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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 August 2016 (25.08.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/133884 A1

(51) International Patent Classification:
*G01N 31/22* (2006.01) *G01N 33/18* (2006.01)

(21) International Application Number:
PCT/US2016/018034

(22) International Filing Date:
16 February 2016 (16.02.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
201510084559.1 16 February 2015 (16.02.2015) CN

(71) Applicant: **ECOLAB USA INC.** [US/US]; 370 N. Wabasha Street, St. Paul, Minnesota 55102 (US).

(72) Inventors: **JIN, Ning**; c/o Nalco (China) Environmental Solution, Co., Ltd., Building B & C, Jinqiao Science Park, No. 255 Guiqiao Road, Pudong, Shanghai, 201206 (CN). **JIANG, Lin**; c/o Nalco (China) Environmental Solution, Ltd., Co., Building B & C, Jinqiao Science Park, No. 255 Guiqiao Road, Pudong, Shanghai, 201206 (CN). **XIA, Fei**; c/o Nalco (China) Environmental Solution, Co., Ltd., Building B & C, Jinqiao Science Park, No. 255 Guiqiao Road, Pudong, Shanghai, 201206 (CN). **HAN, Ling Feng**; c/o Nalco (China) Environmental Solution, Co., Ltd., Building B & C, Jinqiao Science Park, No. 255 Guiqiao Road, Pudong, Shanghai, 201206 (CN). **YU, Chun Bo**; c/o Nalco (China) Environmental Solution, Co., Ltd., Building B & C, Jinqiao Science Park, No. 255 Guiqiao Road, Pudong, Shanghai, 201206 (CN).

(74) Agent: **DEMASTER, Eric E.**; 655 Lone Oak Drive - ESC-F7, Eagan, Minnesota 55121 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17**:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

**Published**:

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

WO 2016/133884 A1

(54) **Title**: COMPOSITION AND METHOD FOR MEASURING ANIONIC POLYMER CONCENTRATION IN INDUSTRIAL WATER SYSTEM AND USE OF THE COMPOSITION

(57) **Abstract**: A composition for detecting anionic polymers in industrial water, wherein the composition comprises a combination of anionic dye and cationic surfactant; and a method for detecting anionic polymers in industrial water. Compared to the cationic dyes approach, the disclosed composition and method enables reduction of background interference from conductivity, resulting in accurate measurements.

# COMPOSITION AND METHOD FOR MEASURING ANIONIC POLYMER CONCENTRATION IN INDUSTRIAL WATER SYSTEM AND USE OF THE COMPOSITION

## TECHNICAL FIELD

**[0001]** The application relates to a composition for measuring an anionic water soluble polymer in an industrial water system, a method for detecting the anionic polymer in the industrial water system using said composition and use of said composition.

## BACKGROUND OF THE INVENTION

**[0002]** Generally, a large amount of water is needed in industry, for example, a large of amount of cooling water or water steam is used in heat exchange devices. If untreated water is used in these devices, scaling or deposit formation will usually occur in them, which adversely affects the rate of heat transfer. Removal of such scales or deposits can be troublesome and usually requires shutdown of the devices. In practice, anionic water soluble polymers can be used to effectively prevent scale and deposit formation in devices as, for example, a dirt dispersion agent. These polymers usually contain carboxylate and sulfonate functional groups which can interact with cations, such as calcium, in the industrial water to inhibit scale or deposit formation.

**[0003]** If the amount of the anionic polymer added into the industrial water system is too low, scaling will usually occur. On the contrary, if the amount of the anionic polymer is too high, it will not bring about a better scaling preventing effect, causes waste, and also has a negative impact on corrosive inhibitor performance of the device. Therefore, it is required in industry that when anionic polymers are present in the industrial water the concentration of these polymers must be checked checked with the goal of maintaining the polymer concentration at an optimal range for individual industrial water system.

**[0004]** Currently, in order to measure these anionic polymers, a cationic dye is often used to interact with the anionic polymers in the aqueous solution, causing a color change from which the concentration of the anionic polymers in the water system can be determined quantitatively with a colorimetrical method. A series of cationic dyes directed to common anionic polymers in industrial water have been disclosed, for example, US 6,214,617 used the dye Nile blue, WO 2008/147618 A1 employed dyes 1,9-dimethyl methylene blue (DMMB), basic blue 17, and New methylene blue N. US 4,894,346 also describes a number of dyes which include pinacyanol chloride, Nile blue A, neutral red,

safrin O, methylene blue, methyl red, toluidine blue, new methylene blue, quinalizarin, tetrechrome, brilliant blue G, and mordant black II. All these dyes have a similar feature in that they carry one or two positive charges and their main UV-Vis spectra peak usually broadens and shortens when interacted with the anionic polymers in aqueous solution. Such changes in the spectral peaks can be used to assay the anionic polymer concentration in the aqueous solution quantitatively.

**[0005]** Certain shortcomings are associated with the current method for measuring the concentration of the anionic polymers in industrial water using cationic dyes. First, since the electrostatic interaction is an important factor for the association between the cationic dye and the anionic polymer, conductivity of the water can severely affect the accuracy of the measurement. Moreover, the cationic dyes described in most publications carry no more than two positive charges, thus, their interactions with the anionic polymers are often weak and prone to interferences by conductivity and other substances. Secondly, the colorimetric measurement has a high background because the UV-Vis spectral peaks of the dyes typically become shorter with the increase of the anionic polymer. Any minor error in the dye concentration of the measuring device might cause great error in the measurement.

**[0006]** The object of the invention is to overcome these defects and provide a more reliable and accurate way to measure the concentration of the anionic polymer in an industrial water system.

## SUMMARY OF THE INVENTION

**[0007]** The invention provides a composition for measuring the concentration of an anionic polymer in an industrial water system. The invention further provides a method for measuring the concentration of the anionic polymer in the industrial water system using said composition and use of said composition as a detection reagent for measuring the concentration of the anionic polymer in the industrial water system. By using the composition of the invention, the concentration of the anionic polymer in the industrial water system can be rapidly measured, and the measurement is more accurate and reliable with higher sensitivity as compared to convention methods.

**[0008]** It has surprisingly been found that the concentration of an anionic polymer in an aqueous solution can be measured by combining an anionic dye and a cationic surfactant. On such bases, the invention provides a composition for measuring the concentration of an anionic polymer in industrial water, wherein the composition comprises an anionic

dye and a cationic surfactant. The combination of the anionic dye and the cationic surfactant enables use of said composition of the invention to measure the concentration of the anionic polymer in the industrial water system.

**[0009]** The invention further provides a kit for measuring the concentration of an anionic polymer in industrial water, wherein the kit comprises the aforesaid composition comprising an anionic dye and a cationic surfactant.

**[0010]** The invention further provides a method for measuring the concentration of an anionic polymer in industrial water comprising

(i) taking a sample from industrial water;

(ii) mixing the aforesaid composition with the industrial water sample into a solution and allow it to develop a color; and

(iii) measuring concentration of anionic polymers with a colorimetrical method.

**[0011]** The invention further provides use of said composition as a detection reagent for measuring the concentration of an anionic polymer in an industrial water system.

BRIEF DESCRIPTION OF THE DRAWINGS

**[0012]** Figure 1: A UV-Vis spectrum after the interaction between the composition of the invention and Nalco-HSP (terpolymer of acrylamide, acrylic acid, and acrylamidomethanesulfonic acid) at certain concentrations, as measured using a UV-Vis spectrometer. The background absorption at 700 nm was eliminated using a borax buffer system. 2-4 measurements were taken at each concentration of the polymer before plotted together.

**[0013]** Figure 2: A UV-Vis spectrum of Nalco-HSP2 (copolymer of acrylamide and 2-acrylamido-2-methylpropane sulfonic acid) at certain concentrations using the composition of the invention, as measured using a UV-Vis spectrometer. The background absorption at 700 nm was not subtracted from said spectrum. Tris buffer system was used. 2-3 measurements were taken at each concentration of the polymer before plotted together.

**[0014]** Figure 3: The calibration curve for measuring HSP and HPS2. After the background at 700 nm was eliminated, the curve was plotted using the mean of the absorbance readings at 606 nm and 615 nm verse the polymer concentration.

DETAILED DESCRIPTION OF THE INVENION

**[0015]** A composition comprising an anionic dye in combination with a cationic

surfactant is disclosed. The composition can be used to measure the concentration of an anionic polymer in a water system. When said combination is used to measure the anionic polymer, the anionic polymer competes with the anionic dye in the combination for the binding of the cationic surfactant as the substrate. While not wishing to be bound by a particular theory, it is believed that the anionic polymer, as a polymer, will be favored over the small molecular anionic dye to bind to the cationic surfactant in the combination. In the invention, an appropriate amount of an anionic dye and a cationic surfactant are added into a solution containing an anionic polymer, and then the anionic polymer will displace the anionic dye to bind to the cationic surfactant which releases the anionic dye into the solution. The concentration of the anionic polymer in the water system is measured using a colorimetric method by the color change exhibited by the anionic dye released.

**[0016]** On such basis, the invention provides a composition for measuring the concentration of an anionic polymer in industrial water, wherein the composition comprises a combination of an anionic dye and a cationic surfactant.

**[0017]** Anionic polymers used in current industrial water system are known to a skilled artisan, which include those anionic polymers containing carboxylate and sulfonate groups. For anionic polymers used in the art, for example, those disclosed in "Industrial Polymers, Specialty Polymers, and Their Applications" (Manas Chanda, Salil K. Roy, disclosed on July 18, 2008) can be used as reference (said disclosure is herein incorporated in its entirety).

**[0018]** All common cationic surfactant can be used as the cationic surfactant in the combination of the cationic surfactant and anionic dye in the invention. Preferably, the cationic surfactant can be selected from those having low critical micelle concentrations (CMC). Without wishing to be bound by theory, it is believed that a cationic surfactant having low critical micelle concentrations have higher tendency to aggregate in an aqueous solution and is more suitable for an anionic dye to aggregate on its surface and develop a color. Moreover, when said anionic dye is displaced by an anionic polymer and released, it can cause more significant color change, thus favors measuring the concentration of the anionic polymer in the water system by a colorimetric method. In the invention, it is desired that the critical micelle concentration of the cationic surfactant be about 0.001-20mmol/L, preferably about 0.1-5 mmol/L, and more preferably about 0.1-1mmol/L. The cationic surfactant used in the invention is for example a quaternary cationic surfactant, such as laureltrimethylammonium chloride,

myristyltrimethylammonium chloride, cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, laureltrimethylammonium bromide, myristyltrimethylammonium bromide, cetyltrimethylammonium bromide, and stearyltrimethylammonium bromide.

**[0019]** As a binding matrix, the cationic surfactant is used in an amount also dependent on the level of the anionic polymer contained in the industrial water to be measured. Currently, the concentration of the anionic polymer in usual industrial water is about 0-100ppm. Given such a concentration of the anionic polymer, the level of the cationic surfactant in the composition is usually about 5-500ppm, preferably about 10-300ppm, and more preferably about 20-100ppm. Alternatively, the concentration of the cationic surfactant in the industrial water is preferably about 0.05-2mmol/L, preferably about 0.05-1mmol/L, and more preferably about 0.1-0.4mmol/L. The aforesaid ppm concentration is on the basis of the total weight of the solution obtained by mixing with industrial water containing the anion-containing polymer. The level of the cationic surfactant depends on the parameters such as concentration and charge density of the anionic polymer contained in the industrial water to be measured.

**[0020]** In the invention, the anionic dye is selected from those having electrostatic interaction with the cationic surfactant in the water system and having color change when displaced by an anionic polymer. Preferably, the anionic dye is selected from those having many negative charges and having large spectral change when interacting with the cationic surfactant. Preferably, the anionic dye carries four or more anions which can greatly reduce the interference from the water system itself and allow stable color development due to strong electrostatic interaction with the cationic surfactant. A skilled artisan is able to select the anionic dye. In the invention, calcium and magnesium indicators such as methylthymol blue, ortho cresolphthalein complexone, arsenazo III, and chlorophosphonazo III can be selected as the anionic dye.

**[0021]** The amount of the anionic dye used depends on the concentration of the anionic polymer in the industrial water. In industry, the level of the anionic polymer in a water system is generally about 0-100ppm. Given such an amount of the anionic polymer in the water system, the corresponding level of the anionic dye is generally about 5-500ppm, preferably about 10-300ppm, and more preferably, about 20-100ppm. The aforesaid ppm concentration is on the basis of the total weight of the solution obtained by mixing with industrial water containing the anion-containing polymer. The level of the anionic dye depends on the parameters such as concentration and charge density of the anionic

polymer contained in the industrial water to be measured. The concentration of the anionic dye in the industrial water is, for example, about 0.02-1 mmol /L, preferably about 0.02-0.5 mmol/L, and more preferably about 0.04-0.2 mmol/L.

**[0022]** In practice, the optimum amounts of the anionic dye and the cationic surfactant are associated with the concentration, charge of the anionic polymer, which can be determined by a person skilled in the art according to the disclosure herein. Moreover, the amounts of the cationic surfactant and anionic dye used also depend on the types of the cationic surfactant and the anionic dye specifically chosen. Generally, the amount of the anionic dye or cationic surfactant used is comparative to the level of the anionic polymer to be measured, for example, 0.2 to 5 times, preferably 0.3 to 3 times, and more preferably 0.5 to 2 times of the mole number of the charge carried by the anionic polymer.

**[0023]** Industrial water generally further contains divalent metal ions such as calcium and magnesium. These metal ions can bind to the anionic polymer or the anionic dye to interfere with the measurement. In order to eliminate the effect of the metal ions contained in the water system on the measurement, a masking agent can be used to mask these metal ions in the water system. Generally, a masking agent inert to other components of the system and able to effectively mask the metal ions in the water system is selected. Depending on different water systems, the masking agent can totally mask divalent ions calcium and magnesium under appropriate conditions (for example, pH). A skilled artisan is able to determine the type and level of the masking agent used according to specific circumstance. For a common industrial water system, for example, ethylenediamine tetraacetic acid can be used as the masking agent. The amount of the masking agent used is, for example, about 10-20 mmol/L.

**[0024]** In order to maintain the pH of the industrial water system, an appropriate buffer system is required. Any buffer system that can maintain the water system close to neutral or close to alkaline range can be used in the invention, for example, those buffer systems that can maintain the pH of the water system at the range of 5-13. The buffer system can be selected from, for example, Borax or Tris-HCl buffer system.

**[0025]** The composition of the invention can further comprise other chemical reagents such as filler or a preservative whose level can be determined by a skilled artisan.

**[0026]** The invention provides a kit for measuring the anionic polymer in industrial water. The kit comprises the composition of the invention and a calibration curve (standard curve) for determining the concentration of the anionic polymer. This kit

enables rapid measurement of the color developed in an industrial water system and determination of the concentration of the anionic polymer contained in the industrial water system according to the calibration curve. This kit can further comprise other active components for measuring the industrial water. These components can be included in said composition or packaged separately from said composition.

**[0027]** The composition for measuring the concentration of an anionic polymer in industrial water of the invention can be prepared by mixing the various components of the composition. The composition of the invention can be in various forms, such as in a form of a mixed powder or concentrated solution.

**[0028]** The invention provides a method for measuring the concentration of an anionic polymer in industrial water comprising

(i) taking a sample from industrial water;

(ii) mixing the aforesaid composition with the industrial water sample into a solution and allow it to develop a color; and

(iii) measuring the concentration of said anionic polymer with a colorimetric method.

**[0029]** In step (ii), the composition of the invention can be added into a water sample and mixed thoroughly to form a color development solution. Alternatively, the anionic dye and the cationic surfactant contained in the composition can be added into the industrial water sample separately to form the solution that contains the composition of the invention. In order to obtain the solution, the anionic dye can be first added and then the cationic surfactant is added into the water sample of the industrial water, and vice versa.

**[0030]** In step (iii), the US-Vis absorption of the water sample is measured at predetermined wavelength using a spectrometer (colorimeter). The concentration of the anionic polymer in the industrial water is obtained by comparing it colorimetrically with a absorption curve (calibration curve) of a stand solution containing the anionic polymer obtained beforehand.

**[0031]** In order to obtain the aforesaid calibration curve, water samples of equial volume having different known anionic polymer concentrations can be placed under UV-Vis analysis to measure the absorption at each concentration. Subsequently, a absorption vs. anionic polymer concentration curve is plotted according to the measured data, which is the aforesaid calibration curve.

**[0032]** The composition of the invention allows measurement of anionic polymers of

different concentration range. The desired measurement result can be obtained by modifying the cationic surfactant and anionic dye in amounts according to need. Generally, the composition of the invention can be used to measure an anionic polymer in a level within the range of about 0-50 ppm, preferably about 0 up to 30 ppm, and more preferably about 0 up to 20 ppm in an industrial water system.

**[0033]** The industrial water described in the invention comprises primary production water, supplementary production water and auxiliary production water. The main production water includes water directly used for the industrial production, including process water and indirect cooling water. The supplementary production water is the water used in the supplementary production devices that in turn serves the main production devices, including water used for maintenance, boiler water treatment station, air compression station, sewage treatment plant, storage and transportation, air blower station, oxygen station, electrical repair, detection and testing, and the like. The auxiliary production water is a collective name for various kinds of water for life use or other use that serves the production within the plant area. When the aforesaid industrial water contains an anionic polymer, the concentration of the anionic polymer in the water can be measured using the composition described in the invention.

**[0034]** In the invention, an anionic ion dye is released by using the superior ability of an anionic polymer to the anionic dye to bind to a cationic surfactant. Without being bound by theory, when an anionic polymer is present in a solution, the anionic dye is displaced from the surface of the micelle of the cationic surfactant and exhibits its normal spectrum. Therefore, with the increase of the polymer concentration, the absorption at the most sensitive wavelength or wavelength range will increase. The high background absorption produced in the current techniques using the cationic dye-anionic polymer system for color development is reduced due to color development from free anionic dye, which increases the precision of the measurement.

**[0035]** Moreover, the cationic dyes used in the current techniques seldom carry more than two positive charges. On the contrary, many anionic dyes have three, four or more negative charges. Therefore, stronger electrostatic interaction is generated by using anionic dyes with more negative charges in the dye-surfactant interaction in the invention, which reduces the interference from the conductivity of the industrial water and other factors.

EXAMPLES

**[0036]** The invention is not limited by the following examples. The following examples are provided for the purpose of illustration, rather than limiting the scope of the invention, which is based on the appended claims.

**[0037]** Example 1

**[0038]** The formulation shown in Figure 1 was used to measure 0-20 ppm of Nalco HSP (terpolymer of acrylamide, acrylic acid, and acrylamidomethanesulfonic acid). The solution contains calcium (1000 ppm, in CaCO3) and has conductivity of 0-8ms/cm did not interfere with the measurement. Borax buffer system was used. The spectra for the HSP measurement are shown in Figure 1.

Table 1

| Reagents | concentration (mmol/L) in the industrial water |
|---|---|
| Methylthymol blue | 0.059 |
| Stearyltrimethylammonium chloride | 0.21 |
| Sodium tetraborate | 80 |
| EDTA (disodium) | 12 |

**[0039]** EXAMPLE 2

**[0040]** The formulation shown in Figure 2 was used to measure 0-20 ppm of Nalco HSP-2 (copolymer of acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid). The solution contains calcium (1000 ppm, in CaCO3) and has conductivity of 0-8ms/cm, which did not interfere with the measurement. Tris buffer system was used. The spectra for the HSP-2 measurement are shown in Figure 2.

Table 2

| Reagents | Concentration (mmol/L) |
|---|---|
| Methylthymol blue | 0.059 |
| Stearyltrimethylammonium Chloride | 0.21 |
| Tris-hydroxymethyl amino methane | 200 |
| Tris-HCl | 40 |
| EDTA (disodium) | 12 |

**[0041]** The duration of color development in Examples 1 and 2 was 1-2 minutes.

**[0042]** As shown in Figures 1 and 2, it can be seen that background absorption exists in the whole wavelength range due to the interaction of the anion polymer and the cation surfactant in the aqueous solution. The effect of said background absorption on the measurement can be eliminated by manually subtracting the background absorption at the 700-900nm interval.

**[0043]** Figure 3 shows the calibration curve for Nalco HSP and Nalco HSP-2 of the above Examples.

**[0044]** As compared to the conventional method using a cationic dye, the composition of the invention enables reduction of background absorption and interference from conductivity. The measurement is convenient, rapid and accurate. The composition of the invention can also be packaged in a kit which is convenient to carry and measure an industrial water system.

CLAIMS

1. A composition for detecting anionic polymers in industrial water, wherein the composition comprises a combination of anionic dyes and cationic surfactants.

2. The composition according to claim 1, wherein the cationic surfactant has a critical micelle concentration of about 0.001-20mmol/L.

3. The composition according to claim 1 or 2, wherein the cationic surfactant is a quaternary ammonium salt surfactant.

4. The composition according to any one of claims 1 to 3, wherein the anionic dyes have three or more, preferably 3 to 4 anionic charges.

5. The composition according to any one of claims 1 to 4, wherein the anionic dye is selected from a group consisting of calcium indicators and magnesium indicators.

6. The composition according to any one of claims 1 to 5, wherein the anionic dyes are selected from methylthymol blue, ortho cresolphthalein complexone, arsenazo III, and Chlorophosphonazo III.

7. The composition according to claim 1, wherein the cationic surfactants are selected from dodecyltrimethylammonium, tetradecyltrimethylammoniu, hexadecyltrimethylammonium, octadecyltrimethylammonium chloride and bromide.

8. The composition according to any one of claims 1 to 7, wherein the molar ratio of cationic surfactants to anionic polymers is from about 1.5:1 to 10:1.

9. The composition according to any one of claims 1 to 8, wherein the molar ratio of anionic dyes to anionic polymers is from about 1.5:1 to 5:1.

10. The composition according to any one of claims 1 to 9, further compries a buffer system of pH at about 5 to 13.

11. The composition according to any one of claims 1 to 10, further comprises a

masking agent for divalent metallic ions in the industrial water, preferably EDTA.

12. The composition according to claim 1, comprises

about 20 ppm to 100 ppm methylthymol blue;

about 20 ppm to 100 ppm octadecyltrimethylammonium chloride;

about 0 to 5000 ppm Borax or Tris-HCl; and

about 0 to 5000 ppm EDTA.

13. A method for detecting anionic polymers in industrial water, wherein the method comprises

(i) taking a sample from the industrial water;

(ii) mixing the composition according to any one of claims 1 to 12 with the industrial water sample into a solution and allow it to develop a color; and

(iii) measuring concentration of anionic polymers with a colorimetrical method.

14. The method according to claim 13, wherein in the solution, the anionic dye has a concentration of about 0.02-1mmol/L, preferably about 0.02-0.5mmol/L, preferably about 0.04-0.2mmol/L; and the cationic surfactant has a concentration of about 0.05-2mmol/L; preferably about 0.05-1mmol/L, preferably about 0.1-0.4mmol/L.

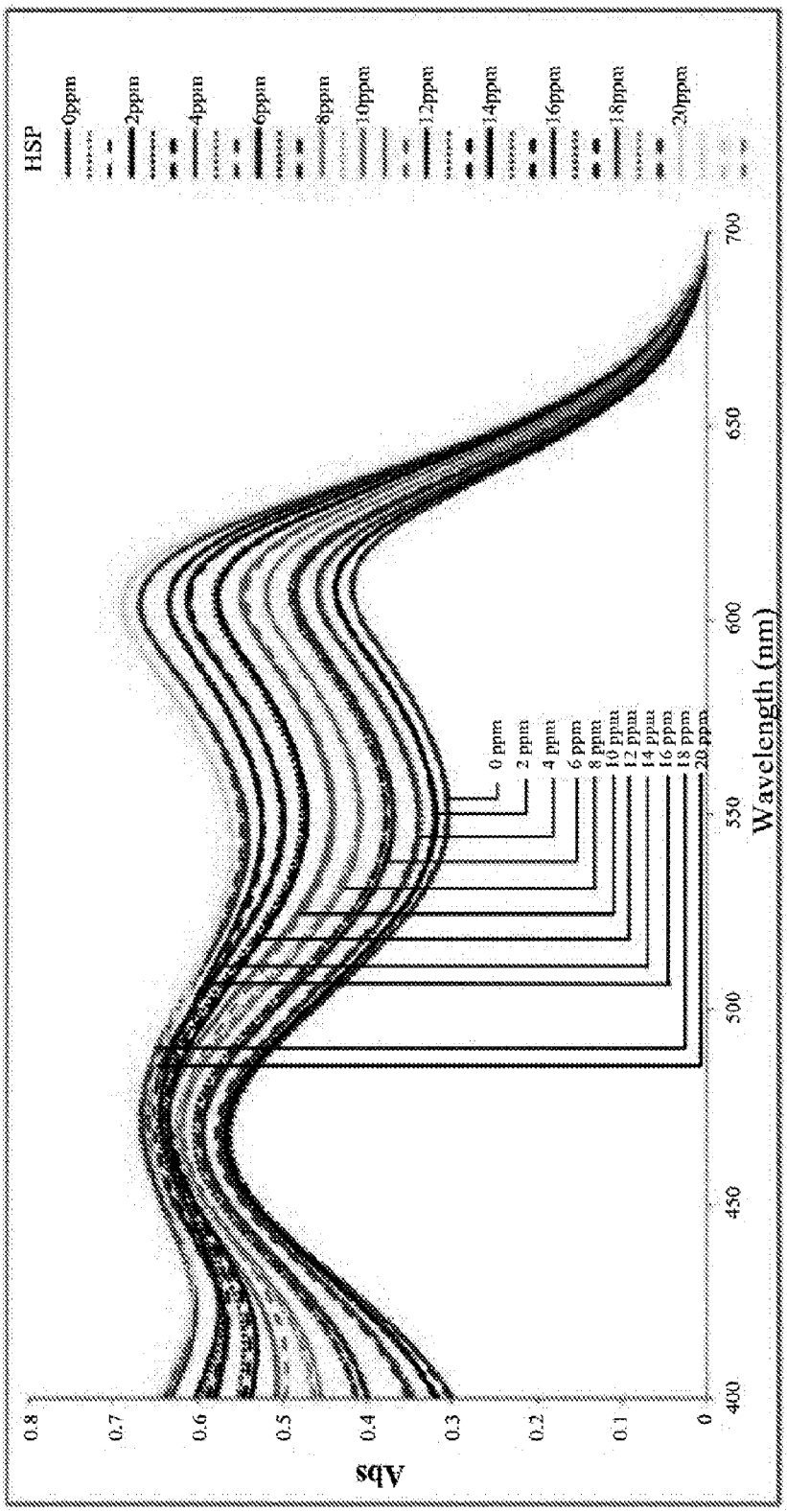
HSP
0ppm
2ppm
4ppm
6ppm
8ppm
10ppm
12ppm
14ppm
16ppm
18ppm
20ppm
0 ppm
2 ppm
4 ppm
6 ppm
8 ppm
10 ppm
12 ppm
14 ppm
16 ppm
18 ppm
20 ppm
Abs
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
400
450
500
550
600
650
700
Wavelength (nm)

Figure 1

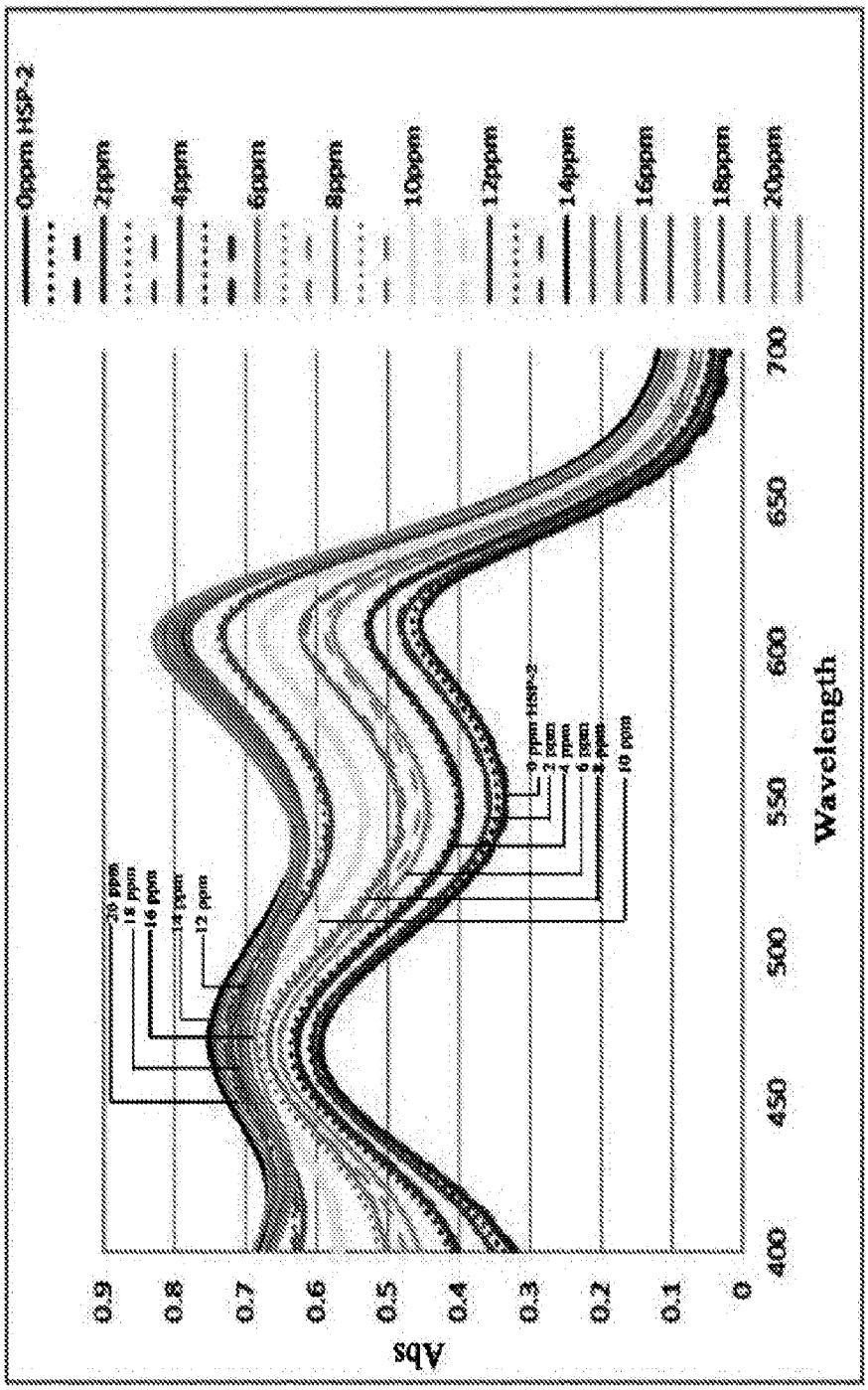
0ppm HSP-2
2ppm
4ppm
6ppm
8ppm
10ppm
12ppm
14ppm
16ppm
18ppm
20ppm
Abs
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
400
450
500
550
600
650
700
Wavelength
20 ppm
18 ppm
16 ppm
14 ppm
12 ppm
0 ppm HSP-2
2 ppm
4 ppm
6 ppm
8 ppm
10 ppm

Figure 2

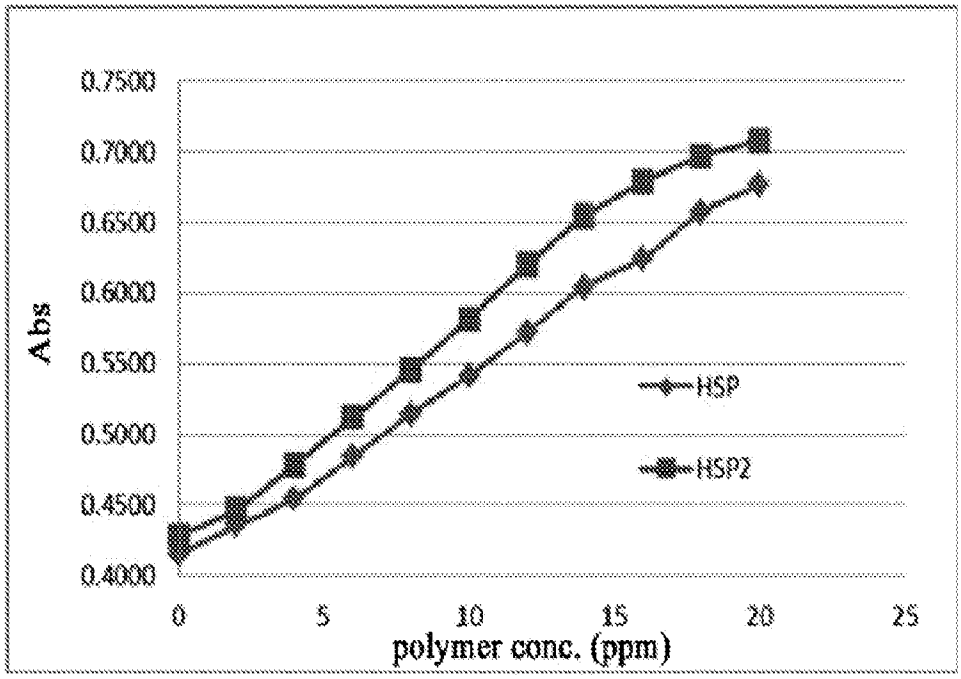
0.7500
0.7000
0.6500
0.6000
0.5500
0.5000
0.4500
0.4000
Abs
0
5
10
15
20
25
polymer conc. (ppm)
HSP
HSP2

Figure 3

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/018034

A. CLASSIFICATION OF SUBJECT MATTER
IPC (2016.01) G01N 31/22, G01N 33/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC (2016.01) G01N

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Databases consulted: Esp@cenet, Google Patents, Google Scholar, FamPat database
Search terms used: Anionic polymer ,anionic Dye , cationic Surfactant , colorimetric, Industrial water, scale inhibitor, analysis

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 4369250 A GINDLER E. M.<br>18 Jan 1983 (1983/01/18)<br>Abstract; col. 2 lines 11-13, col. 2 lines 36-44, col. 4 lines 12-19, col. 4 lines 34-50, col. 5 lines 1-3, col. 5 lines 39-42; col. 6 lines 17-19, col. 6 line 49 – col. 7 line 3 | 1-12 |
| Y | | 13,14 |
| X | US 2007092973 A1 POTYRAILO R. A. et al.<br>26 Apr 2007 (2007/04/26)<br>Para. [0065] | 1-9 |
| Y | US 6214627 B1 CIOTA S. R. et al.<br>10 Apr 2001 (2001/04/10)<br>Abstract ; claim 1 ; examples | 13,14 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 30 May 2016 | 31 May 2016 |

| Name and mailing address of the ISA: | Authorized officer |
|---|---|
| Israel Patent Office<br>Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel<br>Facsimile No. 972-2-5651616 | GUTMAN Ariel<br><br>Telephone No. 972-2-5657816 |

**INTERNATIONAL SEARCH REPORT**
Information on patent family members

International application No.
PCT/US2016/018034

| Patent document cited search report | Publication date | Patent family member(s) | Publication Date |
|---|---|---|---|
| US 4369250 A | 18 Jan 1983 | US 4369250 A | 18 Jan 1983 |
| US 2007092973 A1 | 26 Apr 2007 | US 2007092973 A1 | 26 Apr 2007 |
| | | US 7807473 B2 | 05 Oct 2010 |
| | | AU 2006306398 A1 | 03 May 2007 |
| | | AU 2006306398 B2 | 30 Aug 2012 |
| | | BR PI0619337 A2 | 27 Sep 2011 |
| | | CA 2625626 A1 | 03 May 2007 |
| | | CA 2625626 C | 29 Dec 2015 |
| | | CA 2851934 A1 | 03 May 2007 |
| | | CN 101297197 A | 29 Oct 2008 |
| | | CN 101297197 B | 10 Oct 2012 |
| | | EP 1949092 A1 | 30 Jul 2008 |
| | | HK 1125455 A1 | 19 Jul 2013 |
| | | JP 2009513977 A | 02 Apr 2009 |
| | | JP 5091147 B2 | 05 Dec 2012 |
| | | KR 20080066688 A | 16 Jul 2008 |
| | | KR 101329895 B1 | 15 Nov 2013 |
| | | MY 146554 A | 30 Aug 2012 |
| | | NZ 567588 A | 24 Dec 2010 |
| | | RU 2008120676 A | 10 Dec 2009 |
| | | RU 2427834 C2 | 27 Aug 2011 |
| | | US 2011014087 A1 | 20 Jan 2011 |
| | | US 8647883 B2 | 11 Feb 2014 |
| | | WO 2007050463 A1 | 03 May 2007 |
| US 6214627 B1 | 10 Apr 2001 | US 6214627 B1 | 10 Apr 2001 |
| | | AR 023168 A1 | 04 Sep 2002 |
| | | AU 3497000 A | 16 Oct 2000 |
| | | BR 0007284 A | 10 Sep 2002 |
| | | CA 2354015 A1 | 05 Oct 2000 |

**INTERNATIONAL SEARCH REPORT**
Information on patent family members

International application No.
PCT/US2016/018034

| Patent document cited search report | Publication date | Patent family member(s) | Publication Date |
|---|---|---|---|
| | | CA 2354015 C | 27 Apr 2010 |
| | | CO 5121092 A1 | 30 Jan 2002 |
| | | EP 1166105 A1 | 02 Jan 2002 |
| | | EP 1166105 A4 | 23 Apr 2003 |
| | | WO 0058725 A1 | 05 Oct 2000 |
| | | ZA 200104586 A | 20 May 2002 |