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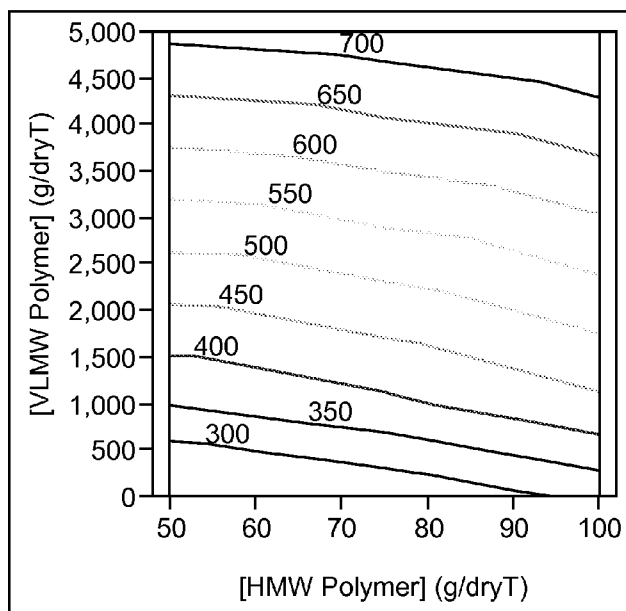


Figure 5

(57) Abstract: A process for treating a tailings stream which comprises sand, clay fines and water, the process comprising the steps of: (i) adding one or more very low molecular weight anionic polymers; or one or more phosphate compounds; or a mixture thereof; and one or more high molecular weight polymer flocculants to the tailings stream; and (ii) separating the solids from the flocculated stream.

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## PROCESSES FOR FLOCCULATING TAILINGS STREAMS OF THE OIL PROSPECTION

**FIELD OF THE ART**

[0001] The present disclosure relates generally to processes for flocculating and dewatering tailings streams.

**BACKGROUND**

[0002] Bituminous sands, or oil sands, are a type of petroleum deposit. The sands contain naturally occurring mixtures of sand, clay, water, and a dense and extremely viscous form of petroleum technically referred to as bitumen (or colloquially "tar" due to its similar appearance, odor, and color). Oil sands are found in large amounts in many countries throughout the world, and most abundantly in Canada and Venezuela. Oil sand deposits in northern Alberta in Canada (Athabasca oil sands) contain approximately 1.6 trillion barrels of bitumen, and production from oil sands mining operations is presently approximately one million barrels of bitumen per day.

[0003] Oil sands reserves have only recently been considered to be part of the world's oil reserves, as higher oil prices and new technology enable them to be profitably extracted and upgraded to usable products. They are often referred to as unconventional oil or crude bitumen, in order to distinguish the bitumen extracted from oil sands from the free-flowing hydrocarbon mixtures known as crude oil traditionally produced from oil wells.

[0004] Conventional crude oil is normally extracted from the ground by drilling oil wells into a petroleum reservoir, and allowing oil to flow into them under natural reservoir pressures. Although artificial lift and techniques such as water flooding and gas injection are usually required to maintain production as reservoir pressure drops towards the end of a field's life. Because extra-heavy oil and bitumen flow very slowly, if at all, towards producing wells under normal reservoir conditions, the sands may be extracted by strip mining or the oil made to flow into wells by in situ techniques which reduce the viscosity, such as by injecting steam, solvents, and/or hot air into the sands. These processes can use more water and require larger amounts of energy than conventional oil extraction, although many conventional oil fields also require large amounts of water and energy to achieve good rates of production.

[0005] Water-based oil sand extraction processes include ore preparation, extraction and tailings treatment stages wherein a large volume of solids-laden aqueous tailings is produced. One such extraction process is called the hot water process. In the hot water process the displacement of bitumen from the sands is achieved by wetting the surface of the sand grains with an aqueous solution containing a caustic wetting agent, such as

sodium hydroxide, sodium carbonate or sodium silicate. The resulting strong surface hydration forces operative at the surface of the sand particles give rise to the displacement of the bitumen by the aqueous phase. The name of the process comes from the fact that the system is operated at temperatures near the boiling point of water. Once the bitumen has been displaced and the sand grains are free, the phases can be separated by froth flotation based on the natural hydrophobicity exhibited by the free bituminous droplets at moderate pH values (Hot water extraction of bitumen from Utah tar sands, Sepulveda *et al.* S. B. Radding, ed., Symposium on Oil Shale, Tar Sand, and Related Material - Production and Utilization of Synfuels: Preprints of Papers Presented at San Francisco, California, August 29 – September 3, 1976; vol. 21, no. 6, pp. 110–122 (1976)).

**[0006]** Hydrophilic and biwetted ultrafine solids, mainly clays and other charged silicates and metal oxides, tend to form stable colloids in water and exhibit a very slow settling and dewatering behavior, resulting in tailing ponds that can take several years to manage. The slow settling of fine (<45 µm) and ultrafine clays (<0.3 µm) and the large demand of water during oil sand extraction process have promoted research and development of new technologies during the last 20 years to modify the water release and to improve settling characteristics of tailings streams. These include process additives such as variations in pH, salinity and addition of chemical substances. Currently, two technologies commonly used in the oil sands industry are the consolidated tailings (CT) process and the paste technology. Gypsum is used in the CT technology as a coagulant while polyelectrolytes, generally polyacrylamides of high density, are used as flocculants in the paste technology. Flocculants, or flocculating agents, are chemicals that promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a floc. Flocculants are used in water treatment processes to improve the sedimentation or filterability of small particles.

**[0007]** Various inorganic and/or organic flocculants are currently in use in tailings treatments. The adequate dosage of gypsum and/or flocculants during the tailings disposition improves the oil sands process efficiency because these substances act as modifiers of the interaction forces responsible for holding particles together. Consequently, the addition of these chemicals can enhance the settling rate of tailings and promote the recovery of water and its recirculation in the oil sands process. Recently some silicates and silica microgel have been proposed for treating tailing and separation of ultrafine solids. Silica could cause some problems, however, because it could be precipitated by the presence of too much calcium and magnesium. The resulting silicate scale could foul pipe surfaces and other surfaces.

**[0008]** When tailings are treated with gypsum (calcium sulfate) to flocculate the particles there is a problem that excess calcium can be present in the water recycled from the tailings, and this calcium can make it very hard to extract bitumen from oil sands.

[0009] A common chemical method of treating tailings is to dose them with a single anionic polymer. This approach is easy to administer, but it can be difficult, if not impossible, to achieve acceptable compaction of flocculated solids.

[0010] Canadian Patent Application No. 2364854 describes a method for settling an aqueous suspension of fine solid material including adding to the suspension a mixture of a first anionic polymer having a molecular weight of 250,000, 15,000,000 or 18,000,000 Daltons and a second anionic polymer having a molecular weight of at least 5,000,000 Daltons.

[0011] The Canadian government has recently required all companies exploiting the Canadian Oil Sands to have plans to treat their aqueous dispersions of tailings so that the tailings will be trafficable within ten years. There remains a need to develop better and more efficient processes for flocculating and dewatering tailings streams.

#### BRIEF SUMMARY

[0012] A process is provided for treating a tailings stream which comprises sand, clay fines and water, the process comprising the steps of:

- (i) adding to the tailings stream one or more very low molecular weight anionic polymers having a molecular weight of about 1,000 to about 50,000 Daltons; or one or more phosphate compounds; or a mixture thereof; and one or more high molecular weight polymer flocculants having a molecular weight of greater than about 1,000,000 Daltons; and
- (ii) separating the solids from the flocculated stream.

#### BRIEF DESCRIPTION OF THE FIGURES

[0013] Figures 1 and 2 show a typical particle size distribution of oil sand process tailings. Figure 1 shows the coarse tailings, which contain about 3% of fine particles. Figure 2 shows typical fine tailings, which contain about 67% of fine particles ("fine" defined as particles below 44 microns in diameter).

[0014] Figures 3 and 4 show results from comparison of flocculating abilities of different polymers. Figure 3 shows the flocculated bed solids (wt%) and Figure 4 shows the supernatant solids (wt%).

[0015] Figures 5 and 6 show the effect of VLMW and HMW polymers concentrations on the initial sedimentation rates of paraffinic froth tailings. Figure 5 shows the initial sedimentation rate (absolute, units mL/min) as a function of HMW and VLMW doses. Figure 6 shows the initial sedimentation rate (relative) as a function of HMW and VLMW doses.

**[0016]** Figures 7 and 8 show the effect of VLMW and HMW polymer concentrations on flocculated bed solids. Figure 7 shows the flocculated bed solids (absolute, units wt%) as a function of HMW and VLMW doses. Figure 8 shows the flocculated bed solids (relative) as a function of HMW and VLMW doses.

**[0017]** Figures 9 and 10 show the effect of VLMW and HMW polymer concentrations on supernatant solids. Figure 9 shows the supernatant solids (absolute, units wt%) as a function of HMW and VLMW doses. Figure 10 shows the supernatant solids (absolute, units wt%) as a function of HMW and VLMW doses.

**[0018]** Figure 11 shows the effect of adding different concentrations of VLMW polymer to tailings treated with 75 g/dryT of a 30 mol% anionic flocculant.

#### DETAILED DESCRIPTION

**[0019]** Processes for treating tailings streams are provided, wherein the tailings are treated with one or more very low molecular weight (VLMW) anionic polymers; or one or more phosphate compounds; or a mixture thereof; and with one or more high molecular weight (HMW) anionic or nonionic polymeric flocculants to produce flocculated solids. After the treatment the flocculated solids are usually let to settle and then they are separated.

**[0020]** It has been surprisingly discovered that tailings streams, in particular oil sands tailings streams, when first treated with one or more VLMW anionic polymer; or one or more phosphate compounds; or both; and one or more HMW anionic or nonionic polymeric flocculant; generally outperformed typical treatment methods for dewatering tailings streams. In particular, this combination led to enhanced formation of compact flocs that settled quickly. Additionally, the flocculated solids dewatered well after impounding, resulting in a sufficient increase in yield strength of the separated solids to achieve the trafficable quality, for example a yield stress of 10 kPa (as specified by the Canadian government).

#### **[0021] Tailings**

**[0022]** The expressions “tailings”, “tailings stream”, “process oil sand tailings”, or “in-process tailings” as used herein refer to tailings that are directly generated as bitumen is extracted from oil sands. Process tailings contain a majority of coarse particles, and are essentially comprised of silicates and clays. Fine tailings are generated after the process tailings are sent to a settling pond. Eventually, the coarse tailings settle to the bottom of the pond, leaving a weak gel of fine tailings (average diameter <44 μm) suspended in the water. Fine tailings tend to be almost entirely composed of clays. While fine tailings primarily consist of particles that are smaller than 44 μm in diameter, the majority of the solids in the process tailings have diameters between 44 and 1000 μm and above. The tailings can be one or more of any of the tailings streams produced in a process to extract bitumen from an oil

sands ore. The tailings are one or more of the coarse tailings, fine tailings, and froth treatment tailings. In exemplary embodiments, the tailings may comprise paraffinic or naphthenic tailings, for example paraffinic froth tailings. The tailings may be combined into a single tailings stream for dewatering or each tailings stream may be dewatered individually. Depending on the composition of the tailings stream, the additives may change, concentrations of additives may change, and the sequence of adding the additives may change. Such changes may be determined from experience with different tailings streams compositions.

**[0023]** In one embodiment, the tailings stream is produced from an oil sands ore and comprises water, sand and clay fines. In one embodiment, the tailing stream comprises at least one of the coarse tailings, fine tailings or froth treatment tailings.

**[0024]** As used herein, the terms “polymer,” “polymers,” “polymeric,” and similar terms are used in their ordinary sense as understood by one skilled in the art, and thus may be used herein to refer to or describe a large molecule (or group of such molecules) that contains recurring units. Polymers may be formed in various ways, including by polymerizing monomers and/or by chemically modifying one or more recurring units of a precursor polymer. A polymer may be a “homopolymer” comprising substantially identical recurring units formed by, e.g., polymerizing a particular monomer. A polymer may also be a “copolymer” comprising two or more different recurring units formed by, e.g., copolymerizing two or more different monomers, and/or by chemically modifying one or more recurring units of a precursor polymer. The term “terpolymer” may be used herein to refer to polymers containing three or more different recurring units.

**[0025] Very Low Molecular Weight Anionic Polymers**

**[0026]** In the embodiments described herein, a very low molecular weight (VLMW) anionic polymer may have a molecular weight between about 1,000 to about 50,000 Daltons; about 1,000 to about 10,000 Daltons; about 1,000 to about 5,000 Daltons; or about 1,000 to about 2,000 Daltons. In certain embodiments, the molecular weight of the VLMW anionic polymers is less than about 50,000 Daltons; less than about 10,000 Daltons; less than about 5,000 Daltons; or less than about 2,000 Daltons.

**[0027]** In one embodiment, the VLMW anionic polymer contains one or more monomers selected from the group consisting of acrylic acid, acrylamide, acrylate, itaconic acid, allyl sulfonate, maleic anhydride, 2-acrylamido-2-methylpropane sulfonic acid, another monomer containing carboxylic functionality and combinations thereof. In certain embodiments, the VLMW anionic polymer contains one or more monomers selected from the group consisting of acrylic acid, maleic anhydride, itaconic acid, another monomer containing carboxylic functionality, and combinations thereof. In certain embodiments, the VLMW anionic polymer contains one or more monomers which have one carboxylic

functionality per repeat unit. In a particular embodiment, the VLMW anionic polymer contains one or more monomers which have two carboxylic functionality per repeat unit.

**[0028]** In certain embodiments, the VLMW anionic polymer is selected from poly(acrylic acid), poly(acrylic acid-co-hydroxyethyl methacrylate), poly(itaconic acid), poly(acrylic acid-co-itaconic acid), poly(acrylic acid-co-maleic anhydride-co-sulfoethyl methacrylate), poly(sodium allyl sulfonate-co-maleic anhydride), poly(acrylic acid-co-acrylamide), poly(acrylic acid-co-acrylamide), and combination thereof.

**[0029]** In certain embodiments, the VLMW anionic polymer is selected from poly(acrylic acid), poly(acrylic acid-co-hydroxyethyl methacrylate) (73/27 mol% AA/HEMA), poly(itaconic acid), poly(acrylic acid-co-itaconic acid) (73/27 mol% AA/IA), poly(acrylic acid-co-maleic anhydride-co-sulfoethyl methacrylate) (84/15.5/0.5 mol% AA/MA/SM), poly(sodium allyl sulfonate-co-maleic anhydride) (50/50 mol% SAS/MA), poly(acrylic acid-co-acrylamide) (75/25 mol% AA/AMD), poly(acrylic acid-co-acrylamide) (50/50 mol% AA/AMD), and combinations thereof.

**[0030]** In certain embodiments, the charge density of the VLMW anionic polymer is from about 25 to about 100 mol%; about 30 to about 100 mol%; about 40 to about 100 mol%; about 50 to about 100 mol%; or about 60 to about 100 mol%. In one embodiment, the charge density of the VLMW anionic polymer at least about 25%, at least about 30%, at least about 40%, at least about 50%, or at least about 60%.

#### **[0031] Phosphate Compounds**

**[0032]** In the embodiments described herein, a phosphate compound is, for example, an inorganic polyphosphate compound such as a salt of hexametaphosphate, a salt of trimetaphosphate, or other salts or esters of polymeric oxyanions formed from tetrahedral PO<sub>4</sub> structural units linked together by sharing oxygen atoms and the like. Exemplary embodiments of the phosphate compounds include, for example, sodium hexametaphosphate (SHMP), trisodium phosphate (TSP), and sodium trimetaphosphate (STMP).

#### **[0033] High Molecular Weight Polymer Flocculants**

**[0034]** In the embodiments described herein, a high molecular weight (HMW) polymer flocculant may have a molecular weight between about 50,000 to about 60,000,000 Daltons; about 50,000 to about 10,000,000 Daltons; about 50,000 to about 2,000,000 Daltons; about 100,000 to about 2,000,000 Daltons; about 250,000 to about 2,000,000 Daltons; or about 500,000 to about 2,000,000 Daltons. In certain embodiments, the molecular weight of the HMW polymer flocculants is greater than about 50,000 Daltons; greater than about 100,000 Daltons; greater than about 250,000 Daltons; greater than about 500,000 Daltons; greater than about 1,000,000 Daltons; greater than about 2,000,000 Daltons.

**[0035]** In exemplary embodiments, the HMW polymer flocculants may be anionic or nonionic. Any high molecular weight anionic or nonionic polymer flocculants known in the art may be used in the processes described herein. Nonlimiting examples of exemplary

HMW polymer flocculants include, for example, flocculant-grade homopolymers, copolymers, and terpolymers prepared from monomers such as (meth)acrylic acid, (meth)acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and ethylene oxide. In one embodiment, the one or more HMW polymer flocculants are anionic polymers. In one embodiment, the one or more HMW polymer flocculants are nonionic polymers. In one embodiment, the HMW polymer flocculants are a mixture of anionic polymers and nonionic polymers. In one example, the HMW polymer is flocculant-grade poly(acrylamide(70)-co-acrylate(30)).

**[0036] Flocculation and Dewatering Process**

**[0037]** It is an objective of the exemplary processes described herein to flocculate and dewater the solids, while enabling recovery of as much of the water as possible. Surprisingly, by using the exemplary processes, a faster separation rate and a more complete separation of the solids from the water has been achieved, improving process efficiency relative to conventional processes for treating tailings streams.

**[0038]** In an exemplary embodiment, a process for treating a tailings stream which comprises sand, clay fines and water may comprise the steps of: (i) adding one or more very low molecular weight anionic polymers having a molecular weight of about 1,000 to about 50,000 Daltons; or one or more phosphate compounds; or a mixture thereof; and one or more high molecular weight polymer flocculants having a molecular weight of greater than about 1,000,000 Daltons to the tailings stream; and (ii) separating the solids from the flocculated stream.

**[0039]** In certain embodiments, the process comprises the steps of: (i) adding one or more VLMW anionic polymers having a molecular weight of about 1,000 to about 50,000 Daltons; and one or more HMW polymer flocculants having a molecular weight of greater than about 1,000,000 Daltons to the tailings stream; and (ii) separating the solids from the flocculated stream.

**[0040]** In one embodiment, the process comprises the steps of: (i) adding one or more phosphate compounds; and one or more HMW polymer flocculants having a molecular weight of greater than about 1,000,000 Daltons to the tailings stream; and (ii) separating the solids from the flocculated stream.

**[0041]** In another embodiment, the process comprises the steps of: (i) adding a mixture of one or more VLMW anionic polymers having a molecular weight of about 1,000 to about 50,000 Daltons and one or more phosphate compounds; and one or more HMW polymer flocculants having a molecular weight of greater than about 1,000,000 Daltons to the tailings stream; and (ii) separating the solids from the flocculated stream.

**[0042]** According to the embodiments, the separation step may be accomplished by any means known to those skilled in the art, including but not limited to centrifuges, hydrocyclones, decantation, filtration or another mechanical separation method.



**[0043]** The addition step of the embodiments results in the production of flocculated solids. The step of adding one or more VLMW anionic polymers; and/or one or more phosphate compounds to the tailings stream may be simultaneous or sequential with the step of adding one or more HMW anionic or nonionic polymer flocculant to the tailings stream. In certain embodiments, the process comprises adding sequentially the one or more VLMW anionic polymers; and/or one or more phosphate compounds to the tailings stream, then adding the one or more HMW anionic or nonionic polymer flocculants to the tailings stream. In other embodiments, the process comprises adding simultaneously the one or more VLMW anionic polymers; and/or one or more phosphate compounds; and the one or more HMW anionic or nonionic polymer flocculants to the tailings stream.

**[0044]** In preferred embodiments, one or more HMW anionic or nonionic polymer flocculants having a molecular weight of greater than 1,000,000 Daltons may be added to the tailing stream during or after the one or more VLMW polymers and/or one more phosphate compounds is added to the tailings stream.

**[0045]** In certain embodiments, the clays in the supernatant, which may be present as a very dilute suspension, can be removed if desired or necessary by any means known in the art, or by the addition of more of the VLMW polymer. In a particular embodiment, the process comprises adding organic or inorganic cationic coagulant or flocculant to the supernatant.

**[0046]** In certain embodiments, the process may optionally comprise adding a cationic coagulant or cationic flocculant to the tailings stream. The cationic coagulant or flocculant may be added to the tailings stream before or at the same time as the HMW flocculant, or added to the flocculated stream after the separation step. In an exemplary embodiment, the cationic coagulant or flocculant may be added to the supernatant. In exemplary embodiments, the cationic flocculants or cationic coagulant is a poly(diallyl dimethyl ammonium chloride) compound; an epi-polyamine compound; an aluminum chloride compound, a ferric chloride compound; a polymer that contains one or more quaternized ammonium groups, such as acryloyloxyethyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, methacrylamidopropyltrimethylammonium chloride, acrylamidopropyltrimethylammonium chloride; or a mixture thereof

**[0047]** In the exemplary embodiments, the process may provide enhanced flocculation of the solid materials in the tailings, better separation of the solids from water, an increased rate of separation of the solids from the water, and/or may expand the range of operating conditions which can be tolerated while still achieving the desired level of separation of solids from water within a desired period of time.

**[0048]** The exemplary processes described herein may provide flocculant bed with higher densities, leading to compact beds that can dewater faster and build yield strength

faster than when the tailings are treated with only a flocculant, or with an anionic or nonionic polymer with a molecular weight between 50,000 and 60,000,000 Daltons and a flocculant. In a particular embodiment, the exemplary processes accelerate dewatering of the tailings.

**[0049]** The exemplary processes described herein also may allow more solids to report to the supernatant. In an exemplary embodiment, the use of certain inorganic cationic coagulants, like calcium or silicates, can be avoided or minimized. In one embodiment, the process does not include the addition of inorganic cationic coagulants, for example calcium compounds or silicates.

**[0050]** In exemplary embodiments, the processes may be used to dewater the tailings so as to provide trafficable solids, or solids which possess a yield stress of greater than about 5000 Pa after one year, or a yield stress of greater than about 10000 Pa within five years. In certain embodiments, the VLMW polymer is added to the tailings stream in conjunction with a HMW polymer flocculant to accelerate dewatering or to produce tailings that achieve trafficability within about 7 days.

**[0051]** In the exemplary embodiments, the dewatered solids may be handled or processed in any manner as necessary or desired. In one embodiment, the dewatered solids should be handled in compliance with governmental regulations. In some embodiments, the resultant solids may be disposed of, sent to a tailings pond for additional settling, or when solids are a concentrated source of minerals, the solids may be used a raw materials or feed to produce compounds for commercial products. In certain embodiments, the solids may be dewatered to the point of supporting 2 kg. In particular embodiments, the solids may be dewatered to the point of being able to tolerate a yield stress of over 10 kPa (i.e. are fully dewatered.) In the exemplary embodiments, the separated water may be handled or processed in any manner as necessary or desired. In one embodiment, the separated water may be recycled to the process (“recycled water”). For example, the recycled water may be added to the crushed oil sands ore for bitumen extraction. Recycled water may also be added to the process at any point where water is added.

**[0052]** In the exemplary embodiments, the processes may be carried out at neutral conditions, such as about pH 6–10.5, or about 6–8. In certain embodiments of the process, it is not necessary to adjust the pH.

**[0053]** In the exemplary embodiments, the processes may be carried out at temperature of about 0°C to about 100°C, or about ambient temperature to about 90°C, or about 20°C to about 90°C.

**[0054]** In certain embodiments, the processes may achieve sedimentation rates of up to about 300 mL/min, up to about 400 mL/min, up to about 500 mL/min, up to about 600 mL/min, up to about 700 mL/min, initial sedimentation rate in a 1L graduated cylinder In a particular embodiment, the process may achieve a sedimentation rate that is greater than the sedimentation rate of comparable processes utilizing flocculant alone, for example greater

than about 200 mL/min initial sedimentation rate in a 1L graduated cylinder. In exemplary embodiments, the processes may achieve sedimentation rates of about 200 mL/min to about 700 mL/min, about 300 mL/min to about 700 mL/min, about 400 mL/min to about 700 mL/min, about 500 mL/min to about 700 mL/min, or about 600 mL/min to about 700 mL/min.

**[0055]** In one embodiment, the processes produce at least about 22 %, at least about 25 %, at least about 30 %, at least about 35 %, at least about 40 %, at least about 45 %, or at least about 50 %, by weight, flocculated bed solids.

**[0056]** In one embodiment, the processes produce less than about 2 wt%, less than about 1.5 wt%, less than about 1 wt%, less than about 0.5 wt%, or less than about 0.3 wt% solids in the supernatant.

**[0057]** In the exemplary embodiments, the dosage of the one or more VLMW anionic polymers or phosphate compounds can be any dosage that will achieve a necessary or desired result. In one embodiment, the dosage of the one or more VLMW anionic polymers or phosphate compound is about 100 ppm to about 16,500 ppm, about 100 ppm to about 10,000 ppm, about 8,000 ppm to about 10,000 ppm, about 100 ppm to about 5,000 ppm, about 100 ppm to about 1,000 ppm, about 100 ppm to about 500 ppm, about 100 ppm to about 400 ppm, about 100 ppm to about 300 ppm, or about 100 ppm to about 200 ppm. In one embodiment, the dosage of the VLMW anionic polymer or phosphate compound is less than about 16,500 ppm, less than about 10,000 ppm, less than about 5,000 ppm, less than about 1,000 ppm, less than about 500 ppm, less than about 400 ppm, less than about 300 ppm, or less than about 200 ppm.

**[0058]** In the exemplary embodiments, the dosage of the one or more VLMW anionic polymers or phosphate compounds can be any dosage that will achieve a necessary or desired result. In one embodiment, the dosage of the one or more VLMW anionic polymers or phosphate compound is about 100 g/dry T (grams of dry additive per metric ton of dry tailings) to about 16,500 g/dry T, about 100 g/dry T to about 10,000 g/dry T, about 8,000 g/dry T to about 10,000 g/dry T, about 100 g/dry T to about 5,000 g/dry T, about 100 g/dry T to about 1,000 g/dry T, about 100 g/dry T to about 500 g/dry T, about 100 g/dry T to about 400 g/dry T, about 100 g/dry T to about 300 g/dry T, or about 100 g/dry T to about 200 g/dry T. In one embodiment, the dosage of the VLMW anionic polymer or phosphate compound is less than about 16,500 g/dry T, less than about 10,000 g/dry T, less than about 5,000 g/dry T, less than about 1,000 g/dry T, less than about 500 g/dry T, less than about 400 g/dry T, less than about 300 g/dry T, or less than about 200 g/dry T.

**[0059]** In the exemplary embodiments, the dosage of the one or more HMW polymer flocculant can be any dosage that will achieve a necessary or desired result. In one embodiment, the dosage of the one or more HMW polymer flocculant is about 50 ppm to about 500 ppm, about 50 ppm to about 400 ppm, about 50 ppm to about 300 ppm, about 50

ppm to about 100 ppm, or about 50 ppm to about 200 ppm. In one embodiment, the dosage of the one or more HMW polymer flocculant is less than about 500 ppm, less than about 400 ppm, less than about 300 ppm, less than about 200 ppm, or less than about 100 ppm.

**[0060]** In the exemplary embodiments, the dosage of the one or more HMW polymer flocculant can be any dosage that will achieve a necessary or desired result. In one embodiment, the dosage of the one or more HMW polymer flocculant is about 50 g/dry T to about 500 g/dry T, about 50 g/dry T to about 400 g/dry T, about 50 g/dry T to about 300 g/dry T, about 50 g/dry T to about 100 g/dry T, or about 50 g/dry T to about 200 g/dry T. In one embodiment, the dosage of the one or more HMW polymer flocculant is less than about 500 g/dry T, less than about 400 g/dry T, less than about 300 g/dry T, less than about 200 g/dry T, or less than about 100 g/dry T.

#### EXAMPLES

##### **[0061] Tailings Substrate**

**[0062]** The tailings evaluated in these tests were process tailings. Figures 1 and 2 show the distribution of particle sizes in the tailings.

**[0063]** Effect of the VLMW Anionic Polymer and HMW Polymer Flocculant Treatment on Process Tailings

**[0064]** Examples 1-15.

**[0065]** A slurry of process tailings was added to a 1 l graduated cylinder. 8,000–10,000 g/dryT of the very low molecular weight (VLMW) polymer was added, and then the slurry was agitated 10 times with a plunger. Next, 60–70 g/dryT of the flocculant was added, and then the slurry was agitated an additional 3 times. The contents of the cylinder were allowed to settle over 20 minutes, and then aliquots of the supernatant and flocculated bed were withdrawn and dried in a 120°C oven. The solids concentrations of these aliquots were calculated from the differences in slurry and dry masses.

**[0066]** It was observed that treating the process tailings with a VLMW polymer followed by a high molecular weight polymer greatly increased the solids content of the flocculated particles. The molecular weight and the chemical composition of the HMW polymer flocculant were typical for practicing the art. The HMW polymer flocculant dose, molecular weight, and composition had less of an effect on solids separation than the dose, molecular weight, and composition of the VLMW polymer. Performance suffered when the molecular weight of the VLMW was above 200,000 g/mol.

**[0067]** It was observed that the supernatant solids increased as the flocculated bed solids increased. These solids could be removed in a subsequent step with a cationic coagulant and an additional anionic or cationic flocculant.

**[0068]** VLMW polymers containing many different monomers were tested, including acrylamide, acrylic acid, maleic anhydride, itaconic acid, allyl sulfonate,

hydroxyethyl methacrylate, and 2-acrylamido-2-methylpropane sulfonic acid. Certain phosphate compounds, silicate compounds and a few higher molecular weight polymers were also tested. The best-performing VLMW polymers contained acrylamide, acrylic acid, and itaconic acid with the charge density between 50 and 100 mol%.

**[0069]** Table 1 shows results from the experiments. The abbreviations are: AA = Acrylic acid, AMD = Acrylamide, HEMA = Hydroxyethyl methacrylate, IA = Itaconic acid, AS = Allyl sulfonate, MA = Maleic anhydride, AMPS = 2-Acrylamido-2-methylpropane sulfonic acid. The example numbers in Table 1 correspond to the experiment numbers in Figures 3 and 4.

Table 1

Ex.	Polymer 1 Composition	Polymer 1 Molecular Weight (g/mol)	Polymer 1 Conc. (g/dryT)	Polymer 2 Composition	Polymer 2 Standard Viscosity (cP)	Polymer 2 Conc. (g/dryT)	Supernatant solids (wt%)	Flocculated bed solids (wt%)
1	None	n/a	n/a	38.7 mol% AA/61.3 mol% AMD	3.5	70	0.20	21.18
2	70 mol% AA / 30 mol% AMD	259950	40	38.7 mol% AA/61.3 mol% AMD	3.5	60	0.62	14.60
3	70 mol% AA / 30 mol% AMD	259950	8000	38.7 mol% AA/61.3 mol% AMD	3.5	60	0.35	15.10
4	75 mol% AA / 25 mol% AMD	1700	8000	38.7 mol% AA/61.3 mol% AMD	3.5	60	0.81	50.97
5	50 mol% AA / 50 mol% AMD	2070	10000	38.7 mol% AA/61.3 mol% AMD	3.5	70	2.79	42.35
6	50 mol% AA / 50 mol% AMD	4140	10000	38.7 mol% AA/61.3 mol% AMD	3.5	70	1.13	44.40
7	60 mol% AA / 40 mol% HEMA	8580	10000	38.7 mol% AA/61.3 mol% AMD	3.5	70	1.13	41.33
8	50 mol% AA / 50 mol% HEMA	1550	10000	38.7 mol% AA/61.3 mol% AMD	3.5	70	0.18	15.66
9	AA	1650	10000	38.7 mol% AA/61.3 mol% AMD	3.5	70	2.94	46.05
10	AA	3420	8000	38.7 mol% AA/61.3 mol% AMD	3.5	60	0.39	42.39

Ex.	Polymer 1 Composition	Polymer 1 Molecular Weight (g/mol)	Polymer 1 Conc. (g/dryT)	Polymer 2 Composition	Polymer 2 Standard Viscosity (cP)	Polymer 2 Conc. (g/dryT)	Supernatant solids (wt%)	Flocculated bed solids (wt%)
11	84 mol% AA / 16 mol% MA	2500	8000	38.7 mol% AA/61.3 mol% AMD	3.5	60	1.25	41.98
12	IA	9940	8000	38.7 mol% AA/61.3 mol% AMD	3.5	60	0.41	32.40
13	73 mol% AA / 27 mol% IA	1660	8000	38.7 mol% AA/61.3 mol% AMD	3.5	60	0.49	44.30
14	50 mol% AS / 50 mol% MA	5200	8000	38.7 mol% AA/61.3 mol% AMD	3.5	60	0.36	36.14
15	85 mol% AA / 15 mol% AMPS	8600	10000	38.7 mol% AA/61.3 mol% AMD	3.5	70	1.64	40.00
16	Sodium hexametaphosphate	612	8000	38.7 mol% AA/61.3 mol% AMD	3.5	70	1.01	32.40
17	Sodium Silicate	Unknown	8000	38.7 mol% AA/61.3 mol% AMD	3.5	70	0.12	24.03

**[0070]** Figures 3 and 4 show the results from comparison of different polymers. Figure 3 shows the flocculated bed solids (wt%) and Figure 4 shows the supernatant solids (wt%).

**[0071]** Example 18.

**[0072]** Samples of process oil sands tailings at a pH of 7.6 and a temperature of 22 °C were treated with either a single high molecular weight (HMW) polymer, or a combination of a very low molecular weight (VLMW) polymer followed by the HMW polymer. The HMW polymer consisted of a flocculant-grade poly(acrylamide(70)-co-acrylate(30)), and the VLMW polymer was a poly(acrylamide(50)-co-acrylate(50)).

**[0073]** Settling tests were performed in 1-L graduated cylinders, and treatment chemicals were mixed into the tailings slurry using a perforated disk mounted on a steel rod. Ten transits of the disk (up and down) through the slurry were sufficient for mixing the VLMW polymer, while three transits were used for mixing the HMW polymer. The volume of the flocculated solids was followed over a period of 20 minutes, after which time the supernatant and flocculated bed were separated and subjected to further analysis.

**[0074]** Particle size distributions were measured on a Malvern Mastersizer S, which measures the angular dependence of scattered light (mainly in the forward direction). Paste samples were dispersed in the impeller driven flow loop of the Mastersizer. The flow loop

contained Milli-Q water without additional chemical dispersants. Particle size distributions were computed as equivalent-sphere size distributions based on Mie scattering and Fraunhofer diffraction formalisms applied to the scattering data. The optical constants ( $\lambda = 432.8$  nm) used for these computations were a complex refractive index of 1.5295, 0.000i for the solids and a real refractive index of 1.3300 for the continuous phase. Measurements were taken during each test at 30, 60, 120, and 240 seconds after addition of the solids to the diluent under continuous agitation at an impeller speed of 1600 rpm. This procedure allowed us to assess whether a steady-state size distribution had been achieved. Typically, the size distributions after 120 sec of mixing were used for comparisons, since steady state was achieved by this time.

**[0075]** Yield stresses were measured on an Anton Paar MCR 300 rheometer equipped with a FL100 spindle. The spindle consisted of six blades measuring 16 mm in height evenly spaced around a central shaft, for an overall diameter of 22 mm. Measurements were accomplished by inserting the spindle into a flocculated sample until the tips of the vanes were covered, and then logarithmically increasing the shear stress from 0.1 Pa until the sample began to flow. The yield stress value was determined by calculating the point at which a log-log plot of shear stress versus viscosity deviated from linearity. ( See Howard A. Barnes, *Journal of Non-Newtonian Fluid Mechanics*, Volume 81, Issues 1-2, 1 February 1999, Pages 133-178, ISSN 0377-0257, 10.1016/S0377-0257(98)00094-9.)

**[0076]** Results and Discussion

**[0077]** Figures 5 and 6 show the effect of VLMW and HMW polymers concentrations on the initial sedimentation rates of paraffinic froth tailings. Figure 5 shows the initial sedimentation rate (absolute, units mL/min) as a function of HMW and VLMW doses. Figure 6 shows the initial sedimentation rate (relative) as a function of HMW and VLMW doses. While increasing the concentration of both components improved sedimentation velocities, the impact of the flocculant was limited, with too much flocculant resulting in large flocs that did not compact or dewater well. Conversely, elevating the amount of VLMW more than doubled sedimentation velocities in some cases, and also increased the dewaterability of the flocculated solids.

**[0078]** Increasing the concentration of flocculant had a minimal effect on the density of flocculated solids, but adding a VLMW polymer increased the solids in the flocculated bed from below 20 wt% to over 50 wt% (see Figures 7 and 8). Carrying out solid-liquid separation in a thickener can even further increase the solids compaction.

**[0079]** Figures 7 and 8 show the effect of VLMW and HMW polymer concentrations on flocculated bed solids. Figure 7 shows the flocculated bed solids (absolute, units wt%) as a function of HMW and VLMW doses. Figure 8 shows the flocculated bed solids (relative) as a function of HMW and VLMW doses.

**[0080]** It was observed that as the VLMW polymer concentration increased, more clays reported to the supernatant, as shown in Figures 9 and 10. However, the structure of the VLMW polymer had been optimized to minimize the amount of fines in the supernatant.

**[0081]** Figures 9 and 10 show the effect of VLMW and HMW polymer concentrations on supernatant solids. Figure 9 shows the supernatant solids (absolute, units wt%) as a function of HMW and VLMW doses. Figure 10 shows the supernatant solids (absolute, units wt%) as a function of HMW and VLMW doses.

**[0082]** Figure 11 shows the effect of adding different concentrations of VLMW polymer to tailings treated with 75 g/dryT of a 30 mol% anionic flocculant.

**[0083]** In the preceding specification, various exemplary embodiments have been described. It will, however, be evident that various modifications and changes may be made thereto, and additional embodiments may be implemented, without departing from the broader scope of the exemplary embodiments as set forth in the claims that follow. The specification and drawings are accordingly to be regarded in an illustrative rather than restrictive sense.



## CLAIMS

We claim:

1. A process for treating a tailings stream which comprises sand, clay fines and water, the process comprising the steps of:
  - (i) adding to the tailings stream one or more very low molecular weight anionic polymers having a molecular weight of about 1,000 to about 50,000 Daltons; or one or more phosphate compounds; or a mixture thereof; and one or more high molecular weight polymer flocculants having a molecular weight of greater than about 1,000,000 Daltons; and
  - (ii) separating the solids from the flocculated stream.
  
2. The process of claim 1, wherein the process comprises the steps of:
  - (i) adding to the tailings stream one or more very low molecular weight anionic polymers having a molecular weight of about 1,000 to about 50,000 Daltons; and one or more high molecular weight polymer flocculants having a molecular weight of greater than about 1,000,000 Daltons; and
  - (ii) separating the solids from the flocculated stream.
  
3. The process of claim 1, wherein the process comprises the steps of:
  - (i) adding to the tailings stream one or more phosphate compounds; and one or more high molecular weight polymer flocculants having a molecular weight of greater than about 1,000,000 Daltons; and
  - (ii) separating the solids from the flocculated stream.
  
4. The process of claim 1, wherein the process comprises the steps of:
  - (i) adding to the tailings stream a mixture of one or more very low molecular weight anionic polymers having a molecular weight of about 1,000 to about 50,000 Daltons and one or more phosphate compounds; and one or more high molecular weight polymer flocculants having a molecular weight of greater than about 1,000,000 Daltons; and
  - (ii) separating the solids from the flocculated stream.
  
5. The process of claim 1, wherein the one or more very low molecular weight anionic polymers having a molecular weight of about 1,000 to about 50,000 Daltons; or the one or more phosphate compounds; or the mixture thereof is added to the tailings stream; and then the one or more high molecular weight polymer flocculants having a molecular weight of greater than about 1,000,000 Daltons is added to the tailings stream.

6. The process of claim 1, wherein the one or more very low molecular weight anionic polymers having a molecular weight of about 1,000 to about 50,000 Daltons; or the one or more phosphate compounds; or the mixture thereof; and the one or more high molecular weight polymer flocculants having a molecular weight of greater than about 1,000,000 Daltons are added to the tailings stream simultaneously.

7. The process of claim 1, wherein the process further comprises adding a cationic coagulant or cationic flocculant to the tailings stream.

8. The process of claim 1, wherein the separation of the solids from the flocculated stream is by centrifuges, hydrocyclones, decantation, filtration or another mechanical separation method.

9. The process of claim 1, wherein the very low molecular weight anionic polymer has a molecular weight of about 1,000 to about 10,000 Daltons.

10. The process of claim 1, wherein the very low molecular weight anionic polymer has a molecular weight of about 1,000 to about 5,000 Daltons.

11. The process of claim 1, wherein the very low molecular weight anionic polymer comprises one or more monomers selected from the group consisting of acrylic acid, acrylamide, acrylate, itaconic acid, allyl sulfonate, maleic anhydride, 2-acrylamido-2-methylpropane sulfonic acid, another monomer containing carboxylic functionality, and combinations thereof.

12. The process of claim 11, wherein the very low molecular weight anionic polymer comprises one or more monomers selected from the group consisting of acrylic acid, maleic anhydride, itaconic acid, another monomer containing carboxylic functionality, and combinations thereof.

13. The process of claim 1, wherein the very low molecular weight anionic polymer comprises one or more monomers which have one carboxylic functionality per repeat unit. In a particular embodiment, the VLMW anionic polymer comprises one or more monomers which have two carboxylic functionality per repeat unit.

14. The process of claim 1, wherein the very low molecular weight anionic polymer is selected the group consisting of: poly(acrylic acid), poly(acrylic acid-co-hydroxyethyl methacrylate), poly(itaconic acid), poly(acrylic acid-co-itaconic acid), poly(acrylic acid-co-

maleic anhydride-co-sulfoethyl methacrylate), poly(sodium allyl sulfonate-co-maleic anhydride), poly(acrylic acid-co-acrylamide), and poly(acrylic acid-co-acrylamide), and combinations thereof.

14. The process of claim 1, wherein the very low molecular weight anionic polymer is selected the group consisting of: poly(acrylic acid), poly(acrylic acid-co-hydroxyethyl methacrylate) (73/27 mol% AA/HEMA), poly(itaconic acid), poly(acrylic acid-co-itaconic acid) (73/27 mol% AA/IA), poly(acrylic acid-co-maleic anhydride-co-sulfoethyl methacrylate) (84/15.5/0.5 mol% AA/MA/SM), poly(sodium allyl sulfonate-co-maleic anhydride) (50/50 mol% SAS/MA), poly(acrylic acid-co-acrylamide) (75/25 mol% AA/AMD), and poly(acrylic acid-co-acrylamide) (50/50 mol% AA/AMD); and combinations thereof.

15. The process of claim 1, wherein the dosage of the one or more very low molecular weight anionic polymers is less than about 200 ppm.

16. The process of claim 1, wherein the dosage of the one or more phosphate compounds is less than about 200 ppm.

17. The process of claim, wherein the dosage of the one or more high molecular weight anionic or nonionic polymers is less than about 200 ppm.

18. The process of claim 1, wherein the one or more very low molecular weight anionic polymers is poly(acrylic acid-co-acrylamide) (50/50 mol% AA/AMD).

19. The process of claim 1, wherein the one or more high molecular weight anionic or nonionic polymers is flocculant grade poly(acrylamide(70)-co-acrylate(30)).

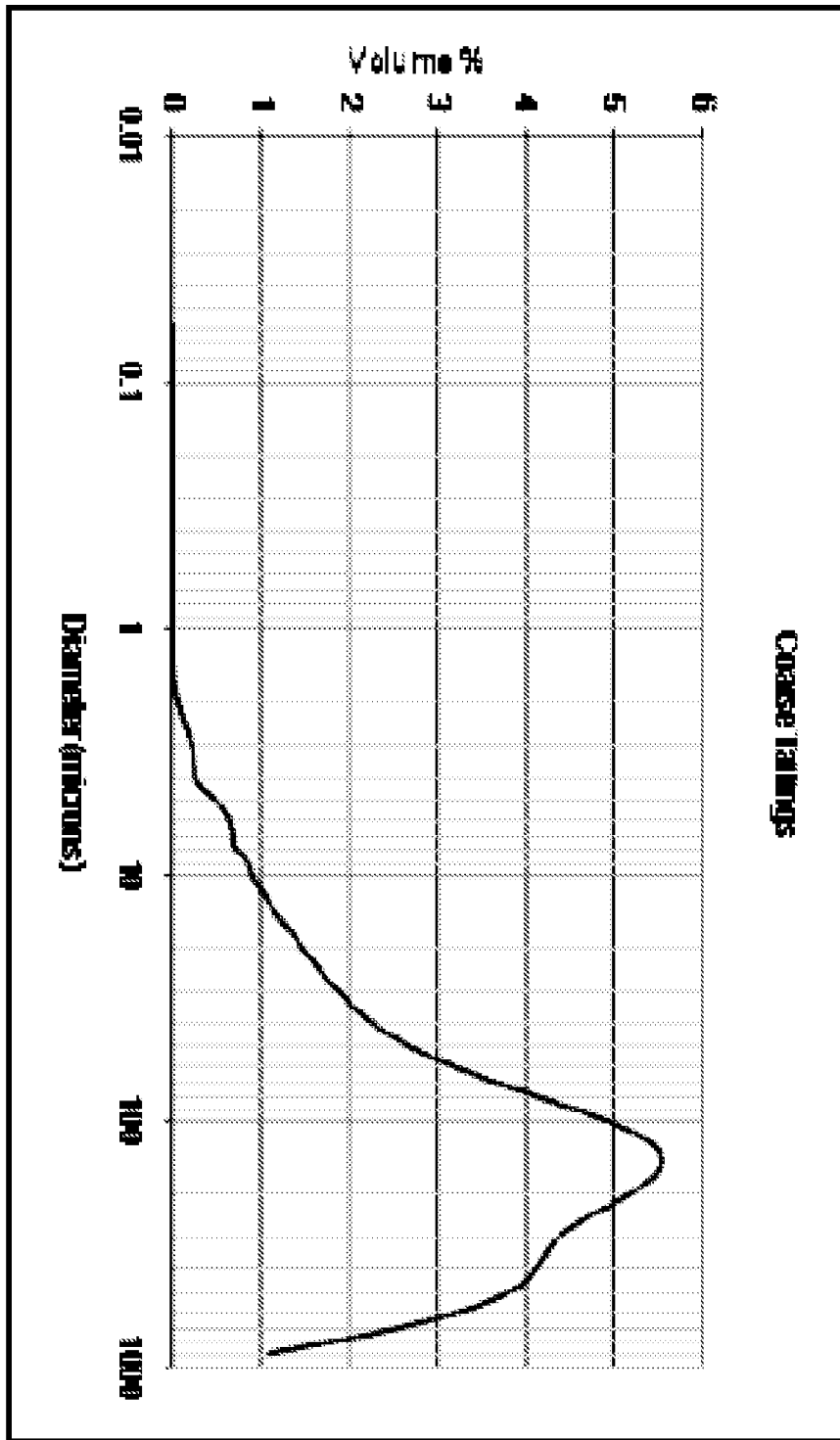


Figure 1

SHEET 2/11

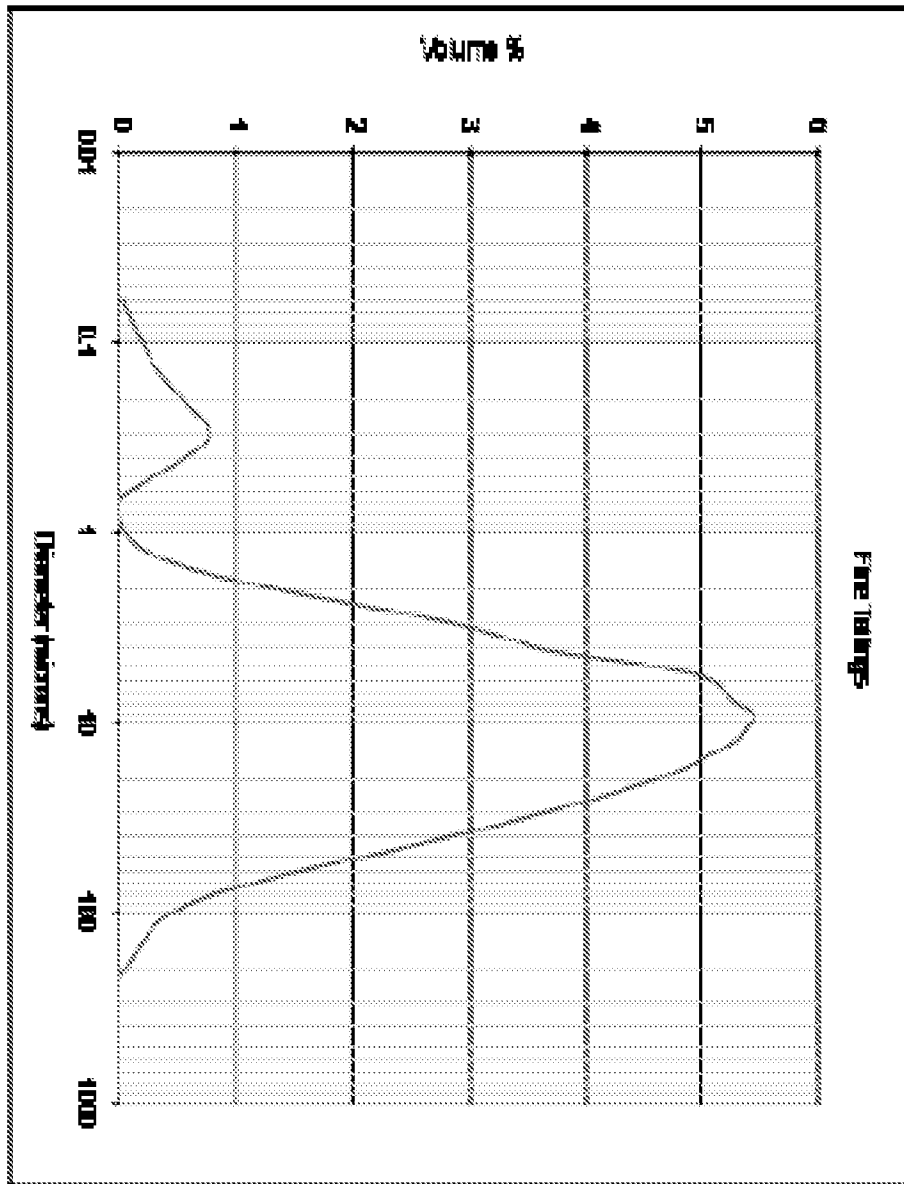


Figure 2

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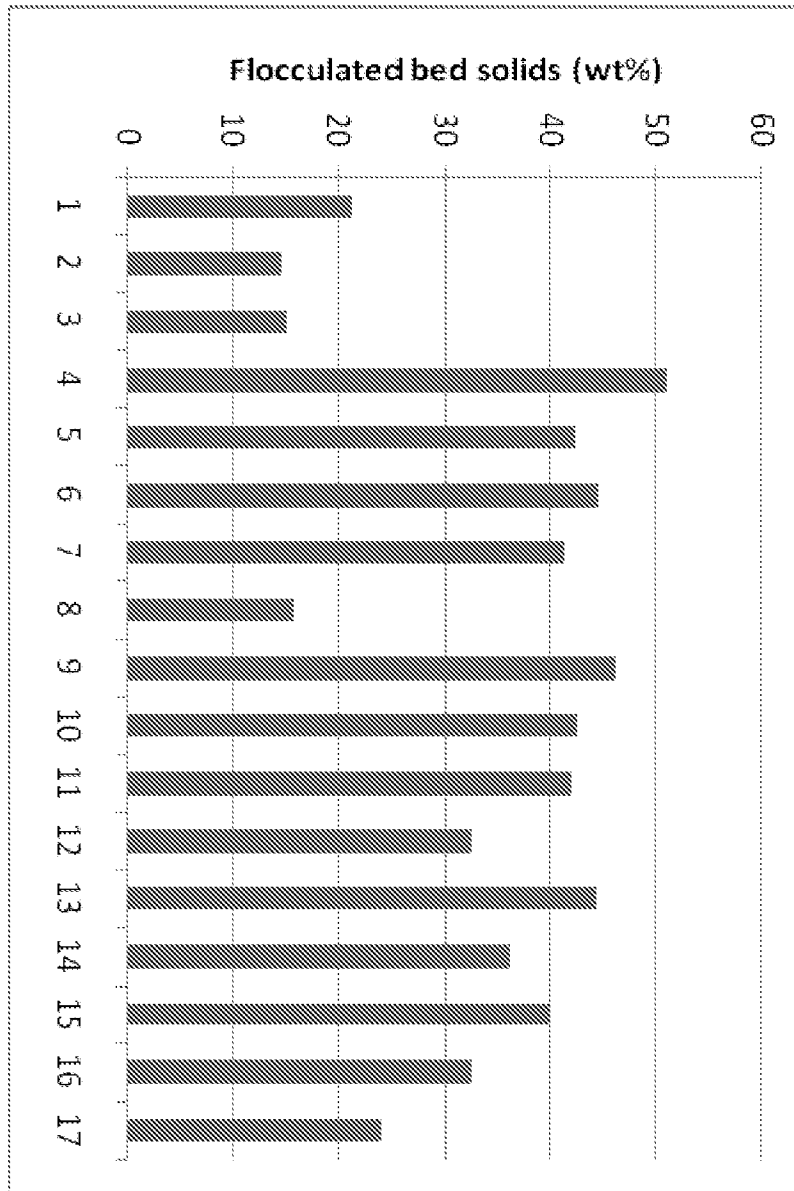


Figure 3

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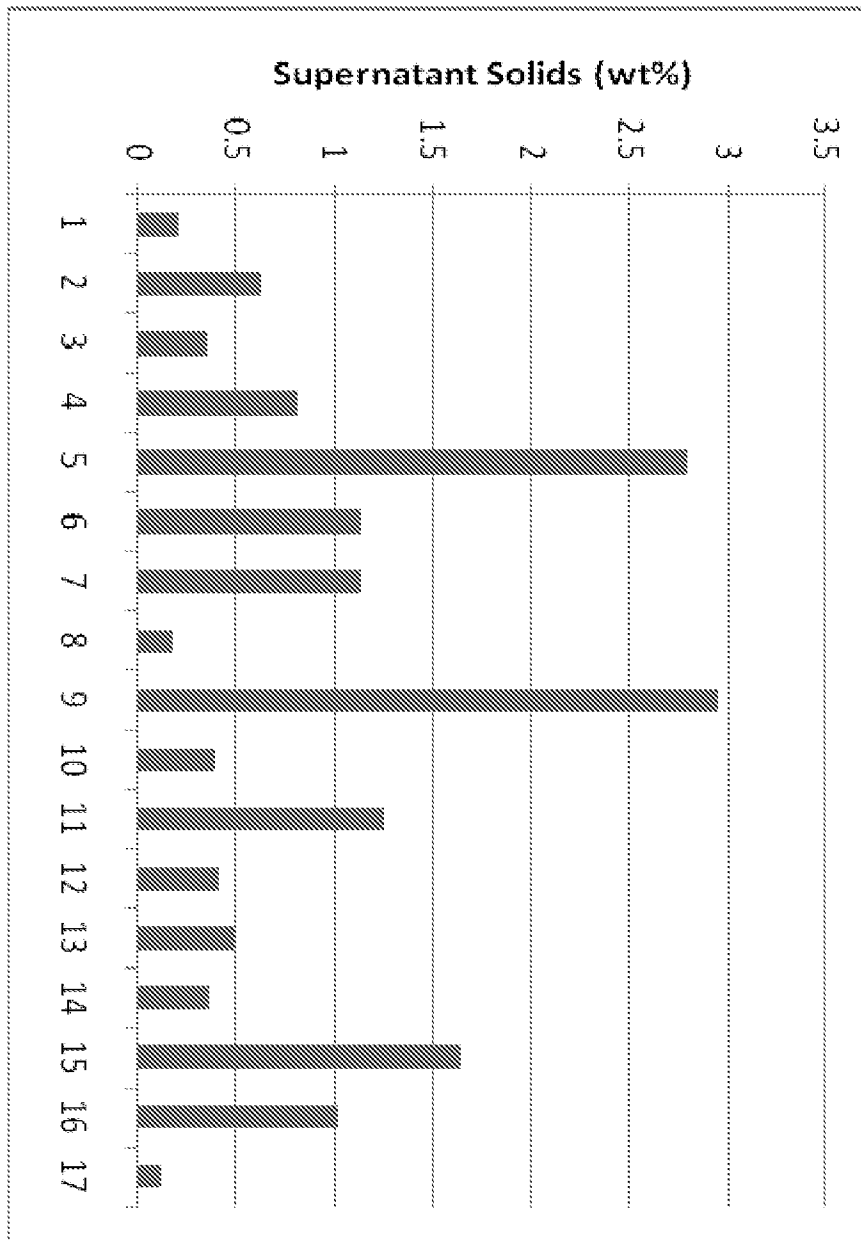


Figure 4

SHEET 5/11

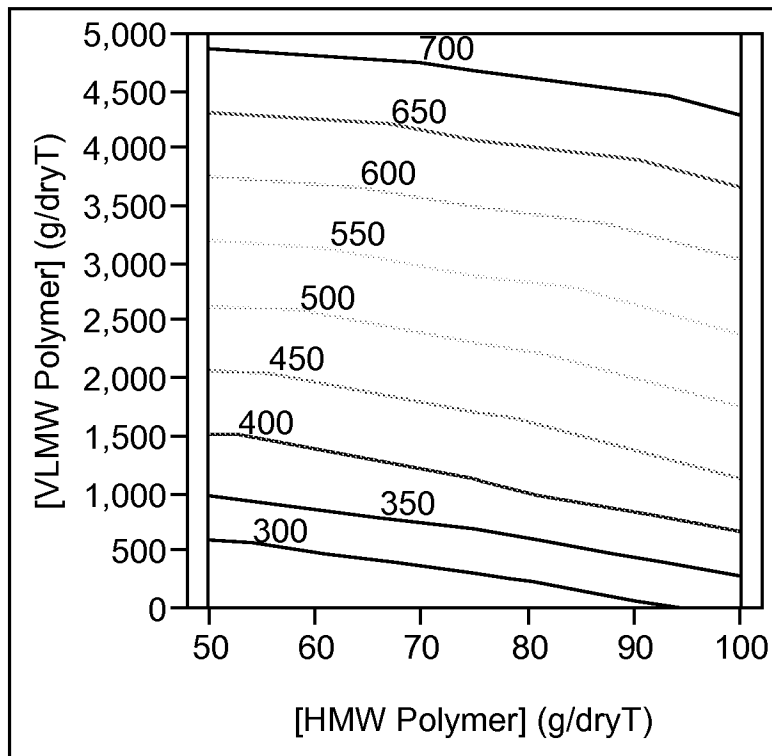


Figure 5



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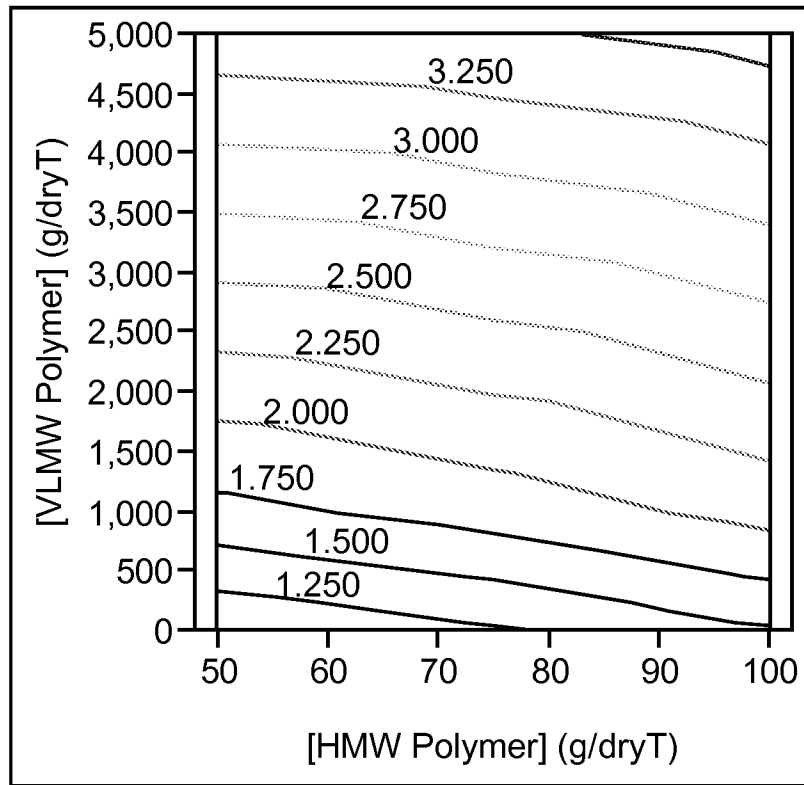


Figure 6

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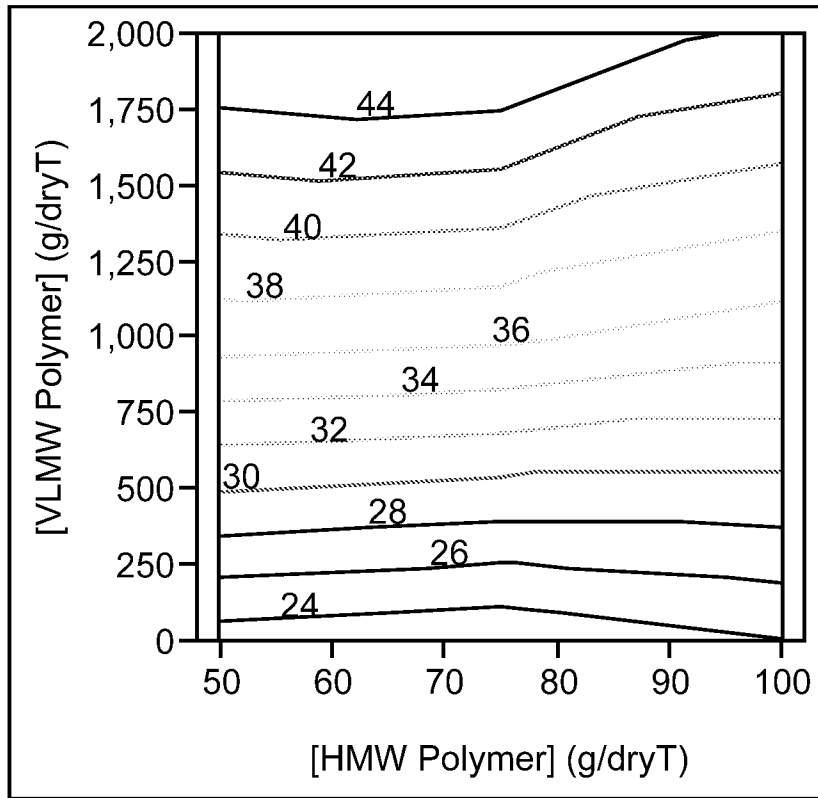


Figure 7

SHEET 8/11

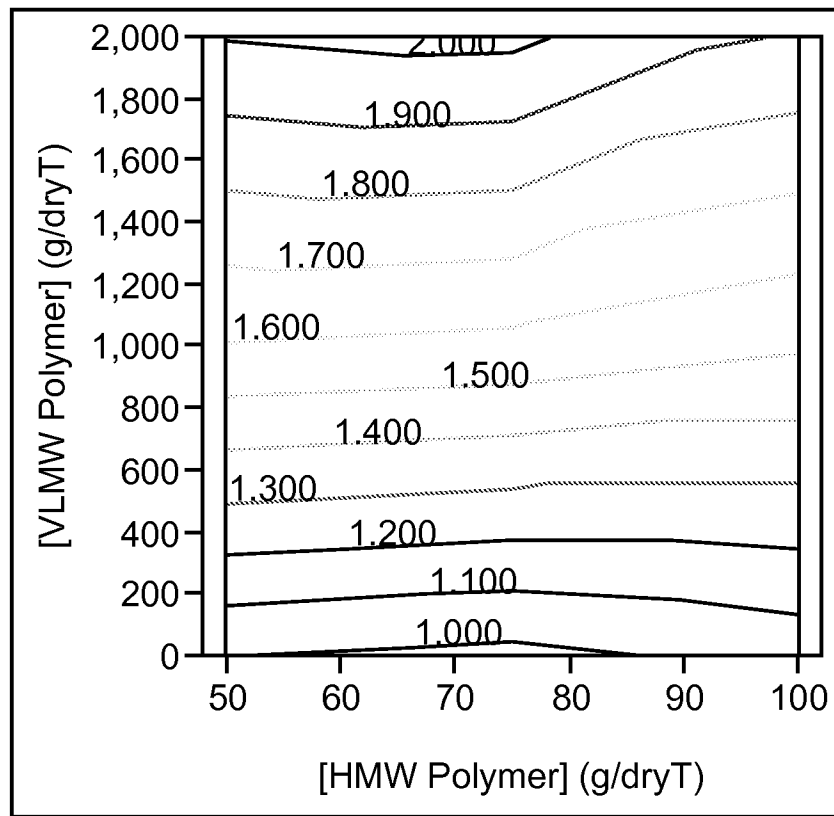


Figure 8

SHEET 9/11

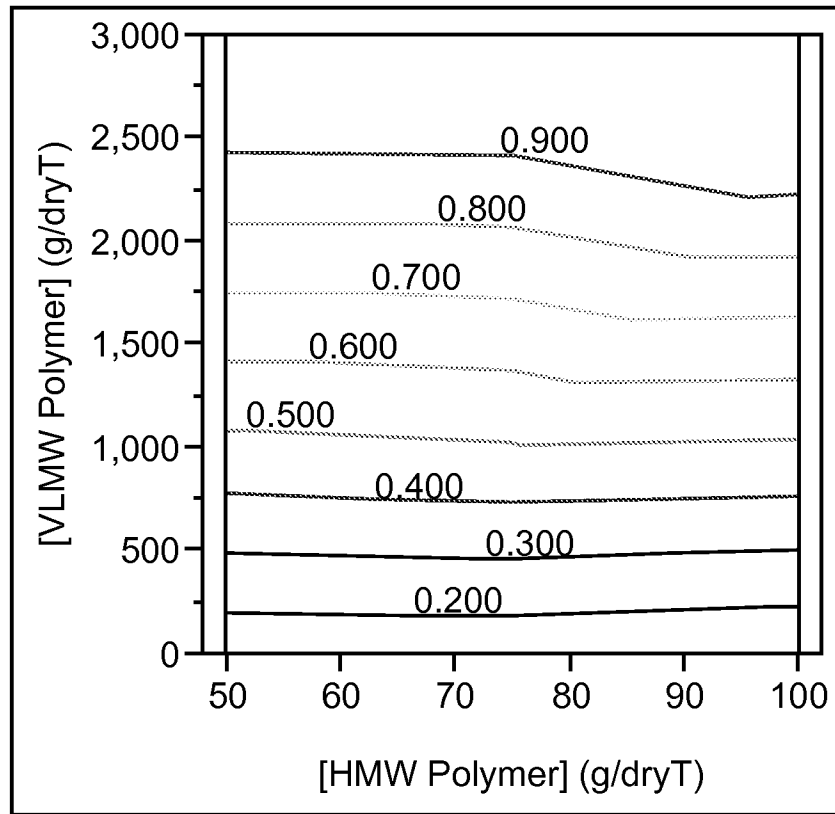


Figure 9

SHEET 10/11

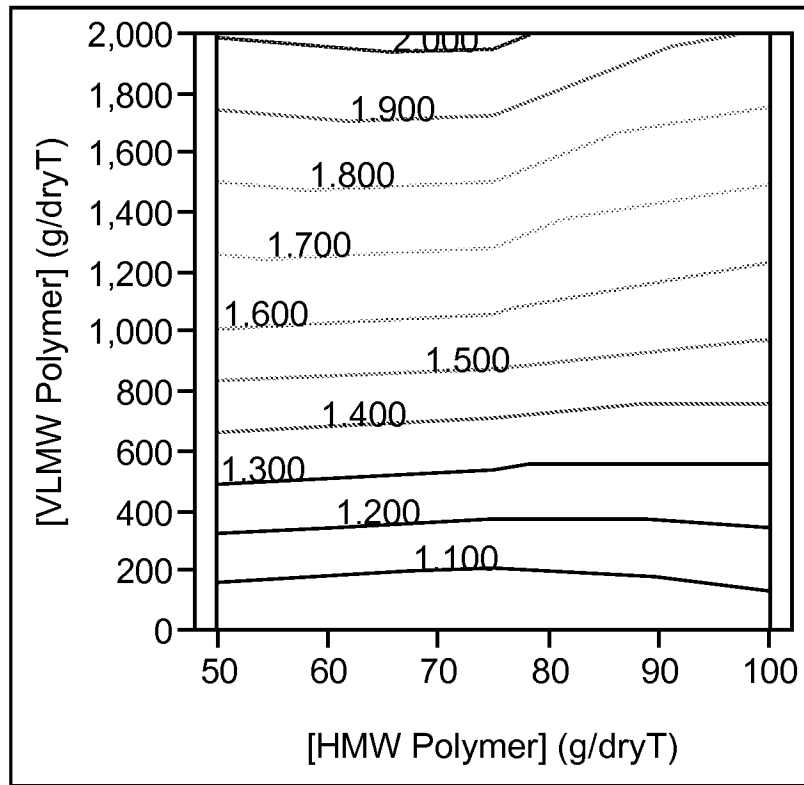


Figure 10

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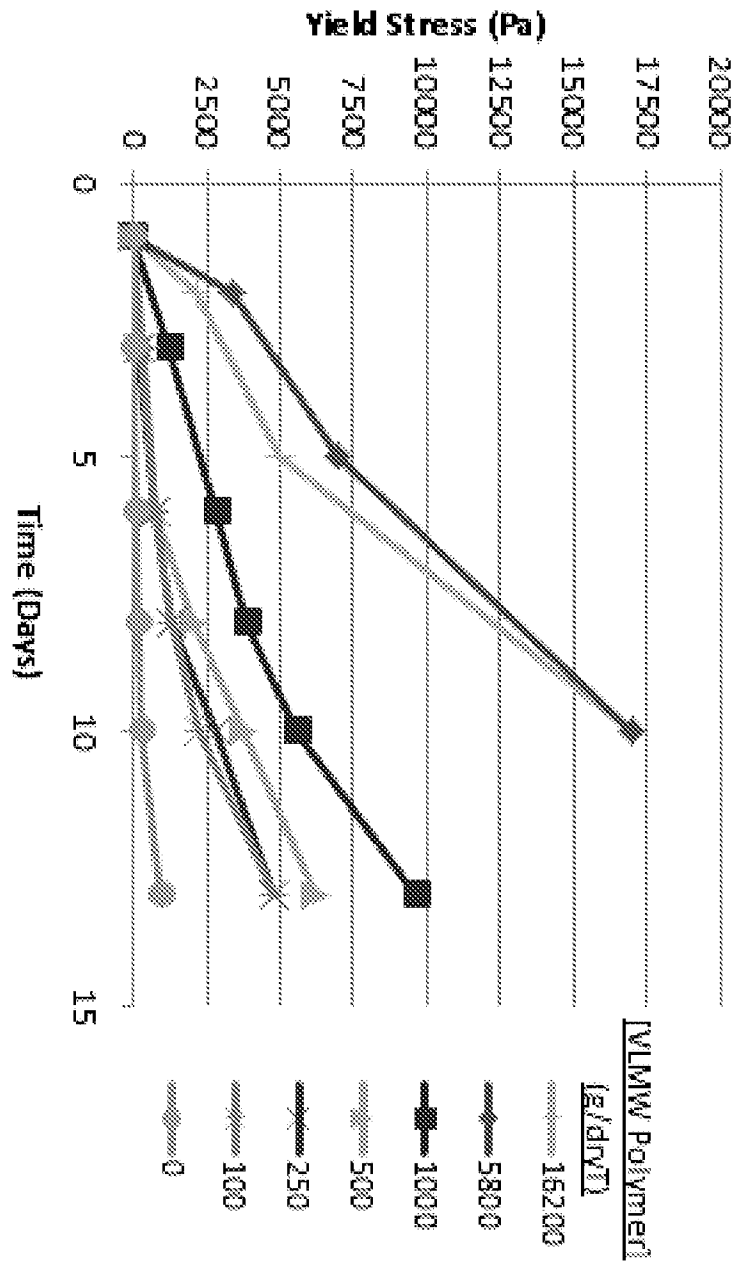


Figure 11

INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2011/066531

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C04B33/04  
ADD.  
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
Minimum documentation searched (classification system followed by classification symbols)  
C04B

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 555 329 A (SYKES ROBERT C [US] ET AL) 26 November 1985 (1985-11-26)	1-19
Y	col. 2, lines 3-28 (points a,b) example II, col. 6, line 11-15; tables, I,II; claims 1-4.	1-19
X	WO 2004/071989 A1 (IMERYS PIGMENTS INC [US]; GARSKA MICHAEL J [US]; PRUETT ROBERT J [US];) 26 August 2004 (2004-08-26) paragraphs[028], [044], [060], [061], [078], [083], [088]	1-19
Y	US 4 798 653 A (RUSHMERE JOHN D [US]) 17 January 1989 (1989-01-17) col. 4, line 10-col.5, line 37	1-19
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Further documents are listed in the continuation of Box C.

See patent family annex.

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Date of the actual completion of the international search  2 March 2012	Date of mailing of the international search report  08/03/2012
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Rumbo, Angel
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## INTERNATIONAL SEARCH REPORT

International application No  
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US 5 296 006 A (REED PETER E [US] ET AL) 22 March 1994 (1994-03-22) see tables 1-3, claims 1-4 -----	1-19
Y	EP 0 643 017 A1 (NALCO CHEMICAL CO [US]) 15 March 1995 (1995-03-15) see examples 1-11 -----	1-19
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