al <sub>2</sub> O <sub>3</sub> | SIVO      |
| TiO <sub>2</sub>                             | TN_SIVO                              | TQ             | TiO <sub>2</sub>               | SIVO      |

5

#### *Physical, chemical and functional characterization*

The prepared samples were characterized in terms of their **surface roughness** and **wettability** by determining their contact angles with water and n-hexadecane, and surface energy. All collected measurements are the result of an average of at least 5 values taken in various areas of the screen so as to map the entire surface.

10

The functional characterizations are defined as such since they were implemented to assess the performance of the materials while simulating the operating conditions in which they are to be used. In particular, two types of functional characterizations were developed; both call for the presence of mud in contact with the surfaces to test the effect of the coatings on mud detachment during filter pressing.

15

Dry detachment (tested on RED MUD): after homogenization of the mud with gentle stirring for 24 hours (rotation on rollers), 3 g of the mud are deposited on a screen slide that is then placed in a ventilated oven at 50°C for 1 hour.

After the heating, mud detachment is assessed by lifting the sample to a 90° vertical position and shaking it until detachment occurs. The tests are always conducted by comparing the coatings to an as-is untreated sample. The comparison comprises a video analysis of the detachment dynamics. The samples were categorized by assigning a score based on a the resulting percentage of detachment area and number of impacts required to obtain the detachment according to the diagram in Table 2.

10 **Table 2** – Evaluation table used to assess DRY DETACHMENT in the presence of mud

| Evaluation table <u>DRY DETACHMENT</u> |              |                |
|----------------------------------------|--------------|----------------|
| Score                                  | clean area % | no. of impacts |
| 0                                      | 0-10%        | ~ 50-70        |
| 1                                      | 10-30%       | ~ 50-70        |
| 2                                      | 30-70%       | ~ 50-70        |
| 3                                      | 70-100%      | ~ 50-70        |
| Score                                  | clean area % | no. of impacts |
| 4                                      | 0-10%        | ~ 1-5          |
| 5                                      | 10-30%       | ~ 1-5          |
| 6                                      | 30-70%       | ~ 1-5          |
| 7                                      | 70-100%      | ~ 1-5          |

Detachment under pressure (tested on RED MUD and MORELOS MUD): After homogenization of the mud in a turbola (20 min), 10 g of mud are appropriately dried and deposited in the middle of two screen slides, which are then pressed by means of a uniaxial press at about **40 bars for 60 minutes, simulating filter pressing conditions**. The detachment evaluation is done by video analysis of the detachment dynamics and the samples are categorized by assigning a score based on the number of impacts required for sliding to occur and for the resulting cake to ultimately become detached.

**Table 3** – Evaluation table used to assess DETACHMENT under PRESSURE

| EVALUATION TABLE<br><u>DETACHMENT under PRESSURE</u> |
|------------------------------------------------------|
|------------------------------------------------------|

5

| Score | no. of impacts for |            |
|-------|--------------------|------------|
|       | sliding            | Detachment |
| 0     | >10                | NO         |
| 1     | <10                | NO         |
| 2     | >10                | YES        |
| 3     | <10                | YES        |
| 4     | <5                 | YES        |

### Results and Discussion

#### 10 Roughness

The surface roughness of samples sandblasted with two different sand particle sizes (**NT\_R1**, **NT\_R3**) were measured and compared to the as-is sample without surface treatment.

The more significant determined parameters are:

- **Sa** (*Surface roughness*), extent of Ra on the surface. Assigns an absolute value to the difference in height between each point and the median line of the surface;
- **Sz** (*surface texture*), defined as the sum of the 5 highest peaks plus the 5 deepest valleys within the area considered.

**Table 4** – Surface roughnesses measured after the various sandblasting treatments

| Label | Finish      | Sa_Surface Roughness (µm) | Sz_Surface Texture (µm) |
|-------|-------------|---------------------------|-------------------------|
| NT    | TQ          | 0.16 ± 0.02               | 1.8 ± 0.4               |
| NT_R1 | Roughness 1 | 0.83 ± 0.16               | 11.9 ± 2.6              |
| NT_R3 | Roughness 3 | 1.74 ± 0.34               | 20.8 ± 4.8              |

20

As expected, the results show increasing values of both surface roughness and surface texture, which is also observed in the surface mapping obtained from the instrument.

#### Wettability

Table 5 shows the wettability results from the samples.

25 **Table 5** – Primary wettability characteristics measured on prepared samples (drop volume 10 µl)

|                                                 | Sample                                | CA°<br>H <sub>2</sub> O | CA°<br>n-hexadecane | Surface energy<br>(mN/m) |
|-------------------------------------------------|---------------------------------------|-------------------------|---------------------|--------------------------|
| Various roughnesses<br>no coating               | TQ                                    | 61.5 ± 6.5              | <10                 | N/A                      |
|                                                 | TQ_R1                                 | 74.5 ± 2.9              | <10                 | N/A                      |
|                                                 | TQ_R3                                 | 84.2 ± 7.7              | <10                 | N/A                      |
| Various polymers                                | TQ_SIVO                               | 105.4 ± 0.5             | 69.0 ± 4.2          | 14.6 ± 1.6               |
|                                                 | TQ_AFW                                | 110.9 ± 3.7             | 71.9 ± 0.9          | 12.7 ± 0.9               |
|                                                 | TQ_D1                                 | 100.4 ± 1.8             | 35.1 ± 5.4          | 23.6 ± 1.7               |
|                                                 | TQ_D2                                 | -                       | -                   | -                        |
| SIVO on various<br>roughnesses                  | TQ_SIVO                               | 105.4 ± 0.5             | 69.0 ± 4.2          | 14.6 ± 1.6               |
|                                                 | SIVO_R1                               | 111.4 ± 6.7             | 72.0 ± 3.4          | 12.6 ± 2.1               |
|                                                 | SIVO_R2                               | 122.4 ± 9.2             | 69.5 ± 2.5          | 12.4 ± 0.8               |
| SiO <sub>2</sub> SIVO<br>Various roughnesses    | SiO <sub>2</sub> SIVO                 | 123.9 ± 3.8             | 80.3 ± 3.7          | 9.3 ± 1.2                |
|                                                 | SiO <sub>2</sub> _SIVO_R1             | 118.3 ± 4.3             | 57.5 ± 11.3         | 16.0 ± 3.5               |
| Al <sub>2</sub> O <sub>3</sub> SIVO             | Al <sub>2</sub> O <sub>3</sub> + SIVO | 123.8 ± 10.9            | 79.3 ± 13.0         | 9.6 ± 4.0                |
| Hydrophilic SiO <sub>2</sub>                    | Si_hydro                              | <10                     | <10                 | -                        |
| SiO <sub>2</sub> SIVO without heat<br>treatment | TQ-SiS-1T-1                           | 110.2 ± 4.7             | 71.4 ± 2.4          | 13.0 ± 1.6               |
| TiO <sub>2</sub>                                | TN_SIVO                               |                         |                     |                          |

In general, the wettability results obtained with the various prepared samples show a marked variation in repellency to water and n-hexadecane between the as-is and treated samples, as evidenced by the increases in the contact angle (n-hexadecane was chosen for its low surface tension in order to simulate oleophobia). The increased roughness caused by sandblasting already leads to an increased contact angle with water, which goes from a value of 61° to 81° from sample TQ to sample TQ\_R3. This trend confirms the Wenzel model known from the literature (14). The increased roughness alone, however, does not influence repellency to n-hexadecane, which is much harder to repel in light of the low surface tension. The samples with the highest contact angles to water are the samples containing fluoroalkylsilane (SIVO), SiO<sub>2</sub>-SIVO, Al<sub>2</sub>O<sub>3</sub> SIVO, R3\_SIVO, and among these the ones with a low surface energy, probably caused by a more homogeneous surface nanostructuring, are SiO<sub>2</sub>-SIVO and Al<sub>2</sub>O<sub>3</sub>\_SIVO.

Hot detachment (RED MUD dried at 50°C)

Hot detachment was assessed by analyzing the videos of each sample after the mud was dried on the screens. In particular, a score is assigned to each sample according to the evaluation table in Table 2 in order to obtain a ranking between the coatings indicating a greater or lesser aptitude for detachment. In every case, each set of tests was conducted with an as-is untreated sample; in addition, the coatings were tested several times to check the reproducibility of the results.

Table 6 shows the overall results of the test, with scores ranging from 1 (for very poor performance) to 7 (for excellent performance).

An overall evaluation of the results shows that the as-is untreated samples confirm a marked trend toward sticking of the mud, which is also confirmed by several consecutive tests. Increased roughness by itself also appears to have a negative impact on performance when there is no coating (perhaps due to an increase in the gripping surface area of the mud), whereas there appears to be no difference with a hydrophobic coating. The hydrophilic coating does not achieve detachment, confirming the need for water repellency.

From this test, the samples that are best at detaching RED MUD are the ones containing SIVO: TQ\_SIVO, R1\_SIVO, R3\_SIVO, AI\_SIVO, and Si\_SIVO; indeed, it seems that the fluorinated polymer plays an important role in the detachment of solids. Polymers D1 and D2 have demonstrated good detachment but not always repeatable, despite the excellent score. However, the coating based on TiO<sub>2</sub> does not appear to perform well, even when coupled with SIVO.

Figure 1 shows the images of two samples after the detachment test: the as-is sample on the left and the Si\_SIVO-treated sample on the right.

**Table 6 – Performance evaluation with regard to RED MUD hot detachment**

|                       | Samples | Impacts<br>(no.) | Detachment area<br>(%) | Score |
|-----------------------|---------|------------------|------------------------|-------|
| As-is reproducibility | TQ      | 53               | 50                     | 2     |
|                       | TQ      | 53               | 50                     | 2     |
|                       | TQ      | 52               | 50                     | 2     |
| Various roughnesses   | TQ      | 77               | 60                     | 2     |
|                       | NT_R1   | 67               | 60                     | 2     |
|                       | NT_R3   | 73               | 20                     | 1     |
| Various polymers      | TQ_SIVO | 1_2              | 100                    | 7     |
|                       | TQ_AFW  | 1_5              | 100                    | 7     |

|                          |                   |            |            |          |
|--------------------------|-------------------|------------|------------|----------|
|                          | <i>TQ_D1</i>      | <i>1_5</i> | <i>100</i> | <i>7</i> |
|                          | <i>TQ_D2</i>      | <i>1_5</i> | <i>100</i> | <i>7</i> |
| SIVO various roughnesses | <i>TQ_SIVO</i>    | 10         | 90         | 5        |
|                          | <i>R1_SIVO</i>    | 1          | 100        | 7        |
|                          | <i>R3_SIVO</i>    | 1          | 100        | 7        |
| Various coatings         | <i>SiO2_IDRO</i>  | 50         | 20         | 1        |
|                          | <i>TiO2_SIVO</i>  | 53         | 70         | 2        |
| SiO2 reproducibility     | <i>Si_SIVO</i>    | 1          | 100        | 7        |
|                          | <i>Si_SIVO</i>    | 1          | 100        | 7        |
|                          | <i>Si_SIVO</i>    | 1          | 100        | 7        |
|                          | <i>TQ_SIVO</i>    | 1          | 100        | 7        |
| Best coatings            | <i>TQ_SIVO</i>    | <i>1_2</i> | 100        | 7        |
|                          | <i>Si_SIVO</i>    | <i>1_2</i> | 100        | 7        |
|                          | <i>Al2O3_SIVO</i> | <i>1_2</i> | 100        | 7        |

#### Detachment under pressure (RED MUD under 40 bars of pressure)

- Detachment under pressure was evaluated by analyzing the videos recorded after opening the two screens (10 x 5 cm), one placed above the other, after remaining under pressure (40 bars, 1 hour) in the presence of mud (10 g). Here again, a score was assigned to each sample according to evaluation Table 3, after observing the detachment dynamics. The objective was to arrive at a ranking between the coatings indicating of the greater or lesser aptitude for detachment, simulated in this case by applying pressure to the screens. The coatings were tested several times to check the reproducibility of the results.
- Table 7 shows the overall results of the test, with scores ranging from 0 (for very poor performance) to 4 (for excellent performance).

**Table 7** – Performance evaluation with regard to detachment under pressure of RED MUD

|                     | Samples | No. of impacts for sliding | Detachment | Score |
|---------------------|---------|----------------------------|------------|-------|
| Various roughnesses | TQ      | 20                         | X - NO     | 0     |
|                     | NT_R1   | 22                         | X - NO     | 0     |
|                     | NT_R3   | 3                          | X - NO     | 1     |
|                     | TQ_SIVO | 8-10                       | V - YES    | 3     |
| Various polymers    | TQ_AFW  | 20                         | X - NO     | 0     |
|                     | TQ_D1   | 26                         | X - NO     | 0     |
|                     | TQ_D2   | 15-20                      | X - NO     | 0     |
|                     | TQ_SIVO | 8-10                       | V - YES    | 3     |

|                                |                       |     |                |          |
|--------------------------------|-----------------------|-----|----------------|----------|
| SIVO various roughnesses       | <b>R1_SIVO</b>        | 8   | <b>V - YES</b> | <b>3</b> |
|                                | <b>R3_SIVO</b>        | 6-8 | <b>V - YES</b> | <b>3</b> |
|                                | <b>Si_Hydrophilic</b> | 15  | <b>V - YES</b> | <b>2</b> |
| Si SIVO on various roughnesses | <b>Si_SIVO</b>        | 4   | <b>V - YES</b> | <b>4</b> |
|                                | <b>Si_SIVO R1</b>     | 5   | <b>V - YES</b> | <b>4</b> |
|                                | <b>Si_SIVO R3</b>     | 5   | <b>V - YES</b> | <b>4</b> |
| Al Sivo                        |                       |     |                | <b>0</b> |
|                                | <b>Al_SIVO</b>        | 20  | <b>X - NO</b>  |          |

The overall evaluation of the results shows that the untreated as-is samples confirm a marked tendency toward adhesion of the pressed mud, which does not detach and does not start to slide, even after repeated impacts, thus confirming the behavior observed for dry detachment.

Unlike the dry tests, in this case improved detachment is observed for the greater roughness, which may be due to less adhesion caused by the presence of surface inhomogeneity despite the larger gripping surface. Polymers D1 and D2 do not confirm the good performance obtained in the dry tests, likewise for the sample containing  $\text{Al}_2\text{O}_3$  (Al\_SIVO). The Si\_SIVO samples applied to the Various roughnesses are confirmed as good performers and SIVO alone applied to the as-is surface (TQ\_SIVO) as well as the sandblasted surfaces (R1\_SIVO, R3\_SIVO). The hybrid coating coupling the  $\text{SiO}_2$  nanostructure with the fluorinated polymer broken down according to the various roughnesses (Si\_SIVO, Si\_SIVO R1, Si\_SIVO R3) is better than SIVO alone (TQ\_SIVO, R1\_SIVO, R3\_SIVO) with a score of 4 versus 3. With regard to SIVO alone in the evaluation of the impacts required to cause detachment, there is a slight improvement in performance as the roughness increases, that is, going from TQ-SIVO to R3\_SIVO.

#### Detachment under pressure (Morelos mud under 40 bars of pressure)

The detachment tests under pressure on Morelos mud were conducted by following the same procedure as for RED MUD, but only testing the most promising coatings (Si\_SIVO). Furthermore, in this case the same pairs of screens were tested repeatedly to evaluate their durability over various cycles.

Table 8 shows the results. Optimum performance is observed for the selected coatings, showing a good capacity for reuse. The untreated as-is samples confirm a poor capacity for detachment. When observing the performance of Si\_SIVO, the best results appear to be achieved with the as-is surface finish and R3 (greater roughness). The results obtained by the

non-heat-consolidated sample (Si\_SIVO\_T1) reused for multiple cycles, also seem comparable.

**Table 8** – Performance evaluation with regard to detachment under pressure of MORELOS mud

|                                    | Samples         | No. of impacts for sliding | Detachment | Score | Score Average |
|------------------------------------|-----------------|----------------------------|------------|-------|---------------|
|                                    | TQ              | 30                         | X-NO       | 0     | 0.7           |
|                                    | TQ_1rip         | 27                         | X-NO       | 0     |               |
|                                    | TQ_2rip         | 20                         | V-YES      | 2     |               |
| SIVO on various roughnesses        | TQ_SIVO         |                            | ND         |       |               |
|                                    | R1_SIVO         |                            | ND         |       |               |
|                                    | R3_SIVO         |                            | ND         |       |               |
| Reused Si SIVO                     | Si_SIVO         | 5                          | V-YES      | 4     | 3.8           |
|                                    | Si_SIVO_1rip    | 5                          | V-YES      | 4     |               |
|                                    | Si_SIVO_2rip    | 5                          | V-YES      | 4     |               |
|                                    | Si_SIVO_3rip    | 10                         | V-YES      | 3     |               |
|                                    | Si_SIVO_4rip    | 4                          | V-YES      | 4     |               |
| Si SIVO R1 and reuse               | Si_SIVO R1      | 12                         | V-YES      | 2     | 3             |
|                                    | Si_SIVO R1_1rip | 5                          | V-YES      | 4     |               |
|                                    | Si_SIVO R1_2rip | 14                         | V-YES      | 2     |               |
|                                    | Si_SIVO R1_3rip | 4                          | V-YES      | 4     |               |
|                                    | Si_SIVO R1_4rip | 9                          | V-YES      | 3     |               |
| Si SIVO R3 and reuse               | Si_SIVO R3      | 7                          | -YES       | 3     | 3.8           |
|                                    | Si_SIVO R3_1rip | 1                          | -YES       | 4     |               |
|                                    | Si_SIVO R3_2rip | 1                          | -YES       | 4     |               |
|                                    | Si_SIVO R3_3rip | 5                          | V-YES      | 4     |               |
|                                    | Si_SIVO R3_4rip | 5                          | V-YES      | 4     |               |
| Non-consolidated Si SIVO and reuse | Si_SIVO T1      | 4                          | V-YES      | 4     | 3.6           |
|                                    | Si_SIVO T1_1rip | 10                         | V-YES      | 3     |               |
|                                    | Si_SIVO T2_2rip | 7                          | V-YES      | 4     |               |
|                                    | Si_SIVO T3_3rip | 4-5                        | V-YES      | 4     |               |
|                                    | Si_SIVO T4_4rip | 5-6                        | V-YES      | 3     |               |

5

The Si\_SIVO\_R3 and Si\_SIVO coatings were applied to 50x50 cm Vee-wire screens for applications in filter pressing pilot plants, and have also shown optimum mud detachment results on a pilot scale, including with repeated consecutive cycles, consistent with the functional characterization determined in the laboratory.

- 10 Figure 2 shows the detachment test results on a pilot scale, highlighting the difference between an untreated Vee-wire screen (on the left) and a screen treated with Si\_SIVO\_R3 (on the right).

### Example 2

#### Effect of anti-ice coatings on Vee-wire screens for water intake

## Materials and methods

### *a) Preparation of type a coatings (SiO<sub>2</sub> + polymer)*

The Vee-wire screens made of stainless steel (AISI 316) are coated with a coating based on inorganic nanoparticles coupled with various types of polymers. Inorganic nanoparticles of SiO<sub>2</sub> dispersed in an aqueous solvent (commercial product LUDOX HS 40) at a dilution of 4% wt are applied to the Vee-wire screens.

A layer of commercial polymer, enriched in some cases with inorganic phases, is then applied. In order to evaluate the effect of the type of polymer coupled with SiO<sub>2</sub>, various commercial polymers as listed below were applied: fluoroalkylsilane (SIVO, Evonik), polysilazane (A1220, Chem Spec), silicone elastomer (NUSIL R-2180, Avantor), oxide micro nanoparticles in propylene glycol methyl ether (NANOMYTE SuperAi, NEI Corporation), and organosilane in an 8% wt alcohol suspension activated with an acid catalyst (METALCOAT+enhancer, Chem Spec). The SiO<sub>2</sub> and polymers are deposited on the Vee-wire plates by dip-coating (dipping and removal at a controlled rate of 2 mm/s, with a hold time of 5 seconds for the inorganic suspensions and 120 seconds for the polymers). Application can also be done by spraying or percolation, which requires homogeneous contact with the surfaces.

Once the inorganic phase has been deposited, the process calls for a heat treatment at 200°C for 1 hour. For the polymers, however, the heat treatments are as follows:

SIVO 150°C for 30 minutes, A1220 180°C for 1 hour, NuSil R-2180 75°C for 45 minutes and 150°C for 135 minutes, NANOMYTE SuperAi 105°C for 15 minutes, Metalcoat 170°C for 30 minutes and enhancer applied after under the same conditions.

The resulting samples are called: LUDOX+SIVO, LUDOX+A1220, LUDOX+NuSil, LUDOX+Nanomyte, LUDOX+Metalcoat+enhancer.

### *b) Preparation of type d coatings (SiO<sub>2</sub>)*

This preparation is conducted according to the same method as example 2a), but without a subsequent polymer application. The resulting sample is called LUDOX.

### *c) Preparation of type c coatings (comparison polymers)*

This preparation is conducted according to the same method as example 2a) but with only the polymer coating being applied to the surface of the screen. The various types of polymer were compared: polysilazane (A1220, Chem Spec), silicone elastomer (NUSIL R-2180, Avantor), oxide micro nanoparticles in propylene glycol methyl ether (NANOMYTE SuperAi, NEI

Corporation), and organosilane in an 8% wt alcohol suspension activated with an acid catalyst (METALCOAT+enhancer, Chem Spec).

The heat treatments after application were done according to the method indicated in example 2a) for the various polymer phases.

- 5 The samples thus produced on Vee-wire screens are called: A1220, Nanomyte, NuSil, and Metalcoat+enhancer.

*d) Preparation of type d coatings ( $Al_2O_3$  with silicone oils)*

- 10 The  $Al_2O_3$  nanoparticles were made by sol/gel synthesis in isopropyl alcohol according to the procedure described in WO2013190587, and were then applied to the metal screens treated with the fluoroalkylsilane polymer SIVO (Evonik) according to the method of example 2a) and infused with silicone oil (Sigma Aldrich, 100 cSt) with an immersion time of 5 minutes and then percolating the excess for 48 hours at ambient temperature. The sample thus produced on Vee-wire screens is called:  $Al_2O_3$ +SIVO+100cSt silicone oil.

Table 9 summarizes all the samples prepared for testing in the anti-frazil ice application.

- 15 **Table 9** – Summary of all prepared and tested coatings

| Sample                                               | Type of coating                    |
|------------------------------------------------------|------------------------------------|
| <b>LUDOX+SIVO</b>                                    | $SiO_2$ + Polymer                  |
| <b>LUDOX+A1220</b>                                   | $SiO_2$ + Polymer                  |
| <b>LUDOX+Nanomyte</b>                                | $SiO_2$ + Polymer                  |
| <b>LUDOX+NuSil</b>                                   | $SiO_2$ + Polymer                  |
| <b>LUDOX+Metalcoat+enhancer</b>                      | $SiO_2$ + Polymer                  |
| <b>LUDOX</b>                                         | $SiO_2$                            |
| <b>A1220</b>                                         | Polymer                            |
| <b>Nanomyte</b>                                      | Polymer                            |
| <b>Primer+Nanomyte</b>                               | Polymer                            |
| <b>NuSil</b>                                         | Polymer                            |
| <b>Metalcoat+enhancer</b>                            | Polymer + Acidic activator         |
| <b><math>Al_2O_3</math>+SIVO+100cSt Silicone oil</b> | $Al_2O_3$ + Polymer (Silicone Oil) |

Physical, chemical and functional characterization

- 20 Wettability is a physical property that may be correlated indirectly to the anti-ice capability. Consequently, the static contact angles (CA) with water and n-hexadecane, drop mobility (hysteresis of the contact angle, HCA), and surface energy of the samples were evaluated. All collected measurements are the result of an average of at least 3 values taken in various areas of the screen so as to map the entire surface.

The functional characterization aims to evaluate the performance of the materials by simulating the operating conditions in which they are to be applied.

In order to reproduce the application in waterways and underground basins, and consequently the formation and adhesion of ice and frazil ice on the surfaces and walls of submerged equipment, we designed an experimental setup enabling a comparison between the prepared coatings.

#### Ice adhesion test

The experiments were conducted using a cryostat (Julabo F 34). 3 liters of bidistilled water were thermostatically set to  $-0.2^{\circ}\text{C}$  with mechanical stirring (200 rpm); a small super-cooling was set so that the slightest external phenomenon can give rise to heterogeneous ice nucleation.

The Vee-wire screens were in a freezer at  $-18^{\circ}\text{C}$  for 20 minutes to promote instantaneous heterogeneous ice nucleation on the surface of the sample when immersed.

The test was conducted by immersing the screen cooled to  $-18^{\circ}\text{C}$  in the water supercooled to  $-0.2^{\circ}\text{C}$ , while continuing to stir the water for 1 minute; during this time ice nucleation was observed until a mixture of ice and water was obtained. The sample was kept submerged and, after being removed, was placed in a low-temperature chamber ( $\sim 0^{\circ}\text{C}$ ), where we evaluated the behavior of the ice in terms of: percentage of coating on the surface (ice adhesion) and the ability to be detached by means of repeated impacts (ice detachment). The samples were tapped (at a rate of 100 impacts per minute) and the number of impacts required for complete detachment was considered a key descriptor for ranking the performance of the sample.

The samples were categorized by assigning a score based on the percentage of ice adhesion and the number of impacts required to achieve detachment according to the diagram in Tables 10 and 11.

**Table 10** – Evaluation table used for ice adhesion

| Adhesion area % | Score |
|-----------------|-------|
| 0-10%           | 10    |
| 11-20%          | 9     |
| 21-30           | 8     |
| 31-40           | 7     |
| 41-50           | 6     |

|        |   |
|--------|---|
| 51-60  | 5 |
| 61-70  | 4 |
| 71-80  | 3 |
| 81-90  | 2 |
| 91-100 | 1 |

**Table 11** – Evaluation table used for ice detachment

| Number of impacts | Score |
|-------------------|-------|
| 0-1               | 10    |
| 2-5               | 9     |
| 6-25              | 8     |
| 26-50             | 7     |
| 51-75             | 6     |
| 76-100            | 5     |
| 101-150           | 4     |
| 151-200           | 3     |
| 201-300           | 2     |
| >300 (melting)    | 1     |

5 The overall evaluation takes into account the average values assigned for adhesion and detachment.

### **Results and discussion**

#### **Wettability and functional characterization of anti-ice coatings**

The wettability properties of the 5x5 cm Vee-wire screens were measured after application of the various types of coatings.

10 Table 12 shows the wettability properties measured after application of just the polymers to the surface, prepared according to the method described in example 2c) Preparation of type c coatings (comparison polymers).

**Table 12** – Primary wettability measurements on samples prepared according to the method of type 2c)

| Sample                   | H <sub>2</sub> O CA<br>(°) | H <sub>2</sub> O HCA<br>(°) | N-hexadecane<br>CA (°) | Surface energy<br>(mN/m) |
|--------------------------|----------------------------|-----------------------------|------------------------|--------------------------|
| Uncoated Vee-wire screen | 97 ± 2                     | 42 ± 5                      | 7 ± 3                  | 29 ± 1                   |
| Metalcoat+enhancer       | 113 ± 9                    | 34 ± 29                     | 68 ± 13                | 15 ± 3                   |
| A1220                    | 99 ± 17                    | 45 ± 16                     | ND                     | ND                       |
| Nanomyte                 | 98 ± 17                    | 15 ± 4                      | 16 ± 12                | 29 ± 4                   |
| NuSil                    | 109 ± 10                   | 25 ± 8                      | 49 ± 17                | 19 ± 6                   |

The inherent inhomogeneities typical of Vee-wire screen surfaces involve high standard deviations of the determined values.

When not determined (ND), the measurement was not possible due to the high hydrophilic/oleophilic property and rapid permeation of the fluid into the channels of the screen.

With the exception of A1220, the coatings showed a slight improvement in terms of hydrophobia and hysteresis, as demonstrated by the CA and HCA measured with respect to water drop, respectively. Only Metalcoat and Nusil promote hydrophobia and oleophobia with significant increases in the contact angle and a good reduction of surface energy.

Table 13 shows the wettability properties measured after application of the coatings prepared according to the methods described in the examples: 2a), 2b), and 2d), i.e. containing inorganic nanoparticles (SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>) alone or coupled with polymers

**Table 13** – Primary wettability measurements on prepared samples

| Sample                   | H <sub>2</sub> O CA<br>(°) | H <sub>2</sub> O HCA<br>(°) | N-hexadecane<br>CA (°) | Surface energy<br>(mN/m) |
|--------------------------|----------------------------|-----------------------------|------------------------|--------------------------|
| Uncoated Vee-wire screen | 97 ± 2                     | 42 ± 5                      | 7 ± 3                  | 29 ± 1                   |
| LUDOX                    | ND<br>(Hydrophilic)        | ND<br>(Hydrophilic)         | ND<br>(Oleophilic)     | ND                       |
| LUDOX+Metalcoat+enhancer | 112 ± 6                    | 43 ± 20                     | 61 ± 11                | 16 ± 4                   |
| LUDOX+A1220              | 95 ± 14                    | 65 ± 18                     | ND                     | ND                       |

|                                                             |          |         |         |        |
|-------------------------------------------------------------|----------|---------|---------|--------|
| LUDOX+Nanomyte                                              | 105 ± 14 | 20 ± 9  | 17 ± 9  | 27 ± 2 |
| LUDOX+NuSil                                                 | 110 ± 10 | 27 ± 1  | 42 ± 8  | 21 ± 3 |
| LUDOX+SIVO                                                  | 111 ± 7  | 46 ± 7  | 79 ± 10 | 12 ± 3 |
| Al <sub>2</sub> O <sub>3</sub> +SIVO+100cSt<br>Silicone oil | 109 ± 15 | 28 ± 13 | 82 ± 11 | 12 ± 5 |

- As expected, the product based on LUDOX SiO<sub>2</sub> alone promotes hydrophilic behavior and rapid penetration of the water drop and oil. The data obtained show that the presence of the inorganic layer increases performance slightly, but does not strongly modify the behavior in terms of hydrophobia, oleophobia, and surface energy. The wettability properties appear to be independent of the inorganic layer, but the presence of inorganic nanoparticles is important in improving functionality during use and durability.

#### Functional ice adhesion and detachment tests

- 10 The prepared and characterized coatings were tested by following the procedures indicated in the earlier section on functional characterization.

**Table 14 – Ice adhesion and detachment tests**

| Sample                                                      | Adhesion area % | Number of impacts | Effectiveness score |
|-------------------------------------------------------------|-----------------|-------------------|---------------------|
| Uncoated Vee-wire screen                                    | 100             | 600               | 1                   |
| Metalcoat+enhancer                                          | 2               | 1                 | 10                  |
| LUDOX                                                       | 5               | 50                | 8.5                 |
| LUDOX+enhancer                                              | 5               | 25                | 9                   |
| LUDOX+Metalcoat+enhancer                                    | 1               | 5                 | 10                  |
| A1220                                                       | 60              | 100               | 5                   |
| LUDOX+A1220                                                 | 80              | 150               | 3.5                 |
| Nanomyte                                                    | 95              | 350               | 1                   |
| LUDOX+Nanomyte                                              | 85              | 280               | 2                   |
| NuSil                                                       | 95              | 75                | 3.5                 |
| LUDOX+NuSil                                                 | 95              | 130               | 2.5                 |
| LUDOX+SIVO                                                  | 100             | 500               | 1                   |
| Al <sub>2</sub> O <sub>3</sub> (S)+SIVO+100cSt silicone oil | 100             | 450               | 1                   |

Table 14 contains the functional results in terms of the effectiveness score of the samples after the first immersion test. The results are shown comparing the samples containing the layer of inorganic nanoparticles coupled with the polymer, versus the sample coated only with the corresponding polymer. The percentage of surface covered with ice and the number of impacts required for complete detachment contribute to the effectiveness score.

Figure 3 shows the result of an adhesion and detachment test conducted on the untreated screen (a) and on the best performing sample, that is, the sample coated with Ludox+Metalcoat+enhancer (c). Generally, the typical behavior for uncoated screens or for ineffective coatings consists of complete adhesion of ice on the macroscopic level (100% of the sample area) and uninitiated detachment only after 600 impacts due only to gradually melting of the ice.

Moreover, for the best performing samples, ice adhesion is extremely limited after immersion and only a few impacts are required to detach the ice crystals (Figure 3).

Functional results of samples prepared with polymer only according to preparation method 2c)

Commercial polymers A1220 and SIVO were not specifically designed for anti-ice applications, but rather to impart water repellency. Indeed, under the test conditions they achieve a low effectiveness score both alone and coupled with nanoparticles (effectiveness score ranging from 1 to 5).

Although both Nanomyte and Nusil are marketed as anti-ice products, when applied alone they show massive ice adhesion, probably because the experimental conditions, which involve prolonged immersion in very shallow water, are too severe for this category of product.

Coupling these polymers with inorganic silicon nanoparticles leads to a slight improvement in performance, indicating that the primary role is fulfilled by the external organic polymer, but the presence of an inorganic support layer could improve the overall behavior.

We selected silicon nanoparticles to support the organic polymers thanks to their low cost and good performance already demonstrated in the field of protective coatings.

Functional results of samples prepared with SiO<sub>2</sub> nanoparticles optionally coupled with polymers according to preparation methods 2a) and 2b)

Table 14 shows that the treatments based on SiO<sub>2</sub> (LUDOX and LUDOX+enhancer) lead to promising behaviors, with effectiveness scores ranging from 8.5 to 9, but coupling with an

organosilane (LUDOX+Metalcoat+enhancer) further improves performance, achieving an effectiveness score of 10.

The LUDOX treatment provides good ice detachment, with a macroscopically clean area, however the microcrystals of ice remain firmly attached to the surface (Figure 3b). This behavior is probably due to the hydrophilic characteristic, which promotes strong attachment of the microcrystals of ice, but sliding and detachment of large and heavy portions of ice.

Metalcoat applied with acid catalyst "enhancer" and coupled with LUDOX silicon leads to excellent performance, showing functional results consistent with the wettability data and confirming its effectiveness at limiting and preventing ice adhesion to the surface.

Functional results of samples prepared with  $Al_2O_3$  nanoparticles infused with silicone oil and prepared according to method 2d)

The coating containing  $Al_2O_3$  infused with silicone oil shows poor performance, with effectiveness scores of 4.5 and 1, respectively.

#### Durability test

In order to evaluate the durability of the coatings, the prepared samples were exposed to a second cycle of immersion tests in supercooled water. The ice adhesion properties were then checked after each subsequent immersion cycle to track any changes in the properties of the coatings.

#### *Functional tests: change in ice adhesion*

Table 15 compares the effectiveness scores after the first and second immersion tests. Although the wettability data are not significantly influenced by the immersion cycles, the functional results show a general drop in the performance of the coating after the second immersion cycle.

The harmful behavior caused by the immersion tests probably includes a macroscopic effect brought to light by the ice adhesion tests, whereas on the microscopic level the wettability properties appear to be stable.

Deterioration of the coating is evident in all the best performing samples, with the exception of the Metalcoat coupled with LUDOX.

**Table 15** – Comparison of effectiveness scores after the first and second immersion cycles

| Samples | Effectiveness score | Effectiveness score |
|---------|---------------------|---------------------|
|---------|---------------------|---------------------|

|                                                             | 1 <sup>st</sup> cycle | 2 <sup>nd</sup> cycle |
|-------------------------------------------------------------|-----------------------|-----------------------|
| Uncoated Vee-wire screen                                    | 1                     | 2.5                   |
| Metalcoat+enhancer                                          | 10                    | 8                     |
| LUDOX                                                       | 8.5                   | 3.5                   |
| LUDOX+enhancer                                              | 9                     | 2                     |
| LUDOX+Metalcoat+enhancer                                    | 10                    | 10                    |
| A1220                                                       | 5                     | 3                     |
| LUDOX+A1220                                                 | 3.5                   | 2.5                   |
| Nanomyte                                                    | 1                     | 1.5                   |
| Primer+Nanomyte                                             | 1.5                   | 2                     |
| LUDOX+Nanomyte                                              | 2                     | 1.5                   |
| NuSil                                                       | 3.5                   | 4.5                   |
| LUDOX+NuSil                                                 | 2.5                   | 2                     |
| LUDOX+SIVO                                                  | 1                     | 1.5                   |
| Al <sub>2</sub> O <sub>3</sub> (S)+SIVO+100cSt silicone oil | 1                     | 6.5                   |

The most significant data in Table 15 are also shown in the graphic in Figure 4.

The commercial inorganic coating Metalcoat+enhancer is very effective at preventing ice adhesion, with good resistance in the subsequent cycle.

- 5 Here again, the silicon layer (LUDOX+Metalcoat+enhancer sample) makes it possible to maximize performance in the second cycle by still preventing ice adhesion. The SiO<sub>2</sub> layer probably acts as a stronger starting point for the coating, synergistically allowing for prolonged durability.

- 10 Figure 3c reveals the performance achieved by the best coating, with no attachment shown for either of the two immersion cycles.

Furthermore, the LUDOX silicon either alone or treated only with the acid catalyst "enhancer," shows rapid deterioration after the first cycle.

### Conclusions

- 15 The wettability characterization and functional test in supercooled water were conducted to select the most promising solutions. The evaluations were repeated after two immersion cycles to study the durability of the coating in a simulated environment.

Although the wettability data are not influenced by the immersion cycles in supercooled water, the frazil ice simulation appears to be a severe condition, particularly for repeated cycles.

We noticed that the introduction of a silicon layer favors the functional performance of the polymer coatings, thus improving the barrier effect and the ability of the ice to detach during the immersion test.

In general, for non-severe conditions, samples with silicone oils are suggested in the literature as the appropriate technology for preventing ice adhesion, but the frazil ice simulation conditions appear to be too severe, particularly in terms of durability.

The coatings with an inorganic base have proven to be the best performing and the most resistant to repeated immersion cycles, even in comparison to some polymers marketed as durable anti-ice coatings.

Of all the tested solutions, we have identified the best solution as the coating consisting of silicon nanoparticles (LUDOX) coupled with an organosilane (Metalcoat) applied with the acid catalyst (enhancer). Indeed, the product called **LUDOX+Metalcoat+enhancer** achieves excellent functional performance, showing optimum durability for immersion cycles, augmented by the presence of the inorganic layer based on LUDOX.

### **Example 3 – Coatings for the separation of oil/water emulsions**

#### **Materials and methods**

##### **Metal screens**

Fine-mesh screens made of stainless steel (AISI 316) were chosen as the substrate to be functionalized with coatings for oil/water separation.

##### **Coating preparation**

The behavior of hydrophilic/oleophobic coatings, in which only the aqueous phase can flow through the sample, was studied (Figure 5).

This configuration makes it possible to use gravity as the driving force for separation, since water, which is denser than the oil phase, tends to flow spontaneously through the screen, especially in the case of vertical geometries; in addition, the flow of the aqueous phase reduces the phenomena of filter screen soiling and fouling typically caused by the flow of oil phases. Indeed, the flow of oil through the filter is prevented or limited by the oleophobic

coating, which, by minimizing interactions with the filter mesh, limits soiling and enables the filter to be reused for repeated separation cycles.

In the literature, polymer phases functionalized with the addition of surfactants are usually used to produce these coatings. However, for this functionality as well, the coupling of inorganic nanoparticles with the polymer phase makes it possible to impart a hierarchical structuring aimed at improving the hydrophilic/oleophobic properties and consequently oil/water separation.

#### Inorganic nanoparticles

Silicon dioxide nanoparticles ( $\text{SiO}_2$  nanoparticles) in powder form are used in the preparations; in particular, the commercial product CAB-O-SIL (Cabot, fumed silica) was used.

#### Polymers

The polymer phase used is poly(diallyldimethylammonium chloride), PDDA, a cationic polymer with a high charge density.

The types of coatings prepared are described below.

#### 15      *a) Preparation of type a coatings (PDDA/FS/ $\text{SiO}_2$ )*

Synthesis is conducted in an aqueous medium. The anionic fluorosurfactant (FS) Capstone FS-63 (DuPont) and the  $\text{SiO}_2$  nanoparticle powder (Cabot) are added to a diluted suspension (2% w/v) of PDDA. The suspension was treated with ultrasound for 1 hour and the precipitate was washed and dried. The powder thus made is ground and dispersed in ethanol by means of ultrasound at a concentration of 1% w/v, ready to be deposited on metal substrates.

The coating was applied by dip-coating (immersion/removal at a controlled rate of 2 mm/s, static hold time 120 seconds). Alternatively, other methods of application capable of leading to the formation of a homogeneous surface (such as spray coating, percolation) may be used.

The samples are kept at ambient temperature for 10 minutes to slowly evaporate the solvent, and are heat treated at 150°C for 30 minutes. Two successive deposition runs were performed.

The resulting samples are called: COATING A.

#### *b) Preparation of type b coatings (PDDA/PFOA/ $\text{SiO}_2$ )*

$\text{SiO}_2$  nanoparticles (Cabot) are dispersed in diluted PDDA (0.1% w/v) and subsequently treated with ultrasound for 30 minutes, then a perfluorooctanoic acid solution (PFOA, 0.1 M) is added

drop by drop. The precipitate is washed and dried. The powder thus obtained is ground and dispersed in ethanol by means of ultrasound at a concentration of 1% w/v.

The application and heat treatment are conducted according to the same method as example 3a).

- 5 The resulting samples are called: COATING B.

*c) Preparation of type c coatings (MTM/HCl)*

The methyltrimethoxysilane (MTM) is mixed with hydrochloric acid (HCl) and sonicated in an ice bath for 5 minutes to induce hydrolysis. The product is applied immediately after synthesis to prevent an excessive increase in the viscosity of the suspension during the following  
10 condensation step.

The application and heat treatment are conducted according to the same method as example 3a).

The resulting samples are called: COATING C.

**Physical, chemical, and functional characterization**

- 15 The samples were characterized by determining the static contact angle with water and n-hexadecane. All the results are derived from an average of at least 3 values acquired in various areas of the sample in order to map the entire surface.

The functional characterization aims to evaluate the performance of the materials by simulating the operating conditions in which they are to be applied.

- 20 The purpose of the experimental equipment is to simulate on a small scale a metal filter used to separate a flow consisting of an oil/water emulsion. The simulation is conducted without the use of any kind of driving force other than gravity. The samples were placed between two section, the upper cylindrical section and the lower conical section (for easy collection of the filtrate in a graduate cylinder). Biodiesel was used as the oil phase, which was mixed with  
25 water, thus creating an emulsion in a water-to-biodiesel volume ratio of 70:30 or 90:10. Before use, the mixture is stirred to create a genuine emulsion (separation by density starts within a short time); once the liquid is poured, the time to finish the filtration is measured. At the end of filtration, the separation effectiveness can be determined by a simple measurement of the volumes of water and oil that have passed through the filter. The  
30 parameters of interest are given in Table 16.

**Table 16** – Experimental parameters of the setup for functional characterization

| Parameters                              | Values              |
|-----------------------------------------|---------------------|
| Water-to-biodiesel ratio                | 70:30 or 90:10% v/v |
| Filtered volume                         | 100 mL              |
| Filtration surface                      | 14 cm <sup>2</sup>  |
| Hydrostatic pressure of 100 mL of water | 440 Pa              |
| Drying temperature *                    | 70°C                |

\*the filters were washed and dried in an oven after each test

The measurement of the time required for filtration makes it possible to estimate the flow resistance caused by the sample, which typically should be as low as possible in a real-world application. As the filtration progresses, the reduced hydrostatic pressure causes the flow to slow down. In terms of filtration effectiveness, the optimum result is complete permeation of the water and quantitative retention of the biodiesel. The results are expressed as a percentage of oil held back in the filter.

## 10 **Results and discussion**

### **Wettability**

The most significant wettability results are shown in Table 17 and Figure 7, and are expressed in terms of contact angle with water (water CA) and contact angle with n-hexadecane (oil CA).

**Table 17** – Contact angle measurements with water and n-hexadecane

| Sample    | Contact angle with water (°) | Contact angle with n-hexadecane (°) |
|-----------|------------------------------|-------------------------------------|
| Uncoated  | 112                          | 0*                                  |
| Coating A | 91 ± 3                       | 98 ± 1                              |
| Coating B | 94 ± 6                       | 115 ± 12                            |
| Coating C | 84 ± 2                       | 24 ± 4                              |

15 \*Flows through the substrate

The uncoated sample has good hydrophobicity, a contact angle with water of 112°, and also exhibits high oleophilicity since the n-hexadecane spreads and immediately tends to filter through the two samples. These are precisely the opposite of the desired properties for the proposed application, so we need to observe how these properties are changed by the prepared coatings. Indeed, with coatings A and B it was possible to observe an increase in hydrophilicity (decreased contact angle with water) and a significant increase in oleophobia (noteworthy increase in the contact angle with n-hexadecane).

Coating C proved slightly more hydrophilic but not oleophobic (contact angle with n-hexadecane  $\approx 30^\circ$ ), so an application of only the polymer phase is not considered to be capable of performing the required oil/water separation.

*Functional characterization of the coatings for oil-water separation*

- 5 The functional characterization of the prepared samples was conducted by evaluating the separation effectiveness of a water-biodiesel emulsion. The stainless steel screens were used as the filter media to allow water to flow and prevent permeation of the oil phase.
- The first test was conducted on uncoated screens to evaluate their behavior and compare the results to the functionalized substrates. First, the individual water and biodiesel flows were
- 10 determined, followed by tests to determine the ability to separate the two phases in the emulsion.

**Table 18** – Characterization of flow through the uncoated screens

| Sample   | Fluid composition (volume %) | Beginning volume (mL) | Time (s) | Filtered volume (mL) |
|----------|------------------------------|-----------------------|----------|----------------------|
| Uncoated | Water 100                    | 100                   | 5        | 100                  |
| Uncoated | Oil 100                      | 30                    | 10       | 30                   |

- 15 Table 18 shows that no retention was achieved either for water or for oil. Permeation is very fast for all the sample; the oil requires more time on account of its higher viscosity. The results reveal that selective filtration is not feasible using uncoated materials.
- The data collected for the filtration of water through the coated samples are given in Table 19. Obstacles must not be created as they could cause excessive slowing of the flow.
- 20 Accordingly, by keeping pressure losses low, it is possible to entertain the idea of separation using only gravity as the driving force of the process.

**Table 19** – Permeation of water flow through coated screens

| Sample    | Fluid | Beginning volume (mL) | Time (s) | Filtered volume (mL) |
|-----------|-------|-----------------------|----------|----------------------|
| Coating A | Water | 100                   | 3        | 100                  |
| Coating B | Water | 100                   | 4        | 100                  |

- 25 The permeation time of water through the filter is 3-4 s, slightly faster than with the coated screens (5 s). This confirms that the modified surface properties allow for better water flow

despite the slight reduction of the opening in the mesh due to the thickness of the coatings. In order to evaluate the performance of the prepared coatings, the separation effectiveness was evaluated by processing 100 mL of water/biodiesel emulsion in a volume ratio of 90:10 or 70:30. The most significant results are given in the following Table 20 and in Figure 6.

5

**Table 20** – Separation test on a mixture with the following starting composition: water 90 mL and biodiesel 10 mL

| Sample    | Total filtrate volume (mL) | Time (s) | Volume of filtered water (mL) | Volume of filtered biodiesel (mL) |
|-----------|----------------------------|----------|-------------------------------|-----------------------------------|
| Uncoated  | 100                        |          | 90                            | 10                                |
| Coating A | 95                         | 180      | 89                            | 6                                 |
| Coating B | 92                         | 180      | 90                            | 2                                 |

**Table 21** – Separation test on a mixture with the following starting composition: water 70 mL and biodiesel 30 mL

10

| Sample    | Total filtrate volume (mL) | Time (s) | Volume of filtered water (mL) | Volume of filtered biodiesel (mL) |
|-----------|----------------------------|----------|-------------------------------|-----------------------------------|
| Uncoated* | 100                        |          | 90                            | 10                                |
| Coating A | 98                         | 300      | 70                            | 28                                |
| Coating B | 89                         | 600      | 70                            | 30                                |

\*since no retention capability was demonstrated in the ratio of 90:10, the test was not repeated under more severe conditions (70:30)

The coatings show a heightened separation effectiveness; water permeates quickly and quantitatively ( $\approx 99\%$ ) and the oil is held back considerably with an average calculated quantity of  $\approx 80\%$  over repeated tests. The water flows quickly between 10 and 90 seconds, followed by slow dripping of the biodiesel; the tests were stopped when the dripping was considered completed, between 180 and 300 seconds.

15

The data suggest that repeated applications increase the separation effectiveness. A thicker and more homogeneous coating may ensure greater oleophobicity, thereby improving biodiesel retention. The observed trends are summarized below:

20

- Multiple applications make it possible to achieve more marked and homogeneous properties on the surface, leading to improved performance. Excellent results are already achieved with 2 applications;

- Of the synthesized coatings, coating A appears to be the most promising solution. It must be stressed that coating A provides the best results, including when tested under the more severe conditions (water/biodiesel 70:30);

## 5 Conclusions

We prepared three different coatings based on a polymer matrix doped with inorganic nanoparticles and functional surfactants. These products were applied to metal screens.

First, we determined the wettability of the coated samples.

The functional characterization was conducted by evaluating the separation effectiveness of water-biodiesel emulsions.

In general, the best performing and most durable coating is COATING A, obtained by coupling SiO<sub>2</sub> nanoparticles with a polymer phase (PDDA) in the presence of a fluorinating agent added to maximize oil repellency.

Simple synthesis processes and the use of off-the-shelf products as raw materials make these coatings simple and potentially readily scalable to larger facilities.

Bibliography

- 1 M. Richard and B. Morse, *Cold Reg. Sci. Technol.*, 2008, **53**, 131–149.
- 2 B. Turcotte, B. Morse, M. Dubé and F. Anctil, *Cold Reg. Sci. Technol.*, 2013, **94**, 21–36.
- 3 L. Cao, A. K. Jones, V. K. Sikka, J. Wu and D. Gao, *Langmuir*, 2009, **25**, 12444–12448.
- 5 4 S. Farhadi, M. Farzaneh and S. A. Kulinich, *Appl. Surf. Sci.*, 2011, **257**, 6264–6269.
- 5 M. J. Kreder, J. Alvarenga, P. Kim and J. Aizenberg, *Nat. Rev. Mater.*, DOI:10.1038/natrevmats.2015.3.
- 6 L. Zhang, Z. Zhang and P. Wang, *NPG Asia Mater.*, DOI:10.1038/am.2012.14.
- 7 L. Jiang, Z. Tang, K. J. Park-Lee, D. W. Hess and V. Breedveld, *Sep. Purif. Technol.*, 2017,  
10 **184**, 394–403.
- 8 O. Arslan, Z. Aytac and T. Uyar, *ACS Appl. Mater. Interfaces*, 2016, **8**, 19747–19754.
- 9 Y. N. Guo, L. Y. Liang, S. X. Bao, F. P. Du and X. Wen, *J. Appl. Polym. Sci.*, 2020, **137**, 1–11.
- 10 Z. Yin, Y. Li, T. Song, M. Bao, Y. Li, J. Lu and Y. Li, *Sep. Purif. Technol.*, 2020, **236**,  
15 116308.
- 11 Y. Wang and X. Gong, *J. Mater. Chem. A*, 2017, **5**, 3759–3773.
- 12 H. C. Wang, C. Y. Wu, C. C. Chung, M. H. Lai and T. W. Chung, *Ind. Eng. Chem. Res.*, 2006, **45**, 8043–8048.
- 13 O. K. Park and Y. S. Kang, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2005, **257–258**,  
20 261–265.
- 14 X. Dai, B. B. Stogin, S. Yang and T. S. Wong, *ACS Nano*, 2015, **9**, 9260–9267.

## CLAIMS

1. A filter metal plate coated with at least one of the following coatings:
  - a) metal oxide nanoparticles coupled with one or more fluoroalkylsilanes and/or one or more organosilanes and/or one or more polymers functionalized with fluoroalkylsilanes and/or with organosilanes;
  - b) metal oxide nanoparticles coupled with a polymeric matrix functionalized with fluorinated molecules or groups.
2. The plate according to claim 1, wherein said filter metal plate is made of stainless steel.
3. The plate according to claim 1 or 2, wherein said filter metal plate is of the Vee-wire type.
4. The plate according to any one of claims 1-3, wherein said metal oxide is silicon dioxide ( $\text{SiO}_2$ ).
5. The plate according to any one of claims 1-4, wherein said coating a) comprises metal oxide nanoparticles coupled with one or more fluoroalkylsilanes and is obtained by applying to the plate an inorganic layer of metal oxide nanoparticles and subsequently an organic layer based on fluoroalkylsilane.
6. The plate according to any one of claims 1-4, wherein said coating a) comprises metal oxide nanoparticles coupled with one or more organosilanes or organosilane polymers and is obtained by applying to the plate an inorganic layer of metal oxide nanoparticles and subsequently a layer comprising the organosilane, optionally together with an enhancer.
7. The plate according to claim 6, wherein the layer comprising the organosilane also comprises additional metal oxide nanoparticles.
8. The plate according to any one of claims 1-4, wherein said coating b) comprises metal oxide nanoparticles coupled with a polymeric matrix made of a polymer selected from polydiallyldimethyl ammonium chloride, polydimethylsiloxane, methyltrimethoxysilane, methyltriacetoxysilane, perfluoropolyether and chitosan-polyvinyl alcohol functionalized with fluorinated molecules or groups selected from

perfluorooctanoic acid, anionic fluorosurfactant, and 1H,1H,2H,2H-perfluorooctyltriethoxysilane.

- 5 9. The plate according to any one of claims 1-4, wherein said coating b) is obtained by precipitation of a suspension of metal oxide nanoparticles in poly(diallyldimethylammonium chloride) (PDDA) and perfluorooctanoic acid or by precipitation of a suspension of metal oxide nanoparticles in poly(diallyldimethylammonium chloride) (PDDA) and at least one anionic fluorosurfactant, and subsequent dispersion in an alcoholic solvent.
- 10 10. The plate according to any one of claims 1-9, wherein said plate has undergone a sandblasting treatment prior to applying the coating.
11. Use of the filter metal plate according to any one of claims 1-10 for the filtration of liquids, such as water.
12. Use of the filter metal plate according to any one of claims 1-10 for filter pressing, in particular to remove mud.
- 15 13. Use of the filter metal plate according to any one of claims 1-10 for the filtration of water in very cold environments.
14. Use of the filter metal plate according to any one of claims 1-10 for the separation of oil/water emulsions.
- 20 15. Use of the filter metal plate according to any one of claims 1-10 for the treatment of waste water, for example industrial waste water.
16. Use of:
- a) metal oxide nanoparticles coupled with one or more fluoroalkylsilanes and/or one or more organosilanes and/or one or more polymers functionalized with fluoroalkylsilanes and/or with organosilanes; and/or
- 25 b) metal oxide nanoparticles coupled with a polymeric matrix functionalized with fluorinated molecules or groups,
- for coating a metal filter plate.
17. The use of claim 16, wherein said metal oxide is silicon dioxide (SiO<sub>2</sub>).

18. The use of claim 16, wherein said nanoparticles a) are metal oxide nanoparticles coupled with one or more fluoroalkylsilanes.
19. The use of claim 16, wherein said nanoparticles a) are metal oxide nanoparticles coupled with one or more organosilanes or organosilane polymers.
- 5 20. The use of claim 16, wherein said nanoparticles b) are obtained by precipitation of a suspension of metal oxide nanoparticles in poly(diallyldimethylammonium chloride) (PDDA) and perfluorooctanoic acid or a suspension of metal oxide nanoparticles in poly(diallyldimethylammonium chloride) (PDDA) and at least one anionic fluorosurfactant, and subsequent dispersion in an alcoholic solvent.
- 10 21. A kit for the preparation of one or more of the following coatings:
- a) metal oxide nanoparticles coupled with one or more fluoroalkylsilanes and/or one or more organosilanes and/or one or more polymers functionalized with fluoroalkylsilanes and/or with organosilanes;
  - b) metal oxide nanoparticles coupled with a polymeric matrix functionalized with
- 15 fluorinated molecules or groups.
22. The kit according to claim 21 comprising:
- a) metal oxide nanoparticles; and
  - b) a composition comprising at least one fluoroalkylsilane or organosilane or one or more polymers functionalized with fluoroalkylsilanes and/or organosilanes; or
- 20 b') at least one polymer and at least one compound containing fluorinated molecules or groups.
23. The kit according to claim 22, wherein said kit comprises metal oxide nanoparticles, a polymer selected from polydiallyldimethyl ammonium chloride, polydimethyl siloxane, methyltrimethoxysilane, methyltriacetoxysilane, perfluoropolyether and
- 25 chitosan-polyvinyl alcohol and a compound containing fluorinated molecules or groups selected from perfluorooctanoic acid, anionic fluorosurfactant and 1H,1H,2H,2H-perfluorooctyltriethoxysilane.