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(54) Title: METHOD FOR THE FLOCCULATION OF AQUEOUS DISPERSIONS

(57) Abstract: The invention relates to a method for flocculating aqueous dispersions of high salinity and high dry solids content in the presence of a dicyandiamide condensate and a cationic, non- ionic or amphiphilic acrylamide polymer. Further, the invention relates to the use of said dicyandiamide-formaldehyde condensate and said acrylamide polymer for flocculating drilling mud, bio-fermentation sludge and landfill-leachate.

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Method for the flocculation of aqueous dispersions

FIELD OF THE INVENTION

The invention relates to a method for flocculating aqueous dispersions of high salinity and high dry solids content in the presence of a dicyandiamide condensate and an acrylamide polymer. Further, the invention relates to the use of said dicyandiamide-formaldehyde condensate and said acrylamide polymer for flocculating drilling mud, bio-fermentation sludge or landfill-leachate.

BACKGROUND PRIOR ART

As a result of growing concern for the purity of water resources and in response to growing governmental pressures to maintain the quality of these water resources, industry has been required to investigate and implement methods for reducing chemical pollutants contained in their effluent streams. The danger of chemical pollution in water is mainly due to the presence of toxic constituents and the ability of organic constituents of the effluent streams to bind dissolved oxygen contained in the water. This binding, whether by chemical reaction or simple chemical interaction, prevents the utilization of dissolved oxygen by aquatic life. The effect of this binding is commonly referred to as chemical oxygen demand (COD).

One of the crucial steps in effluent treatment is the addition of flocculants to facilitate the separation of suspended solids and colloidal material from the effluent streams. Typically, polyelectrolytes are used to initiate the flocculation process. The overall flocculation mechanism is thought to involve a molecular bridge or series of bridges between solid particles. The polyelectrolyte is adsorbed to a particle and when another particle comes within close enough proximity, the extended polyelectrolyte chain is adsorbed on to it. This elementary floe grows by bridging with other particles until an optimum floe size is formed.

It is well known that the efficiency of flocculants depends on several properties of the effluent streams such as their pH, ionic strength (salinity) and solids content. It has been recognized that the ionic strength of the effluent may be a limiting factor for the use of polyelectrolytes, since their flocculating ability is significantly decreased at high ionic strength (high salinity). Further, a high solids content may be also a limiting factor, since it has been found that the higher the solids content the less pronounced is the flocculation effect brought about by the added flocculants.

Effluent streams of high salinity and solids content are frequently encountered in the treatment of drilling mud, bio-fermentation sludge and landfill leachate. The treatment of such effluents with flocculants often fails due to the formation of floes of insufficient size or due to the total absence of floe formation.

Therefore, there is a demand for a flocculation method which allows for the efficient treatment of effluent streams of high ionic strength (salinity) and high solids content.

JP 48 072 960 A discloses the clarification of waste water by adjusting the pH to 4-9 and adding polycationic surfactants prepared from dicyandiamide and optionally, polyacrylamide-system macromolecular flocculants. In an example, 200 ppm of a surfactant prepared from dicyandiamide, NH_4Cl and formalin are added to waste water from a milk processing plant after adjusting its pH to 6.5. Then, 10 ppm of an anionic polyacrylamide are added.

SUMMARY OF THE INVENTION

The invention relates to a method for flocculating an aqueous dispersion comprising the step of adding a dicyandiamide condensate and an acrylamide polymer to the aqueous dispersion, so that the relative weight ratio of the dicyandiamide-formaldehyde condensate to the acrylamide polymer in the aqueous dispersion is >10:1 .

It has been surprisingly found that the addition of a dicyandiamide condensate and an acrylamide polymer to aqueous dispersions such as aqueous effluents of high salinity and high dry solids content results in an efficient flocculation of the dispersed solids and colloidal material. Further, it has been surprisingly found that said method results in a decreased COD, a decreased filtration time and an increased clarity of the filtered effluent.

DETAILED DESCRIPTION OF THE INVENTION

A first aspect of the invention relates to a method for flocculating an aqueous dispersion comprising the step of adding a dicyandiamide-formaldehyde condensate and an acrylamide polymer, preferably a cationic, non-ionic or amphiphilic acrylamide polymer, to the aqueous dispersion, so that the relative weight ratio of the dicyandiamide condensate to the acrylamide polymer in the aqueous dispersion is >10:1.

It is apparent to a person skilled in the art that the dicyandiamide condensate and the acrylamide polymer may be, independently of each other, added to the aqueous dispersion in portions or in bulk.

For the purpose of the specification, the term "addition in portions" means preferably that the total amount of the dicyandiamide condensate and/or the total amount of acrylamide polymer are, independently of each other, divided in at least two portions. The respective portions may be separately added to the aqueous dispersion.

For the purpose of the specification, the term "addition in bulk" means that the total amount of the dicyandiamide condensate and/or the total amount of the acrylamide polymer are, independently of each other, added to the aqueous dispersion, i.e. without dividing the respective total amount into portions.

Both the addition in portions and the addition in bulk of the respective components may be performed punctually or continuously. For the purpose of the specification, the term "punctual addition" means the addition of the dicyandiamide condensate and/or the acrylamide polymer to the aqueous dispersion at a certain point in time by adding the intended amount of the respective component at once. The term "continuous addition" means herein that the addition of the dicyandiamide condensate and/or the acrylamide polymer to the aqueous dispersion is performed over a certain time interval. For example, in case that the dicyandiamide condensate is added continuously to the aqueous dispersion, the dicyandiamide condensate may be slowly dropped or poured into the aqueous dispersion over a certain time interval. It is apparent to a person skilled in the art that the punctual addition represents a fast addition step, whereas the continuous addition is considerably slower than the punctual addition.

In a preferred embodiment, the acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer, is added to the aqueous dispersion after the dicyandiamide condensate. In this respect, the acrylamide polymer may be added to the aqueous dispersion after at least a portion of the dicyandiamide condensate has been added to the aqueous dispersion, wherein both components, independently of each other, may be added in bulk or in portions, continuously or punctually.

More preferably, the total amount of the acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer, is continuously or punctually added to the aqueous dispersion after the total amount of dicyandiamide condensate has been added continuously or punctually to the aqueous dispersion.

In a particularly preferred embodiment, the dicyandiamide condensate is allowed to act on the aqueous dispersion (pretreatment) for at least 5 seconds, more preferably at least 30 seconds, still more preferably at least 1 minute, yet more preferably at least 15 minutes, most preferably at least 1 hour and in particular at least 2.0 hours, before the acrylamide polymer is added.

Preferably, the aqueous dispersion has a high dry solids content. A person skilled in the art knows how to measure the dry solids content of an aqueous dispersion. For example, the dry solids content may be determined gravimetrically after removing the liquid phase from a sample of the aqueous dispersion by evaporation.

Preferably, the aqueous dispersion has a dry solids content of at least 0.10 wt.-%, more preferably of at least 1.0 wt.-%, even more preferably of at least 2.5 wt.-%, still more preferably of at least 4.0 wt.-%, most preferably of at least 5.5 wt.-% and in particular of at least 7.0 wt.-% based on the total weight of the aqueous dispersion.

In another preferred embodiment, the aqueous dispersion has a dry solids content within the range of from 0.10 to 20 wt.-%, more preferably of from 0.10 to 17.5 wt.-%, even more preferably of from 0.10 to 15 wt.-%, still more preferably of from 0.10 to 12.5 wt.-%, most preferably of from 0.10 to 10 wt.-% and in particular of from 0.10 to 8.0 wt.-% based on the total weight of the aqueous dispersion.

It is particularly preferred that the aqueous dispersion has a dry solids content of 3.85±3.0 wt.-%, more preferably of 3.85±2.5 wt.-%, even more preferably of 3.85±2.0 wt.-%, still more preferably of 3.85±1.5 wt.-%, most preferably of 3.85±1.0 wt.-% and in particular of 3.85±0.50 wt.-% based on the total weight of the aqueous dispersion.

Preferably, the aqueous dispersion has a high ionic strength (salinity). A person skilled in the art knows how to measure the ionic strength of an aqueous dispersion. For example, the salinity may be determined by measuring the electric conductivity of the aqueous dispersion.

Preferably, the aqueous dispersion has a salinity expressed by its electric conductivity of at least 0.10 mS cm^{-1}, more preferably of at least 1.0 mS cm^{-1}, even more preferably of at least

2.5 mS cm^{-1}, still more preferably of at least 5.0 mS cm^{-1}, most preferably of at least 10 mS cm^{-1} and in particular of at least 15 mS cm^{-1}.

In another preferred embodiment, the salinity of the aqueous dispersion as expressed by its electric conductivity is within the range of from 0.10 to 100 mS cm^{-1}, more preferably of from 0.50 to 85 mS cm^{-1}, even more preferably of from 1.0 to 75 mS cm^{-1}, still more preferably of from 2.5 to 50 mS cm^{-1}, most preferably of from 5.0 to 30 mS cm^{-1} and in particular of from 7.5 to 20 mS cm^{-1}.

It is particularly preferred that the electric conductivity of the aqueous dispersion is 18.8±5.0 mS cm^{-1}, more preferably 18.8±4.0 mS cm^{-1}, even more preferably 18.8±3.0 mS cm^{-1}, still more preferably 18.8±2.0 mS cm^{-1}, most preferably 18.8±1.0 mS cm^{-1} and in particular 18.8±0.50 mS cm^{-1}.

In another preferred embodiment, the aqueous dispersion is drilling mud, bio-fermentation sludge or landfill leachate. A person skilled in the art knows the terms "drilling mud", "bio-fermentation sludge" and "landfill leachate".

Preferably, the dicyandiamide condensate is added to the aqueous dispersion to a final concentration of at least 0.10 kg m^{-3}, more preferably of at least 1.0 kg m^{-3}, even more preferably of at least 2.5 kg m^{-3}, still more preferably of at least 5.0 kg m^{-3}, most preferably of at least 10 kg m^{-3} and in particular of at least 15 kg m^{-3}.

In another preferred embodiment, the dicyandiamide condensate is added to the aqueous dispersion to a final concentration within the range of from 0.10 to 100 kg m^{-3}, more preferably of from 1.0 to 75 kg m^{-3}, even more preferably of from 2.5 to 50 kg m^{-3}, still more preferably of from 5.0 to 30 kg m^{-3} and in particular of from 10 to 20 kg m^{-3}.

In a particularly preferred embodiment, the dicyandiamide condensate is added to the aqueous dispersion, such as drilling mud, bio-fermentation sludge or landfill leachate, to a final concentration of 15±5.0 kg m^{-3}, more preferably of 15±4.0 kg m^{-3}, even more preferably of 15±3.0 kg m^{-3}, still more preferably of 15±2.0 kg m^{-3}, most preferably of 15±1.0 kg m^{-3} and in particular of 15±0.50 kg m^{-3}.

Preferably, the acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer, is added to the aqueous dispersion to a final concentration of at least 0.10 g m^{-3}, more preferably of at least 1.0 g m^{-3}, even more preferably of at least 5.0 g m^{-3}, still more preferably of at least 10 g m^{-3}, most preferably of at least 50 g m^{-3} and in particular of at least IOO g rrT^{3}.

In another preferred embodiment, the acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer, is added to the aqueous dispersion to a final concentration within the range of from 0.10 to 3,000 g m^{-3}, more preferably of from 1.0 to 2,000 g m^{-3}, even more preferably of from 10 to 1,500 g m^{-3}, still more preferably of from 25 to 1,000 g m^{-3}, most preferably of from 50 to 800 g nrï ^{3} and in particular of from 100 to 650 g m^{-3}.

It is particularly preferred that the acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer, is added to the aqueous dispersion to a final concentration of 300±150 g m^{-3}, more preferably of 300±120 g m^{-3}, even more preferably of 300±90 g m^{-3}, still more preferably of 300±60 g m^{-3}, most preferably of 300±30 g m^{-3} and in particular of 300±15 g m^{-3}.

The relative weight ratio of the dicyandiamide condensate to the acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer, in the aqueous dispersion is >10:1, preferably >20:1, more preferably >30:1 , still more preferably >40:1, most preferably >50:1 and in particular ≥60:1.

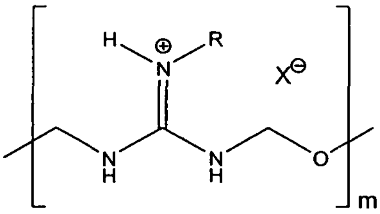
In another preferred embodiment, the relative weight ratio of dicyandiamide condensate to the acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer, in the aqueous dispersion is within the range of from >10:1 to 99:1, more preferably of from 20:1 to 80:1 , even more preferably of form 25:1 to 75:1, still more preferably of from 30:1 to 70:1 , most preferably of from 35:1 to 65:1 wt.-% and in particular of from 40:1 to 60:1 .

It is particularly preferred that the relative weight ratio of dicyandiamide condensate to the acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer, in the aqueous dispersion is (50±30):1, more preferably (50±25):1, even more preferably (50±20):1, still more preferably (50±15):1, most preferably (50±20):1 and in particular (50±5):1.

The term "dicyandiamide condensate" is well accepted in the art. For the purpose of the specification, the term "dicyandiamide condensate" preferably refers to a polymer which contains dicyandiamide and an aldehyde, preferably formaldehyde, as monomer units, wherein the molar ratio of the monomer units dicyandiamide and aldehyde is preferably 1:1.

A person skilled in the art knows how to manufacture dicyandiamide condensates. For example, the respective condensate may be synthesized by subjecting the monomer components dicyandiamide and aldehyde, preferably formaldehyde, to a condensation reaction, wherein both components are preferably present in equimolar amounts. However, one of the components may be also added in excess to influence the properties of the resulting condensate, such as its molecular weight, polydispersity or particle size.

The dicyandiamide condensate is preferably a polymer of general formula (I)



(I)

,

wherein

m is an integer of at least 5, more preferably of at least 10, even more preferably of at least 15, still more preferably of at least 20, most preferably of at least 25 and in particular of at least 30,

R is -H, -CN or $-CONH_2$, and

X^- is selected from the group consisting of F^-, Cl^-, Br^-, I^- and $V_2\ SO_4^{2-}$.

In a preferred embodiment, m is an integer of from 5 to 150, more preferably of from 5 to 75, even more preferably of from 5 to 50, still more preferably of from 5 to 30, and in particular of from 5 to 15.

In a particularly preferred embodiment, R is -CN and X^- is selected from the group consisting of Cl^-, Br^- and $^1/_2\ SO_4^{2-}$.

For the purpose of the specification, the term "polymer" preferably refers to a material composed of macromolecules containing >10 monomer units (cf. G. P. Moss et al. Glossary of Class Names of Organic Compounds and Reactive Intermediates Based on Structure. *Pure & Applied Chemistry* 1995, *67,* 1307-1375).

The dicyandiamide condensate is preferably a copolymer, more preferably an alternating copolymer, even more preferably an alternating bipolymer.

For the purpose of the specification, the term "copolymer" preferably refers to a polymer derived from more than one species of monomer. Copolymers that are obtained by copolymerization of two monomer species are termed bipolymers (cf. A. D. Jenkins et al. Glossary of Basic Terms in Polymer Science. *Pure & Applied Chemistry* 1996, *68,* 2287-231 1).

A person skilled in the art knows the meaning of the terms "alternating copolymer" and "alternating bipolymer". Definitions for these terms may be found preferably in A. D. Jenkins et al. Glossary of Basic Terms in Polymer Science. *Pure & Applied Chemistry* 1996, 68, 2287-231 1.

Preferably, the dicyandiamide condensate is in the form of a dispersion, emulsion or solution. More preferably, the dicyandiamide condensate is in the form of an aqueous dispersion, aqueous emulsion or aqueous solution. Most preferably the dicyandiamide condensate is in the form of an aqueous solution.

Preferably, the pH of the dispersion, emulsion or solution of the dicyandiamide condensate is within the range of from 0.10 to 8.0, more preferably of from 0.20 to 7.5, even more preferably of from 0.30 to 7.0, still more preferably of from 0.40 to 6.5, most preferably of from 0.50 to 6.0 and in particular of from 0.60 to 5.5, at a temperature of 20 ^{0}C.

Preferably, the density of the dispersion, emulsion or solution of the dicyandiamide condensate is within the range of from 1.00 to 2.00 g cm^{-3}, more preferably of from 1.05 to 1.75 g cm^{-3}, most preferably of from 1.10 to 1.50 g cm^{-3} and in particular of from 1.15 to 1.40 g cm^{-3} at a temperature of 20 °C.

Preferably, the dynamic viscosity of the dispersion, emulsion or suspension of the dicyandiamide condensate is within a range of from 1.0 to 250 mPa s, more preferably of from 2.5 to 225 mPa s, even more preferably of from 5.0 to 200 mPa s, still more preferably of from 7.5 to 175 mPa s, most preferably of from 10 to 150 mPa and in particular of from 12.5 to 125 mPa s.

Preferably, the emulsion, dispersion or suspension of the dicyandiamide condensate is completely soluble in water.

Methods for the determination of the pH, density, dynamic viscosity and water solubility are known to a person skilled in the art.

In a preferred embodiment, the dicyandiamide condensate is a dicyandiamide-formaldehyde-ammonium chloride polymer or a blend comprising a dicyandiamide condensate and an aluminium salt.

Preferably, the dicyandiamide-formaldehyde-ammonium chloride polymer is a polymer of formula (I) as defined above, wherein R is -CN and X^- is Cl^-.

Preferably, the pH of the dispersion, emulsion or solution of the dicyandiamide-formaldehyde-ammonium chloride polymer is within the range of from 0.50 to 7.0, more preferably of from 1.0 to 6.5, even more preferably of from 1.5 to 6.5, still more preferably of from 2.0 to 6.0, most preferably of from 2.5 to 5.5 and in particular of from 3.0 to 5.0, at a temperature of 20 ^{0}C.

Preferably, the density of the dispersion, emulsion or solution of the dicyandiamide-formaldehyde-ammonium chloride polymer is within the range of from 1.00 to 1.50 g cm^{-3}, more preferably of from 1.05 to 1.45 g cm^{-3}, still more preferably of from 1.10 to 1.35 g cm^{-3} and most preferably of from 1.15 to 1.25 g cm^{-3} at a temperature of 20 ^{0}C. In a particularly preferred embodiment, the density is 1.19±0.12 g cm^{-3} at a temperature of 20 °C.

Preferably, the dynamic viscosity of the dispersion, emulsion or suspension of the dicyandiamide-formaldehyde-ammonium chloride polymer is within a range of from 5.0 to 225 mPa s, more preferably of from 10 to 200 mPa s, even more preferably of from 20 to 175 mPa s, still more preferably of from 30 to 150 mPa s, most preferably of from 40 to 125 mPa and in particular of from 50 to 100 mPa s.

Preferably, the emulsion, dispersion or suspension of the dicyandiamide-formaldehyde-ammonium chloride polymer is completely soluble in water.

The aluminium salt may be any aluminium salt known to a person skilled in the art. Typical aluminium salts, which may be used in combination with the dicyandiamide condensate, are for example aluminium oxide, aluminum chloride, aluminium nitrate, aluminium hydroxide, sodium aluminate, zeolites, potassium aluminium sulfate and aluminium diacetate.

The molar ratio of aluminium ions of the aluminium salt to the dicyandiamide monomers of the dicyandiamide condensate in the blend is preferably within the range of from 100:1 to 1:100, more preferably within the range of from 50:1 to 1:10, even more preferably within the range of from 25:1 to 1:6, still more preferably within the range of from 10:1 to 1:4, most preferably within the range of from 5:1 to 1:2 and in particular within the range of from 3:1 to 1:1. It is particularly preferred that said mole ratio is (2.0±0.5):1.

Procedures for the manufacturing of blends comprising a dicyandiamide condensate and an aluminium salt are known to a person skilled in the art. For example, the aluminium salt, preferably aluminium oxide, may be added prior to, during or after the condensation reaction for the synthesis of the dicyandiamide condensate.

Preferably, the pH of the dispersion, emulsion or solution of the blend comprising a dicyandiamide condensate and an aluminium salt is within the range of from 0.10 to 2.0, more preferably of from 0.20 to 1.90, even more preferably of from 0.30 to 1.75, still more preferably of from 0.40 to 1.50, most preferably of from 0.60 to 1.30 and in particular of from 0.80 to 1.10, at a temperature of 20 ^{0}C.

Preferably, the density of the dispersion, emulsion or solution, preferably of the aqueous solution, of the blend comprising a dicyandiamide condensate and an aluminium salt is within the range of from 1.00 to 2.00 g cm^{-3}, more preferably of from 1.05 to 1.80 g cm^{-3}, even more preferably of from 1.10 to 1.60 g cm^{-3}, still more preferably of from 1.15 to 1.50 g cm^{-3}, most preferably of from 1.20 to 1.40 g cm^{-3} and in particular of from 1.30 to 1.33 g cm^{-3} at a temperature of 20 ^{0}C.

Preferably, the dynamic viscosity of the dispersion, emulsion or suspension, preferably of the aqueous solution, of the blend comprising a dicyandiamide condensate and an aluminium salt is within a range of from 1.0 to 100 mPa s, more preferably of from 2.5 to 80 mPa s, even more preferably of from 5.0 to 60 mPa s, still more preferably of from 7.5 to 50 mPa s, most preferably of from 10 to 40 mPa s and in particular of from 15 to 30 mPa s.

Preferably, the emulsion, dispersion or suspension of the blend comprising a dicyandiamide condensate and an aluminium salt is completely soluble in water.

The acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer, according to the invention may be in the form of a powder, granulate, dispersion or solution. A person skilled in the art knows the meanings of these terms. For the purpose of the specification, the term dispersion comprises preferably emulsions (oil-in-water, water-in-oil) and suspensions.

For the purpose of the specification, the term "acrylamide polymer", preferably "cationic, non-ionic or amphiphilic acrylamide polymer", preferably refers to any polymer that is obtainable by polymerization of acrylamide and optionally, one or more further monomers.

Accordingly, the term

- "non-ionic acrylamide polymer" stands for a non-ionic polymer which is derived from at least the non-ionic monomer acrylamide, optionally at least one further structurally different non-ionic monomer as defined below, and optionally at least one further non-ionic amphiphilic monomer;
- "anionic acrylamide polymer" stands for an anionic polymer which is derived from at least the non-ionic monomer acrylamide, optionally at least one further structurally different non-ionic monomer, optionally at least one non-ionic amphiphilic monomer, and at least one anionic monomer;
- "cationic acrylamide polymer" stands for a cationic polymer which is derived from at least the non-ionic monomer acrylamide, optionally at least one further structurally different non-ionic monomer, optionally at least one non-ionic or cationic amphiphilic monomer, and at least one cationic monomer; and
- "amphiphilic acrylamide polymer" stands for an amphiphilic polymer which is derived from at least the non-ionic monomer acrylamide, optionally at least one further structurally different non-ionic monomer, and at least one amphiphilic monomer.

The terms "non-ionic monomer", "anionic monomer", "cationic monomer", and "amphiphilic monomer" are defined below.

The acrylamide polymers, preferably cationic, non-ionic or amphiphilic acrylamide polymer, according to the invention may be also polymeric components of mixtures which contain at least two structurally different polymers. In this respect, at least one of the polymers of a corresponding mixture of polymers is a non-ionic, anionic, cationic or amphiphilic acrylamide polymer as defined above. The other polymers in the mixture may be also polymers which do not contain acrylamide as a monomer.

The non-ionic, anionic, cationic and amphiphilic acrylamide polymers are preferably water-soluble or water-swellable.

For the purpose of the specification the term "water-swellable" preferably refers to the increase in volume of polymers associated with the uptake of water (cf. D. H. Everett. Manual of Symbols and Terminology for Physicochemical Quantities and Units. Appendix II, Part I: Definitions, Terminology and Symbols in Colloid and Surface Chemistry. *Pure & Applied Chemistry* 1972, *31,* 579-638). The swelling behavior of polymers may be measured at different temperatures and pH values in water. The swollen weights of the polymers are determined at intervals, after removal of the surface water, until equilibrium swelling is attained. The percent swelling is preferably calculated by the following equation: %swelling = 100 x [(W, - W_0) / W_0], where W_0 is the initial weight and W, the final weight of the gel at time t (cf. I. M. El-Sherbiny et al. Preparation, characterization, swelling and in vitro drug release behaviour of poly[*N*-acryloylglycine-chitosan] interpolymeric pH and thermally-responsive hydrogels. *European Polymer Journal* 2005, *41,* 2584-2591).

The non-ionic, anionic, cationic or amphiphilic water-swellable acrylamide polymer according to the invention may display a %swelling of at least 2.5%, preferably of at least 5.0%, more preferably of at least 7.5%, still more preferably of at least 10%, most preferably of at least 15%, and in particular of at least 20% measured in demineralized water at 20 ^{0}C and pH 7.4 in phosphate buffer after equilibrium swelling is attained.

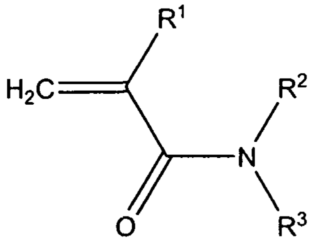
Preferably, the non-ionic, anionic, cationic or amphiphilic acrylamide polymer contains at least 75 wt.-%, more preferably at least 79 wt.-%, still more preferably at least 84 wt.-%, most preferably at least 89 wt.-%, and in particular at least 94 wt.-% water-swellable or water-soluble polymer, based on the total weight of the acrylamide polymer. In a preferred embodiment, the acrylamide polymer essentially consists of water-swellable or water-soluble polymer.

Preferably, the non-ionic, anionic, cationic or amphiphilic polymer is derived from ethylenically unsaturated monomers, preferably from acrylic acid derivatives, such as acrylic acid, acrylic acid esters, acrylic acid amides, acrylonitrile, and the like.

For the purpose of the specification, the term "non-ionic acrylamide polymer" refers to an uncharged material composed of macromolecules containing >10 monomer units, wherein the non-ionic acrylamide polymer contains at least acrylamide, optionally at least one structurally different non-ionic monomer of general formula (II) (see below), and optionally at least one non-ionic amphiphilic monomer.

The non-ionic acrylamide polymers may be homopolymers, which comprise acrylamide as the only monomer component. Further, the non-ionic acrylamide polymers may be also copolymers, i.e. bipolymers, terpolymers, quaterpolymers, etc., which comprise at least acrylamide and at least one further structurally different non-ionic monomer as the only monomer components. Still further, the non-ionic polymers may be also copolymers, i.e. bipolymers, terpolymers, quaterpolymers, etc. preferably prepared from acrylamide, optionally at least one further structurally different non-ionic monomer and at least one uncharged amphiphilic monomer as the only monomer components, provided that the relative weight ratio of the non-ionic monomer units to the uncharged amphiphilic monomer units is >1.0.

Compounds of the following general formula (II) can be used as non-ionic monomers for manufacturing non-ionic acrylamide polymers:



(II),

wherein

R^1 stands for hydrogen or methyl, and

R^2 and R^3 stand, independently of each other, for hydrogen, alkyl with 1 to 5 carbon atoms, or hydroxyalkyl with 1 to 5 carbon atoms.

Typically, at least one of R^1, R^2 and R^3 does not stand for hydrogen, so that the compound of general formula (II) differs from acrylamide.

The non-ionic monomers (meth)acrylamide, N-methyl(meth)acrylamide, N-isopropyl(meth)-acrylamide or N,N substituted (meth)acrylamides such as N,N,-dimethyl(meth)acrylamide, N,N-diethyl(meth)acrylamide, N-methyl-N-ethyl(meth)acrylamide or N-hydroxyethyl(meth)-acrylamide are preferably used for manufacturing the water-soluble or water-swellable polymers according to the invention.

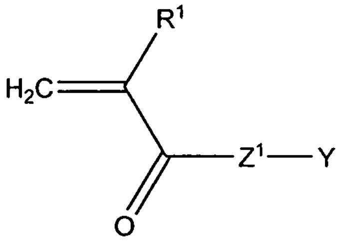
For the purpose of the specification the term "(meth)acryl" covers both, "methacryl" as well as "acryl".

For the purpose of the specification, the term "cationic acrylamide polymer" refers preferably to positively charged material composed of macromolecules containing >10 monomer units, wherein the cationic acrylamide polymer contains acrylamide, optionally at least one further structurally different non-ionic monomer, optionally at least one non-ionic or cationic charged amphiphilic monomer, and at least one cationic monomer of general formula (III) (see below).

In a particularly preferred embodiment, the non-ionic acrylamide polymer contains 100 wt-% acrylamide based on the total weight of the non-ionic acrylamide polymer.

Preferably, the non-ionic acrylamide polymers according to the invention are in the form of a dispersion and in particular in the form of a water-in-oil (W/O) dispersion.

Compounds of the following general formula (III) can be used as cationic monomers for manufacturing cationic acrylamide polymers:



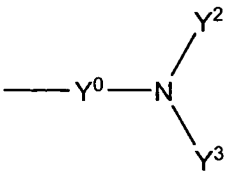
(III),

wherein

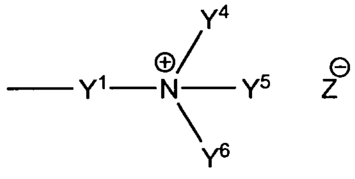
R^1 stands for hydrogen or methyl,

Z^1 stands for O, NH or NR^4, wherein R^4 stands for alkyl with 1 to 4 carbon atoms, and

Y stands for one of the groups



or



,

wherein

Y^0 and Y^1 stand for alkylene with 2 to 6 carbon atoms, optionally substituted with hydroxy groups,

Y^2, Y^3, Y^4, Y^5, and Y^6, independently of each other, stand for alkyl with 1 to 6 carbon atoms, and

Z^- stands for halogen, acetate or methyl sulfate.

Protonated or quaternized dialkylaminoalkyl(meth)acrylates or dialkylaminoalkyl(meth)acrylamides with C_1 to C_3-alkyl or C_1 to C_3-alkylene groups are preferably used as cationic monomers for manufacturing the cationic acrylamide polymers according to the invention. The methyl chloride-quaternized, ethyl chloride-quaternized, propyl chloride-quaternized, or isopropyl-quaternized ammonium salts of N,N-dimethylaminomethyl(meth)acrylate, N,N-dimethylaminoethyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate, N.N-diethylaminomethyl(meth)acrylate, N,N-diethylaminoethyl(meth)acrylate, N,N-diethylaminopropyl(meth)acrylate, N,N-dimethylaminomethyl(meth)acrylamide, N,N-dimethylaminoethyl(meth)acrylamide and/or N,N-dimethylaminopropyl(meth)acrylamide are more preferably used. Instead of the alkyl chlorides (i.e., methyl chloride, ethyl chloride, propyl chloride, and isopropyl chloride), the corresponding bromides, iodides, sulfates, etc. may also be used for the quaternization of said N,N-dialkylaminoalkyl(meth)acrylate and N,N-dialkylaminoalkyl(meth)acrylamide derivatives.

In a preferred embodiment of the invention, the cationic acrylamide polymer comprises cationic copolymers containing acrylamide units and cationic monomer units selected from ADAME-Quat (quaternized N,N-dimethylaminoethyl acrylate) and DIMAPA-Quat (quaternized N,N-dimethylaminopropyl acrylamide).

In a preferred embodiment, the cationic acrylamide polymers contain at least 10 wt.-%, at least 15 wt.-% or at least 20 wt.-%; more preferably at least 25 wt.-%, at least 30 wt.-%, at least 35 wt.-%, at least 40 wt.-% or at least 45 wt.-%; still more preferably at least 50 wt.-%, at least 55 wt.-%, at least 60 wt.-%, at least 65 wt.-% or at least 70 wt.-%; most preferably at least 75 wt.-%, at least 80 wt.-% or at least 85 wt.-%; and in particular at least 88 wt.-%, at least 90 wt.-% or at least 92 wt.-% of cationic monomer units based on the total weight of the cationic acrylamide polymer.

In another preferred embodiment, the cationic acrylamide polymers contain 10-99 wt.-%, more preferably 20-98 wt.-%, still more preferably 30-96 wt.-%, most preferably 50-94 wt.-%, and in particular 75-92 wt.-% of cationic monomer units, preferably ADAME-Quat, based on the total weight of the cationic acrylamide polymer.

In another preferred embodiment, the cationic acrylamide polymers contain 1.0-50 wt.-%, more preferably 2.0-40 wt.-%, even more preferably 4.0-35%, still more preferably 6.0-30 wt.-%, most preferably 8.0-25 wt.-% and in particular 10-20 wt.-% acrylamide based on the total weight of the cationic acrylamide polymer.

In another preferred embodiment, the cationic acrylamide polymers contain acrylamide and ADAME-Quat as the only monomer components, wherein the relative weight ratio of ADAME-Quat to acrylamide is preferably within the range of from 1.25:1 to 20:1, more preferably of from 1.5:1 to 18:1, even more preferably of from 1.75:1 to 16:1, still more preferably of from 2:1 to 14:1, most preferably of from 2.5:1 to 12:1 and in particular of from 3:1 to 10:1.

In another particularly preferred embodiment, the cationic acrylamide polymers contain acrylamide and ADAME-Quat as the only monomer components, wherein the relative weight ratio of ADAME-Quat to acrylamide is preferably (7±5):1 and in particular (7±3):1.

Preferably, the cationic acrylamide polymer is in the form of an emulsion, wherein its cationicity is preferably in the range of from 75 to 95 wt.-% and in particular of from 80 to 90 wt.-%.

For the purpose of the specification the term "anionic acrylamide polymer" refers to a negatively charged material composed of macromolecules containing >10 monomer units, wherein the anionic acrylamide polymer contains acrylamide, optionally at least one further structurally different non-ionic monomer, optionally at least one non-ionic amphiphilic monomer, and at least one anionic monomer.

The anionic acrylamide polymers may be copolymers, i.e. bipolymers, terpolymers, quaterpolymers, etc., which comprise acrylamide and, e.g., at least one further structurally different non-ionic monomer, and at least one anionic monomer.

The following anionic monomers can be used for manufacturing anionic polymers:

- olefinically unsaturated carboxylic acids and carboxylic acid anhydrides, in particular acrylic acid, methacrylic acid, itaconic acid, crotonic acid, glutaconic acid, maleic acid, maleic anhydride, fumaric acid and the water-soluble alkali metal salts thereof, alkaline earth metal salts thereof, and ammonium salts thereof;
- olefinically unsaturated sulfonic acids, in particular aliphatic and/or aromatic vinylsulfonic acids, for example vinylsulfonic acid, allylsulfonic acid, styrenesulfonic acid, acrylic and methacrylic sulfonic acids, in particular sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-methacryloxypropylsulfonic acid and 2-acrylamido-2-methylpropanesulfonic acid, and the water-soluble alkali metal salts thereof, alkaline earth metal salts thereof, and ammonium salts thereof;

- olefinically unsaturated phosphonic acids, in particular, for example, vinyl- and allyl-phosphonic acid and the water-soluble alkali metal salts thereof, alkaline earth metal salts thereof, and ammonium salts thereof; and/or

- sulfomethylated and/or phosphonomethylated acrylamides and the water-soluble alkali metal salts thereof, alkaline earth metal salts thereof, and ammonium salts thereof.

The anionic acrylamide monomers are preferably selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, crotonic acid, glutaconic acid, maleic acid, maleic anhydride, and fumaric acid. More preferably, the anionic monomers are selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, and crotonic acid. The water-soluble alkali metal salts of acrylic acid and in particular potassium acrylate are most preferred according to the invention.

In a preferred embodiment, the anionic acrylamide polymers contain at least 5.0 wt.-%, more preferably at least 25 wt.-%, still more preferably at least 50 wt.-%, most preferably at least 75 wt.-%, and in particular 99 wt.-% of anionic monomer units based on the total weight of the anionic acrylamide polymer.

In another preferred embodiment, the anionic acrylamide polymers contain 1.0-99 wt.-%, more preferably 6.0-80 wt.-%, still more preferably 8.0-60 wt.-%, most preferably 10-50 wt.-%, and in particular 12-35 wt.-% of anionic monomer units.

In another preferred embodiment, the anionic acrylamide polymers contain 1.0-99 wt.-%, more preferably 10-97 wt.-%, even more preferably 20-95 wt.-%, still more preferably 40-93%, most preferably 60-91 wt.-% and in particular 70-89 wt.-% acrylamide based on the total weight of the anionic acrylamide polymer.

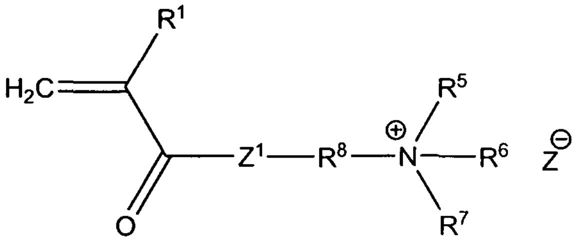
In a particularly preferred embodiment, the anionic acrylamide polymers contain acrylamide and acrylic acid as the only monomer components, wherein the relative weight ratio of acrylamide to acrylic acid is preferably within the range of from 1.5:1 to 15:1 , more preferably of from 1.75:1 to 12.5:1, even more preferably of from 2:1 to 10:1 and in particular 2.2:1 to 8:1.

In another particularly preferred embodiment, the anionic acrylamide polymers contain acrylamide and acrylic acid as the only monomer components, wherein the relative weight ratio of acrylamide to acrylic acid is preferably (4.5±4):1 and in particular (4.5±3):1.

Preferably, the anionic acrylamide polymer is in the form of an emulsion, more preferably in the form of a oil-in-water (O/W) emulsion and in particular in the form of a water-in-oil (W/O) emulsion, wherein its anionicity is preferably within the range of from 5.0 to 50 wt.-% and in particular of from 10 to 40 wt.-%.

For the purpose of the specification, the term "amphiphilic acrylamide polymer" preferably refers to a charged, preferably positively charged, or uncharged material composed of macromolecules containing >10 monomer units, wherein the amphiphilic acrylamide polymer contains preferably acrylamide, and at least one monomer that possesses both a hydrophilic and a hydrophobic group (cf. D. H. Everett. Manual of Symbols and Terminology for Physicochemical Quantities and Units. Appendix II, Part I: Definitions, Terminology and Symbols in Colloid and Surface Chemistry. *Pure & Applied Chemistry* 1972, *31,* 579-638). The amphiphilic polymers according to the invention comprise acrylamide, optionally at least one further structurally different non-ionic monomer, and at least one amphiphilic monomer of general formulae (IV) or (V) as defined below.

Compounds of the following general formulae (IV) or (V) can be used as amphiphilic monomers for manufacturing amphiphilic acrylamide polymers:



(IV),

wherein

Z^1 stands for O, NH or NR^4, wherein R^4 stands for hydrogen or methyl,

R^1 stands for hydrogen or methyl,

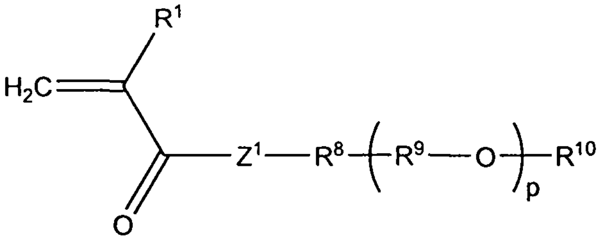
R^5 and R^6 stand, independently of each other, for alkyl with 1 to 6 carbon atoms,

R^7 stands for alkyl, aryl and/or aralkyl with 8 to 32 carbon atoms,

R^8 stands for alkylene with 1 to 6 carbon atoms, and

$Z^{"}$ stands for halogen, pseudohalide ions, methyl sulfate or acetate;

or



(V),

wherein

Z^1 stands for O, NH or NR^4, wherein R^4 stands for alkyl with 1 to 4 carbon atoms,

R^1 stands for hydrogen or methyl,

R^8 stands for alkylene with 1 to 6 carbon atoms,

R^9 stands for alkylene with 2 to 6 carbon atoms, and

R^{10} stands for hydrogen, alkyl, aryl, and/or aralkyl with 8 to 32 carbon atoms, and

p stands for an integer between 1 to 50.

The conversion products of (meth)acrylic acid or (meth)acrylamide with polyethylene glycols (10 to 40 ethylene oxide units) that have been etherified with fatty alcohol are preferably used as amphiphilic monomers for manufacturing the amphiphilic acrylamide polymers according to the invention.

For the purpose of the specification the term "pseudohalide ions" preferably refers to certain ions such as azide, thiocyanate, and cyanide, which resemble halide ions in their chemistry (cf. G. P. Moss et al. Glossary of Class Names of Organic Compounds and Reactive Intermediates Based on Structure. *Pure & Applied Chemistry* 1995, *67,* 1307-1375).

The amphiphilic acrylamide polymers may be copolymers, i.e. bipolymers, terpolymers, quaterpolymers, etc., which preferably comprise acrylamide and at least one amphiphilic monomer or at least two structurally different amphiphilic monomers as the only monomer components.

The acrylamide polymer may be a component of a mixture comprising two or three structurally different amphiphilic polymers as the only polymer components, two or three structurally different non-ionic polymers as the only polymer components, two or three structurally different anionic polymers as the only polymer components, or two or three structurally different cationic polymers as the only polymer components, wherein the respective mixture comprises at least one polymer which contains the non-ionic monomer acrylamide.

Further, the acrylamide polymer may be a component of a mixture comprising at least two polymers independently selected from the group consisting of non-ionic acrylamide polymers, amphiphilic acrylamide polymers, anionic acrylamide polymers and cationic acrylamide polymers, wherein the respective mixture comprises at least one polymer which contains the non-ionic monomer acrylamide.

Still further, the acrylamide polymer may be a component of a mixture comprising at least three polymers selected from the group consisting of non-ionic polymers, amphiphilic polymers, anionic polymers and cationic polymers, wherein the respective mixture comprises at least one polymer which contains the non-ionic monomer acrylamide.

The acrylamide can be cross-linked or not cross-linked. The skilled person knows how to achieve cross-linking. In a preferred embodiment cross-linking is achieved by adding suitable amounts of multifunctional monomers, such as N.N'-methylene bisacrylamide.

Particularly preferred is a mixture comprising at least one polymer A and/or at least one polymer B as defined here below, wherein either polymer A or polymer B, or polymer A and polymer B contain the non-ionic monomer acrylamide.

Polymer A is preferably high-molecular with an average molecular weight (M_w) of $\geq 1.0 \times 10^6$ g/mol, as measured by the GPC method. Polymer B is preferably a low-molecular polymer with an average molecular weight (M_w) of at most 500,000 g/mol, more preferably of at most 400,000 g/mol, still more preferably of at most 300,000 g/mol, most preferably of at most 200,000 g/mol, as measured by the GPC method.

Thus, it is preferred that the average molecular weight of polymer A is greater than the average molecular weight of polymer B. The ratio of the average molecular weights of polymer A to polymer B may be at least 4.0, preferably at least 10, more preferably at least 20, still more preferably at least 25, most preferably at least 30, and in particular at least 40.

In a particularly preferred embodiment, the mixture comprises at least one water-soluble or water-swellable polymer A and/or at least one water-soluble or water-swellable polymer B as the only polymer components, wherein the water-soluble or water-swellable polymer A as well as the water-soluble or water-swellable polymer B are preferably both cationic or both anionic.

The preparation of the polymers according to the invention is known to the person skilled in the art. For example, the polymers according to the invention may be prepared by polymerization techniques according to the procedures described in WO 2005/092954, WO 2006/072295, and WO 2006/072294.

Depending on the procedure used for the preparation of the polymers according to the invention, the respective polymer products may comprise further substances such as polyfunctional alcohols, water-soluble salts, chelating agents, free-radical initiators and/or their respective degradation products, reducing agents and/or their respective degradation products, oxidants and/or their respective degradation products, etc.

According to the invention, the dicyandiamide condensate and the acrylamide polymer preferably cationic, non-ionic or amphiphilic acrylamide polymer, are preferably employed as separate components, i.e. the relative weight ratio of the dicyandiamide condensate and the acrylamide polymer can be freely chosen, and the two components can be supplied in a timed fashion, i.e. not necessarily simultaneously. This is of particular advantage, as it has been surprisingly found that depending upon the substrate to be flocculated, the relative weight ratio of both components can be optimized by simple routine experimentation. This cannot be achieved by one-component systems that contain both components in a predetermined fixed ratio. Further, it has been surprisingly found that it can be advantageous to allow the first component to act on the substrate in the absence of the second component for an initial period of time, and to supplement the second component thereafter. This cannot be achieved by one-component systems either.

A second aspect of the invention relates to the use of a dicyandiamide-formaldehyde condensate as defined above for flocculating an aqueous dispersion, preferably drilling mud, bio-fermentation sludge or landfill leachate, as described in detail above.

A third aspect of the invention relates to the use of an acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer, as defined above for flocculating an aqueous dispersion, preferably drilling mud, bio-fermentation sludge or landfill leachate, as described in detail above.

A fourth aspect of the invention relates to the use of a dicyandiamide condensate, an acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer, and an aluminium salt for flocculating drilling mud, bio-fermentation sludge or landfill leachate, wherein the dicyandiamide condensate, acrylamide polymer and the aluminium salt are defined as above.

The flocculation of the drilling mud, bio-fermentation sludge or landfill leachate is preferably achieved as described in detail above.

A fifth aspect of the invention relates to an aqueous dispersion comprising a dicyandiamide-formaldehyde condensate, and a non-ionic, anionic, cationic or amphiphilic acrylamide polymer, wherein

- the relative weight ratio [dicyandiamide-formaldehyde condensate] : [acrylamide polymer] is >10:1, and
- the aqueous dispersion, the dicyandiamide-formaldehyde condensate and the acrylamide polymer are defined as above.

Preferably, said aqueous dispersion is drilling mud, bio-fermentation sludge or landfill leachate.

A sixth aspect of the invention relates to a kit comprising the components

A) a dicyandiamide-formaldehyde condensate and

B) an acrylamide polymer, preferably cationic, non-ionic or amphiphilic acrylamide polymer,

and

C) optionally an aluminium salt,

for flocculating an aqueous dispersion as described in detail above,

wherein

- the components A), B), and optionally C) are at least partially separated from each other,
- the relative weight ratio of component A) to component B) is >10:1 , and
- the components A), B) and C) are defined as above.

In a preferred embodiment, the components A), B), and optionally C) are fully separated from each other.

Preferably, the relative weight ratio of component A) to component B) is ≥20:1 , more preferably ≥25:1, even more preferably ≥30:1, still more preferably ≥35:1, most preferably >40:1 and in particular >45:1. In a particularly preferred embodiment, the relative weight ratio is (50±10):1.

Preferably, the kit according to the invention comprises at least two containers, which are preferably at least partially attached to each other and/or are packaged together, i.e., said containers are components of an identical outer package.

In another preferred embodiment, the kit comprises two containers, which are preferably at least partially attached to each other and/or are packaged together, wherein the first of said containers contains exclusively component A) and the second of said containers contains exclusively component B).

In another preferred embodiment, the kit according to the invention comprises three containers, which are preferably at least partially attached to each other and/or are package together, wherein the first of said containers contains exclusively component A), the second of said containers contains exclusively component B), and the third of said containers contains exclusively component C).

The mole ratio of aluminium ions of component C) to dicyandiamide monomers of component A) is preferably within the range of from 100:1 to 1:100, more preferably within the range of from 50:1 to 1:10, even more preferably within the range of from 25:1 to 1:6, still more preferably within the range of from 10:1 to 1:4, most preferably within the range of from 5:1 to 1:2 and in particular within the range of from 3:1 to 1:1.

In a particularly preferred embodiment, the aluminium salt (component C)) and the dicyandiamide condensate (component A)) are present in the same container of the kit according to the invention, thereby forming a blend as described above.

In another particularly preferred embodiment, the kit according to the invention comprises two containers, which are preferably at least partially attached to each other and/or are package together, wherein the first of said containers contains exclusively a blend of component A) and C) as described above, and the second of said containers contains exclusively component B).

The following examples further illustrate the invention but should no be construed as limiting its scope.

EXAMPLES

Determination of the dewatering effect by the screen-test method:

This test-method was adapted to the dewatering method used in industry, namely continuous pressure filtration by means of filter presses or centrifugal dewatering.

The method is typically applied to test polymers for their suitability in the conditioning and dewatering of aqueous effluents (aqueous dispersions).

The effluent is conditioned by the use of flocculating agents under controlled conditions. After conditioning, the effluent sample is dewatered by filtration on a metal screen (200 µm mesh). The dewatering time for a given filtrate volume is measured and the clarity of the filtrate is evaluated by the use of a clarity wedge (clarity 0 = no clarification; clarity 46 = best clarification).

Bio-fermentation sludge:

The dewatering effect was tested by the use of bio-fermentation sludge, which was retrieved from a bio-fermentation site in Kevelaer (Germany). The sludge had the following properties:

dry solids content:	7.7 wt.-%
pH:	8.1
electric conductivity:	18.4 mS cm^{-1}
ignition loss (600 ^0C):	77.9 wt.-%

Prior to testing, the sludge was diluted 1:1 by volume with water.

Dicvandiamide condensate:

The resulting sludge was pre-treated with an aqueous solution of dicyandiamide-formaldehyde-ammonium chloride polymer by adding the dicyandiamide condensate and stirring the resulting mixture for 10s at 1000 rpm.

The aqueous solution of the dicyandiamide-formaldehyde-ammonium chloride polymer had the following properties:

pH:	~ 4.0	(20 ^{0}C)
density:	- 1.19 g em^{-3}	(20 °C)
dynamic viscosity:	~ 70 mPa s	(20 ^{0}C)
appearance:	slightly opaque liquid	
water-solubility:	freely soluble	
ionicity:	cationic	
used concentration:	10 wt.-% in aqueous solution	

Acrylamide polymers:

After the pre-treatment, an acrylamide polymer was added to the sludge and the resulting mixture was stirred for 10 s at 1000 rpm.

Three different acrylamide polymers P1 to P3 were tested:

P1: moderately cross-linked cationic polymer (cationicity 70 wt.-%) in the form of a water-in-oil dispersion (C_{16} alkane + emulsifiers); monomers: acrylamide and ADAME-Quat.; density 1.03 g/cm^3; polymer content: 47.8 wt.-% (Praestol® K 233 L).

P2: moderately cross-linked cationic polymer (cationicity 81 wt.-%) in the form of a water-in-oil dispersion (C_{16} alkane + emulsifiers); monomers: acrylamide and ADAME-Quat.; density 1.03 g/cm^3; polymer content: 48.2 wt.-% (Praestol® K 242 L).

P3: mildly cross-linked cationic polymer (cationicity 90 wt.-%) in the form of a water-in-oil dispersion (C_{16} alkane + emulsifiers); monomers: acrylamide and ADAME-Quat.; density 1.03 g/cm^3; polymer content: 47.8 wt.-% (Praestol® K 255 L).

Results:

i) The following table displays the measured dewatering times in seconds for 400 ml filtrate:

	Dosage of acrylamide polymer [g m^{-3}]				
	300	*300*	*300*	*300*	*400*
P1	>120	>120	65	>120	>120
P2	>120	>120	40	>120	>120
P3	>120	>120	36	>120	>120
	0	*10*	*15*	*20*	*20*
	Dosage of dicyandiamide condensate[kg m^{-3}]				

Comparative examples:

	Dosage of acrylamide polymer [g m^{-3}]				
	300	*300*	*300*	300	400
P1	>120	>120	>120	>120	>120
P2	>120	>120	>120	>120	>120
P3	>120	>120	>120	>120	>120
	0	70	15	20	20
	Dosage of iron(III)chloride [kg m^{-3}]				

The use of iron(III)chloride resulted in the formation of gas and foam in each of the experiments. Furthermore, the used sludge was irreversibly thickened in each case.

ii) The following table displays the determined clarity for the obtained filtrates:

	Dosage of acrylamide polymer [g m^{-3}]				
	300	*300*	*300*	*300*	*400*
P1	0	0	15	13	9
P2	0	0	13	14	11
P3	0	0	17	15	10
	0	*10*	*15*	*20*	*20*
	Dosage of dicyandiamide condensate [kg m^{-3}]				

Comparative examples:

	Dosage of acrylamide polymer [g m^{-3}]				
	300	*300*	*300*	*300*	*400*
P1	0	0	1	1	1
P2	0	0	1	1	1
P3	0	0	1	1	1
	0	*10*	*15*	*20*	*20*
	Dosage of iron(III)chloride [kg m^{-3}]				

iii) The following table displays the press stability of the sludge by the use of a plexiglass plate:

	Dosage of acrylamide polymer [g m^{-3}]				
	300	*300*	*300*	*300*	*400*
P1	--	--	+	--	--
P2	--	--	++	--	--
P3	--	--	++	--	--
	0	*10*	*15*	*20*	*20*
	Dosage of dicyandiamide condensate [kg m^{-3}]				

(--) insufficient; (-) unsatisfactory; (o) moderate; (+) good; (++) excellent

Comparative examples:

	Dosage of acrylamide polymer [g m^{-3}]				
	300	*300*	*300*	*300*	*400*

P1	--	--	--	--	--
P2	--	--	--	--	--
P3	--	--	--	--	--
	0	*10*	*15*	*20*	*20*
	Dosage of iron(III)chloride[kg m^{-3}]				

(--) insufficient; (-) unsatisfactory; (o) moderate; (+) good; (++) excellent

Salt and CMC (Carboxymethylcellulose) containing drilling mud: *

The dewatering effect was tested by the use of a mud, which was retrieved from a drilling application in Hungary. The sludge had the following properties:

dry solids content:	16,7 wt.-%
pH:	8.9
electric conductivity:	213 mS cm^{-1}
density:	1,26 g cm^{-1}

Prior to testing, the sludge was diluted 1:1 by volume with water.

A non-ionic acrylamide polymer containing 100 wt-% acrylamide was used (Praestol® N 3100 L).

Results:

i) The following table displays the measured dewatering times in seconds for 50 ml filtrate:

Dosage of (non-ionic) acrylamide polymer [g m^{-3}]		
150	150	150
>120	23	15
0	*10*	*20*
Dosage of dicyandiamide condensate[kg m^{-3}]		

N) The following table displays the determined clarity (photometer) for the obtained filtrates:

Dosage of acrylamide polymer [g m^{-3}]		
300	*300*	*300*
0	28	12
0	*10*	*20*
Dosage of dicyandiamide condensate[kg m^{-3}]		

iii) The following table displays the press stability of the sludge by the use of a plexiglass plate:

Dosage of acrylamide polymer [g m^{-3}]		
300	*300*	*300*

--	+	++
0	***10***	***20***
Dosage of dicyandiamide condensate[kg m^{-3}]		

(-) insufficient; (-) unsatisfactory; (o) moderate; (+) good; (++) excellent

CLAIMS

1. A method for flocculating an aqueous dispersion comprising the step of adding

   - a dicyandiamide-formaldehyde condensate and
   - a cationic, non-ionic or amphiphilic acrylamide polymer

   to the aqueous dispersion, so that the relative weight ratio of the dicyandiamide-formaldehyde condensate to the acrylamide polymer in the aqueous dispersion is >10:1.

2. The method according to claim 1, wherein the acrylamide polymer is added to the aqueous dispersion after the dicyandiamide-formaldehyde condensate.

3. The method according to claim 1 or 2, wherein the aqueous dispersion has a dry solids content of at least 0.10 wt.-%.

4. The method according to any of the preceding claims, wherein the aqueous dispersion has an electric conductivity of at least 0.10 mS cm^{-1}.

5. The method according to any of the preceding claims, wherein the aqueous dispersion is drilling mud, bio-fermentation sludge or landfill leachate.

6. The method according to any of the preceding claims, wherein the dicyandiamide-formaldehyde condensate is added to the aqueous dispersion to a final concentration of 15±5 kg m^{-3}.

7. The method according to any of the preceding claims, wherein the acrylamide polymer is added to the aqueous dispersion to a final concentration of 300±100 g m^{-3}.

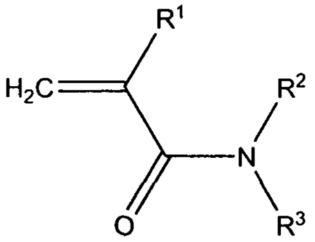
8. The method according to any of the preceding claims, wherein the dicyandiamide-formaldehyde condensate is in the form of a dispersion, emulsion or solution.

9. The method according to any of the preceding claims, wherein the dicyandiamide-formaldehyde condensate is

   - a dicyandiamide-formaldehyde-ammonium chloride polymer or
   - a blend comprising a dicyandiamide-formaldehyde polymer and an aluminium salt.

10. The method according to any of the preceding claims, wherein the acrylamide polymer is in the form of a powder, granulate, dispersion, emulsion or solution.

11. The method according to any of the preceding claims, wherein the acrylamide polymer comprises acrylamide and at least one compound of general formula (II)

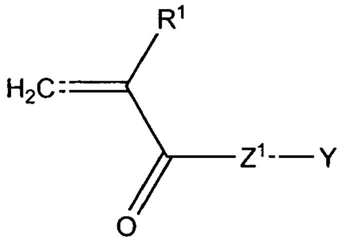


(II),

wherein

- R^1 stands for hydrogen or methyl, and
- R^2 and R^3 stand, independently of each other, for hydrogen, alkyl with 1 to 5 carbon atoms, or hydroxyalkyl with 1 to 5 carbon atoms.

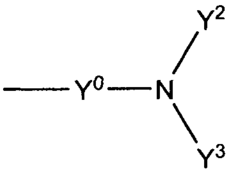
12. The method according to any of the preceding claims, wherein the acrylamide polymer comprises acrylamide and at least one compound of general formula (III)



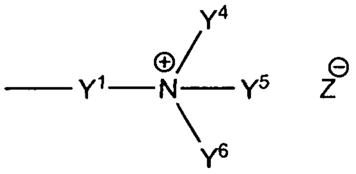
(III),

wherein

- R^1 stands for hydrogen or methyl,
- Z^1 stands for O, NH or NR^4, wherein R^4 stands for alkyl with 1 to 4 carbon atoms, and
- Y stands for one of the groups



or

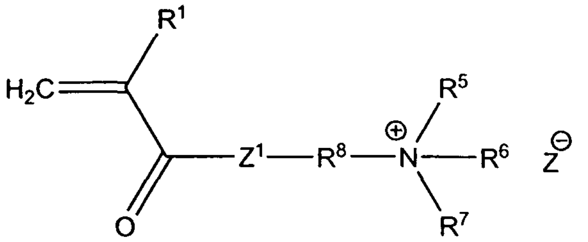


,

wherein

- Y^0 and Y^1 stand for alkylene with 2 to 6 carbon atoms, optionally substituted with hydroxy groups,
- Y^2, Y^3, Y^4, Y^5, and Y^6, independently of each other, stand for alkyl with 1 to 6 carbon atoms, and
- Z" stands for halogen, acetate or methyl sulfate.

13. The method according to any of the preceding claims, wherein the acrylamide polymer comprises acrylamide and at least one compound of general formula (IV)

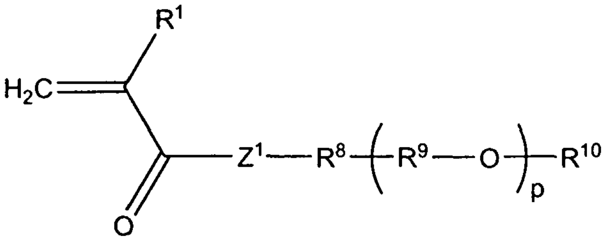


(IV),

wherein

- Z^1 stands for O, NH or NR^4, wherein R^4 stands for hydrogen or methyl,
- R^1 stands for hydrogen or methyl,
- R^5 and R^6 stand, independently of each other, for alkyl with 1 to 6 carbon atoms,
- R^7 stands for alkyl, aryl and/or aralkyl with 8 to 32 carbon atoms,
- R^8 stands for alkylene with 1 to 6 carbon atoms, and
- Z" stands for halogen, pseudohalide ions, methyl sulfate or acetate;

or general formula (V)



(V),

wherein

- Z^1 stands for O, NH or NR^4, wherein R^4 stands for alkyl with 1 to 4 carbon atoms,

- R^1 stands for hydrogen or methyl,
- R^8 stands for alkylene with 1 to 6 carbon atoms,
- R^9 stands for alkylene with 2 to 6 carbon atoms, and
- R^{10} stands for hydrogen, alkyl, aryl, and/or aralkyl with 8 to 32 carbon atoms, and
- p stands for an integer between 1 to 50.

14. Use of a dicyandiamide-formaldehyde condensate in the method as defined in any of claims 1 to 13.

15. Use of an acrylamide polymer in a method as defined in any of claims 1 to 13.

16. Use of

   - a dicyandiamide-formaldehyde condensate,
   - a cationic, non-ionic or amphiphilic acrylamide polymer, and
   - an aluminium salt

   for flocculating drilling mud, bio-fermentation sludge or landfill leachate.

17. The use according to claim 16, wherein the flocculation is achieved by the method according to any of claims 1 to 13.

18. An aqueous dispersion comprising

   - a dicyandiamide-formaldehyde condensate, and
   - a cationic, non-ionic or amphiphilic acrylamide polymer,

   wherein the relative weight ratio [dicyandiamide-formaldehyde condensate] : [acrylamide polymer] is >10:1.

19. The dispersion according to claim 18, wherein the aqueous dispersion is drilling mud, bio-fermentation sludge, or landfill leachate.

20. A kit comprising the components

   A) a dicyandiamide-formaldehyde condensate and

   B) a cationic, non-ionic or amphiphilic acrylamide polymer and

C) optionally an aluminium salt,

for the method according to any of claims 1 to 13,

wherein

- the components A), B), and optionally C) are at least partially separated from each other, and
- the relative weight ratio of component A) to component B) is >10:1.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/001952

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F1/56
ADD. C02F9/00

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

B. RELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F

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

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

EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 197403 Thomson Scientific, London, GB; Class A91, AN 1974-04656V XP002493421 ISHIHARA: "Treatment of industrial waste water - which contains proteins, oils, and fats." -& JP 48 072960 A (ISHIHARA) 2 October 1973 (1973-10-02) abstract -----	1-20

D 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 document 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 27 July 2009	Date of mailing of the international search report 13/08/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patent laan 2 NL - 2280 HV Ri]SWiJk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Serra, Renato

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2009/001952

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 48072960 A	02-10-1973	NONE	

Form PCT/ISA/210 (patent family annex) (April 2005)