

METHODS OF REMOVING DEPOSITS FROM A SURFACE USING A SALT

FIELD OF THE INVENTION

[0001] The invention relates to the field of removing deposits from a surface, preferably the surface of industrial equipment.

BACKGROUND OF THE INVENTION

[0002] Solutions of hydrogen peroxide are widely used in various commercial cleaning. In most applications diluted solutions are used, normally containing from about 0.1 to about 20 wt % of hydrogen peroxide. The disadvantages of the cleaning method are insufficient efficacy when used for removing deposits on metal surfaces.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0003] As used in the preceding sections and throughout the rest of this specification, unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one skilled in the art to which this invention belongs. All patents and publications referred to herein are incorporated by reference in their entireties.

[0004] The term “a”, “an”, or “the” as used herein, generally is construed to cover both the singular and the plural forms.

[0005] The term “about” as used herein, generally refers to a particular numeric value that is within an acceptable error range as determined by one of ordinary skill in the art, which will depend in part on how the numeric value is measured or determined, i.e., the limitations of the measurement system. For example, “about” can mean a range of $\pm 20\%$, $\pm 10\%$, or $\pm 5\%$ of a given numeric value.

[0006] The term “volume expansion” refers to the increase of volume when an anhydrous salt becomes a hydrate salt and is defined as the ratio of the volume of the hydrate salt over that of the anhydrous salt. For example, the stable forms of sodium sulfate are the decahydrate (mirabilite) and the anhydrite (thenardite). The transition from thenardite to mirabilite and the incorporation of 10 water molecules in the crystal lattice causes a volume expansion of about 320%.

[0007] The disclosure relates to a method of removing various types of deposits from a surface. The deposits can be salt deposits, deposits of a petroleum nature including fouling of heat exchangers, asphaltene-resin-paraffin, and resin and biological (bacterial) deposits. In some embodiments, the deposit is the fouling in a heat exchanger. In an embodiment, the deposit is the fouling in a heat exchanger used in oil refinery. In some embodiments, the surface is the surface of a metal or a glass, or a ceramic material, or a polymer material.

[0008] The method for removing deposits from a surface comprises the steps of

wetting the surface in a first salt solution so that the first salt solution penetrates into the cracks or pores of the deposits;

removing the first salt solution outside the cracks or pores of the deposits;

drying the surface so that the first salt solution inside the cracks or pores of the deposits becomes an anhydrous salt;

wetting the surface in a second salt solution;

wherein the anhydrous salt forms a salt hydrate inside the cracks or pores of the deposits and causes volume expansion, resulting in breaking the deposits from the surface.

[0009] The method described herein takes advantage of volume expansion when an anhydrous salt becomes a hydrate thereof. In some embodiments, the hydrate is in a crystalline form. In some embodiments, any of the steps may be repeated 2, 3, 4, or more times till surface cleaning is achieved.

[0010] In some embodiments, the surface is a metal surface. In some embodiments, the deposits comprise barite deposit or a heavy oil deposit, or petcoke deposit, or a iron oxide/sulfide deposit, or a hardness salt deposit. In some embodiments, the deposit is a thin layer on the surface with an average thickness of about 1 mm, about 2 mm, about 3 mm, about 4 mm, about 5 mm, about 6 mm, about 7 mm, about 8 mm, about 9 mm, about 10 mm, about 11 mm, about 12 mm, about 13 mm, about 14 mm, about 15 mm, about 16 mm, about 17 mm, about 18 mm, about 19 mm, or about 20 mm.

[0011] In some embodiments, the first salt solution is the same as the second salt solution. In some embodiments, the first salt solution is different from the second salt solution.

[0012] In some embodiments, the first salt solution is a saturated solution of the salt.

[0013] In some embodiments, the first salt solution is an unsaturated solution of the salt.

[0014] In some embodiments, the second salt solution is a saturated solution of the salt. In some embodiments, the second salt solution is a unsaturated solution of the salt.

[0015] In some embodiments, the first salt solution and the second salt solution independently comprise a salt selected from the group consisting of copper(II) sulfate, zinc sulfate, calcium chloride, magnesium sulfate, iron(II) sulfate, magnesium chloride, sodium carbonate, sodium thiosulfate, barium hydroxide, iron(II) acetate, zinc nitrate, magnesium ammonium phosphate, iridium(III) bromide, gold chloride, sodium acetate, calcium sulfate, sodium dihydrogen phosphate, sodium sulfate, nickel(II) nitrate, iron(III) chloride, nickel(II) sulfate, manganese(II) sulfate, sodium monohydrogen phosphate, manganese(II) chloride, copper(II) nitrate, calcium nitrate, cobalt(II) chloride, nickel(II) chloride, nickel(II) sulfate, sodium dichromate, copper(II) nitrate, tin(IV) chloride, and mixtures thereof.

[0016] In some embodiments, the concentration of the first salt solution is about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, 55%, about 60%, about 65%, about 70%, or about 75% by the weight of the salt. In some embodiments, the concentration of the second salt solution is about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, 55%, about 60%, about 65%, about 70%, or about 75% by the weight of the salt.

[0017] In some embodiments, wetting the surface includes immersing the surface in the first salt solution or the second salt solution. In some embodiments, wetting the surface includes applying certain amount of the first salt solution or the second salt solution to the surface. The amount of solution is decided by area size of the surface, the solution concentration, temperature, and the volume of the deposits.

[0018] In some embodiments, the first salt solution is a solution of sodium sulfate. In some embodiments, the concentration of the first salt solution is about 14% by weight

[0019] In some embodiments, the second salt solution is a solution of sodium sulfate.

[0020] In some embodiments, the concentration of the second salt solution is about 14%.

[0021] In some embodiments, the first salt solution or the second salt solution independently contains an additive. The additive may be comprised by wetting agent, detergent, and/or chelating agent.

[0022] After the surface is wetted with the first salt solution. The wetting may last an amount of time sufficient to allow the first salt solution to penetrate to the cracks or pores of the

deposits on the surface. In some embodiments, the amount of time for the first salt solution to penetrate to the cracks or pores of the deposits on the surface is selected from the group consisting of about 30 minutes, about 1 hour, about 2 hours, about 3 hours, about 4 hours, about 5 hours, about 6 hours, about 7 hours, about 8 hours, about 9 hours, about 10 hours, about 11 hours, and about 12 hours. In some embodiments, the amount of time for the first salt solution to penetrate to the cracks or pores of the deposits on the surface is about 3-24 hours. Thereafter, the first salt solution outside the cracks or pores of the deposits is removed. Then the surface is dried so that the first salt solution inside the cracks or pores of the deposits evaporates, resulting an anhydrous salt or a partially anhydrous salt. In some embodiments, the surface is dried at a temperature for a certain amount of time. The temperature is selected from the group consisting of about 50°C, about 55°C, about 60°C, about 65°C, about 70°C, about 75°C, about 80°C, about 85°C, about 90°C, about 95°C, about 100°C, about 100°C, about 120°C, about 125°C, about 130°C, about 135°C, about 140°C, about 150°C, about 155°C, about 160°C, about 165°C, about 170°C, about 175°C, about 180°C, about 185°C, about 190°C, about 195°C, and about 200°C. In some embodiments, the temperature is within a range of 50°C-200°C. In some embodiments, the surface is dried at a temperature for about 30 minutes, about 1 hour, about 2 hours, about 3 hours, about 4 hours, about 5 hours, about 6 hours, about 7 hours, about 8 hours, about 9 hours, about 10 hours, or more. In some embodiments, the surface is dried for about one day, two days, three days, four days, five days, six days, or a week. In some embodiments, the surface is dried within a range of time periods 0.5 – 24 hours.

[0023] In some embodiments, the surface is dried by vacuum at room temperature or a high temperature selected from the group consisting of about 50°C, about 55°C, about 60°C, about 65°C, about 70°C, about 75°C, about 80°C, about 85°C, about 90°C, about 95°C, about 100°C, about 100°C, about 120°C, about 125°C, about 130°C, about 135°C, about 140°C, about 150°C, about 155°C, about 160°C, about 165°C, about 170°C, about 175°C, about 180°C, about 185°C, about 190°C, about 195°C, and about 200. In some embodiments, the surface is dried by vacuum at a temperature within a range of 50-90°C.

[0024] In some embodiments, where the vacuum drying is conducted in a vacuum selected from the group consisting of about 1 Torr, about 10 Torr, about 25 Torr, about 50 Torr, about 75 Torr, about 100 Torr, about 125 Torr, about 150 Torr, about 175 Torr, about 200 Torr, about 225 Torr, about 250 Torr, about 275 Torr, about 300 Torr, about 325 Torr, about 350 Torr, about 350 Torr, about 375 Torr, about 400 Torr, about 425 Torr, about 450 Torr, about

475 Torr, about 500 Torr, about 525 Torr, about 550 Torr, about 575 Torr, about 600 Torr, about 625 Torr, about 650 Torr, about 675 Torr, and about 700 Torr.

[0025] In some embodiments, where the vacuum drying is conducted in a vacuum within a range of 10-500 Torr.

[0026] After the drying, the surface is cooled to room temperature. Then a second salt solution is applied to the surface. In some embodiments, the surface is immersed in the second salt solution. The second salt solution is allowed to stay in contact with the surface for certain amount of time sufficient to penetrate the cracks or pores of the deposits. In some embodiments, the amount of time for the second salt solution to penetrate to the cracks or pores of the deposits on the surface is selected from the group consisting of about 30 minutes, about 1 hour, about 2 hours, about 3 hours, about 4 hours, about 5 hours, about 6 hours, about 7 hours, about 8 hours, about 9 hours, about 10 hours, about 11 hours, and about 12 hours. In some embodiments, the amount of time for the second salt solution to penetrate to the cracks or pores of the deposits on the surface is in the range of 3-24 hours. Inside the cracks or pores of the deposits, the second salt solution is in contact with the anhydrous salt or the partially anhydrous salt formed in the drying step. Then, the anhydrous salt or the partially anhydrous salt forms a salt hydrate. In some embodiments, the salt hydrate is in a crystalline form. When the anhydrous salt or the partially anhydrous salt forms a salt hydrate, the salt hydrate tends to have larger volume than the corresponding anhydrous salt or partially anhydrous salt. Such volume expansion inside the cracks or pores of the deposits leads to the break-away of the deposits from the surface. In some embodiments, the volume expansion is at least about 2 times. In some embodiments, the volume expansion is at least about 3 times, at least about 4 times, at least about 5 times, at least about 6 times, at least about 7 times, at least about 8 times, at least about 9 times, or at least about 10 times.

[0027] In some embodiments, the method described herein further comprises the step of removing the second salt solution outside the cracks or pores of the deposits.

[0028] In some embodiments, the first salt solution and the second salt solution independently comprise a salt selected from the group consisting of copper(II) sulfate, zinc sulfate, calcium chloride, magnesium sulfate, iron(II) sulfate, magnesium chloride, sodium carbonate, sodium thiosulfate, barium hydroxide, iron(II) acetate, zinc nitrate, magnesium ammonium phosphate, iridium(III) bromide, gold chloride, sodium acetate, calcium sulfate, sodium dihydrogen phosphate, sodium sulfate, nickel(II) nitrate, iron(III) chloride, nickel(II)

sulfate, manganese(II) sulfate, sodium monohydrogen phosphate, manganese(II) chloride, copper(II) nitrate, calcium nitrate, cobalt(II) chloride, nickel(II) chloride, nickel(II) sulfate, sodium dichromate, copper(II) nitrate, tin(IV) chloride, and mixtures thereof.

[0029] In some embodiments, the salt hydrate is selected from the group consisting of copper(II) sulfate pentahydrate, zinc sulfate heptahydrate, calcium chloride dihydrate, magnesium sulfate heptahydrate, iron(II) sulfate heptahydrate, magnesium chloride hexahydrate, sodium carbonate decahydrate, sodium thiosulfate pentahydrate, barium hydroxide octahydrate, iron(II) acetate tetrahydrate, zinc nitrate hexahydrate, magnesium ammonium phosphate hexahydrate, iridium(III) bromide tetrahydrate, sodium acetate trihydrate, calcium sulfate dihydrate, sodium dihydrogen phosphate heptahydrate, sodium sulfate decahydrate, nickel(II) nitrate hexahydrate, iron(III) chloride hexahydrate, nickel(II) sulfate hexahydrate, manganese(II) sulfate monohydrate, sodium monohydrogen phosphate heptahydrate, manganese(II) chloride tetrahydrate, copper(II) nitrate hexahydrate, calcium nitrate tetrahydrate, cobalt(II) chloride hexahydrate, nickel(II) chloride hexahydrate, nickel(II) sulfate tetrahydrate, sodium dichromate dihydrate, copper(II) nitrate trihydrate, tin(IV) chloride pentahydrate, and mixtures thereof.

[0030] After removing the debris, the method disclosed herein may further comprise the step of the cleaning the surface using a composition comprising hydrogen peroxide, catalyst for decomposing peroxide compounds, SAA, chelating agent, water-soluble calixarene, anti-foaming agent and water. Such step is described in PCT/RU2017/05005 and PCT/RU2018/050154, each of which is hereby incorporated by reference in its entirety.

EXAMPLES

[0031] The embodiments encompassed herein are now described with reference to the following examples. These examples are provided for the purpose of illustration only and the disclosure encompassed herein should in no way be construed as being limited to these examples, but rather should be construed to encompass any and all variations which become evident as a result of the teachings provided herein.

Example 1: Removing deposits from a metal surface using sodium sulfate

The sample is a steel cylindrical part (height 10 cm, diameter 5 cm) of oil production equipment covered with a layer of barite deposit (thickness 5 mm).

1. The sample is immersed in 14 % Na_2SO_4 solution at 25 °C for an hour.
2. Then the sample is dried at 105 °C for an hour.
3. After cooling to 25 °C the sample is immersed again in the same solution for 5 hours.
4. Steps 2-3 are repeated 3 times.

As a result, during first one or two cycles, cracks appear on deposit layer, and during the third cycle deposit pieces are detached from the steel sample.

Following washing by water removes deposits completely.

Example 2: Removing deposits from a CDU preheat train heat-exchanger

[0032] The following prophetic example illustrates the applying of method for clean-up of a shell side of a small-size shell-and-tube heat-exchanger fouled with porous petcoke deposits. The fouling consists mostly of elemental carbon, the average thickness of fouling layer is 5 mm. The median pore diameter is 0.02 mm. 14% solution of sodium sulfate is used for the first and the second immersions.

[0033] The clean-up proceeds as follows:

[0034] The shell side of the heat-exchanger (hereinafter referred to as contour) is filled with sodium sulfate solution and left undisturbed for 6 hours for the solution to soak the deposits. After 3 hours the solution is drained from the contour to the recycle storage tank. The contour is then dried for 1 hour with a 150°C steam supplied to the tube side. After drying the contour is filled with the same sodium sulfate solution and left undisturbed for 3 hours. The contour is then connected to the circulation loop comprising pump and filter units. Circulation of the solution resulted in accumulation of the fouling debris in the filter units. The commissioning of the dismantled tube bundle showed complete removal of all fouling material.

CLAIMS

1. A method for removing deposits from a surface comprising the steps of:
 - wetting the surface in a first salt solution so that the first salt solution penetrates into the cracks or pores of the deposits;
 - removing the first salt solution outside the cracks or pores of the deposits;
 - drying the surface so that the first salt solution inside the cracks or pores of the deposits becomes an anhydrous salt; and
 - wetting the surface in a second salt solution;

wherein the anhydrous salt forms a salt hydrate inside the cracks or pores of the deposits and causes volume expansion, resulting in breaking the deposits from the surface.
2. The method of claim 1, wherein the first salt solution is the same as the second salt solution.
3. The method of claim 1, wherein the first salt solution is different from the second salt solution.
4. The method of claim 1, wherein the first salt solution is a saturated solution of the salt.
5. The method of claim 1, wherein the first salt solution is an unsaturated solution of the salt.
6. The method of claim 1, wherein the second salt solution is a saturated solution of the salt.
7. The method of any one of the claims 1-6, wherein the first salt solution and the second salt solution independently comprise a salt selected from the group consisting of copper(II) sulfate, zinc sulfate, calcium chloride, magnesium sulfate, iron(II) sulfate, magnesium chloride, sodium carbonate, sodium thiosulfate, barium hydroxide, iron(II) acetate, zinc nitrate, magnesium ammonium phosphate, iridium(III) bromide, sodium acetate, calcium sulfate, sodium dihydrogen phosphate, sodium sulfate, nickel(II) nitrate, iron(III) chloride, nickel(II) sulfate, manganese(II) sulfate, sodium monohydrogen phosphate, manganese(II) chloride, copper(II) nitrate, calcium nitrate, cobalt(II) chloride, nickel(II) chloride, nickel(II) sulfate, sodium dichromate, copper(II) nitrate, tin(IV) chloride, and mixtures thereof.

8. The method of claim 1, wherein the first salt solution is a solution of sodium sulfate.
9. The method of claim 8, wherein the concentration of the first salt solution is about 14%.
10. The method of claim 1, wherein the second salt solution is a solution of sodium sulfate.
11. The method of claim 10, wherein the concentration of the second salt solution is about 14%.
12. The method of claim 1, wherein the surface is dried at selected from the group consisting of about 50°C, about 55°C, about 60°C, about 65°C, about 70°C, about 75°C, about 80°C, about 85°C, about 90°C, about 95°C, about 100°C, about 100°C, about 120°C, about 125°C, about 130°C, about 135°C, about 140°C, about 150°C, about 155°C, about 160°C, about 165°C, about 170°C, about 175°C, about 180°C, about 185°C, about 190°C, about 195°C, and about 200°C.
13. The method of claim 1, wherein the surface is dried by vacuum drying.
14. The method of claim 13, where the vacuum drying is conducted in a vacuum selected from the group consisting of about 1 Torr, about 10 Torr, about 25 Torr, about 50 Torr, about 75 Torr, about 100 Torr, about 125 Torr, about 150 Torr, about 175 Torr, about 200 Torr, about 225 Torr, about 250 Torr, about 275 Torr, about 300 Torr, about 325 Torr, about 350 Torr, about 350 Torr, about 375 Torr, about 400 Torr, about 425 Torr, about 450 Torr, about 475 Torr, about 500 Torr, about 525 Torr, about 550 Torr, about 575 Torr, about 600 Torr, about 625 Torr, about 650 Torr, about 675 Torr, and about 700 Torr.
15. The method of claim 1, wherein the salt hydrate is selected from the group consisting of copper(II) sulfate pentahydrate, zinc sulfate heptahydrate, calcium chloride dihydrate, magnesium sulfate heptahydrate, iron(II) sulfate heptahydrate, magnesium chloride hexahydrate, sodium carbonate decahydrate, sodium thiosulfate pentahydrate, barium hydroxide octahydrate, iron(II) acetate tetrahydrate, zinc nitrate hexahydrate, magnesium ammonium phosphate hexahydrate, iridium(III) bromide tetrahydrate, sodium acetate trihydrate, calcium sulfate dihydrate, sodium dihydrogen phosphate heptahydrate, sodium sulfate decahydrate, nickel(II) nitrate hexahydrate, iron(III) chloride hexahydrate, nickel(II) sulfate hexahydrate, manganese(II) sulfate monohydrate, sodium monohydrogen phosphate heptahydrate, manganese(II) chloride tetrahydrate, copper(II) nitrate hexahydrate, calcium nitrate tetrahydrate, cobalt(II) chloride hexahydrate, nickel(II) chloride hexahydrate, nickel(II) sulfate tetrahydrate,

sodium dichromate dihydrate, copper(II) nitrate trihydrate, tin(IV) chloride pentahydrate, and mixtures thereof.

16. The method of claim 1, wherein the anhydrous salt comprises a salt selected from the group consisting of copper(II) sulfate, zinc sulfate, calcium chloride, magnesium sulfate, iron(II) sulfate, magnesium chloride, sodium carbonate, sodium thiosulfate, barium hydroxide, iron(II) acetate, zinc nitrate, magnesium ammonium phosphate, iridium(III) bromide, sodium acetate, calcium sulfate, sodium dihydrogen phosphate, sodium sulfate, nickel(II) nitrate, iron(III) chloride, nickel(II) sulfate, manganese(II) sulfate, sodium monohydrogen phosphate, manganese(II) chloride, copper(II) nitrate, calcium nitrate, cobalt(II) chloride, nickel(II) chloride, nickel(II) sulfate, sodium dichromate, copper(II) nitrate, tin(IV) chloride, and mixtures thereof.
17. The method of claim 1, wherein the salt hydrate is in a crystalline form.
18. The method of claim 1, wherein the volume expansion is at least about 2 times.
19. The method of claim 1, wherein the concentration of the first salt solution is about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, 55%, about 60%, about 65%, about 70%, or about 75% by the weight of the salt.
20. The method of claim 19, wherein the concentration of the second salt solution is about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, 55%, about 60%, about 65%, about 70%, or about 75% by the weight of the salt.