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(71) Demandeur/Applicant:
SORTWELL & CO., US

(72) Inventeur/Inventor:
SORTWELL, EDWIN T., US

(74) Agent: RIDOUT & MAYBEE LLP

(54) Titre : FLOCULENTS ANIONIQUES MULTIACRYLATE

(54) Title: MULTI-ACRYLATE ANIONIC FLOCCULANTS

(57) **Abrégé/Abstract:**

Polymeric compositions are described for dewatering and/or solids reclamation from aqueous slurries. The composition comprises a polymeric product comprising the following monomers: (a) monovalent acrylate; (b) multivalent acrylate; and (c) acrylamide. The polymeric product may comprise a polymeric compound comprising all three of the above monomers in a single compound, or alternatively a mixture of polymeric compounds such as a mixture of two copolymers comprising (a) a monovalent acrylate monomer and an acrylamide monomer; and (b) a multivalent acrylate monomer and an acrylamide monomer. The monovalent acrylate monomer may be sodium acrylate, potassium acrylate, ammonium acrylate, or a combination thereof. Methods for the use of the compositions as flocculants are described, including a pretreatment with a low-molecular weight (LMW) copolymer of 80 to 250 kDa.

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ABSTRACT:

Polymeric compositions are described for dewatering and/or solids reclamation from aqueous slurries. The composition comprises a polymeric product comprising the following monomers: (a) monovalent acrylate; (b) multivalent acrylate; and (c) acrylamide. The polymeric product may comprise a polymeric compound comprising all three of the above monomers in a single compound, or alternatively a mixture of polymeric compounds such as a mixture of two copolymers comprising (a) a monovalent acrylate monomer and an acrylamide monomer; and (b) a multivalent acrylate monomer and an acrylamide monomer. The monovalent acrylate monomer may be sodium acrylate, potassium acrylate, ammonium acrylate, or a combination thereof. Methods for the use of the compositions as flocculants are described, including a pretreatment with a low-molecular weight (LMW) copolymer of 80 to 250 kDa.

MULTI-ACRYLATE ANIONIC FLOCCULANTS

FIELD:

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The invention relates generally to polymers and the use thereof for aggregating mineral or organic components in aqueous slurries to separate out individual components of the slurry, which may then be recovered from the slurry.

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BACKGROUND:

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Many industrial or municipal processes involve the dispersion of minerals and/or organic matter in water to assist in the separation and recovery of the mineral or organic components.

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For mineral processing, the mining industry is the predominant user of such processes, wherein mineral ores are ground and slurried in water to allow separation and recovery of desired components. The residual mineral components in the slurry, referred to as gangue or tailings, are then often deposited in pits or ponds, often called tailings ponds, where solids are expected to settle to allow recovery of the supernatant water, and ultimate consolidation of the remaining mineral solids. Coal, copper and gold mining are but a few of the mining processes that employ this technology. An important use, discussed below, is in bitumen processing from oil sands formations.

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The slow rate of mineral solids setting in tailings ponds is often a serious economic and environmental problem in mining operations. If an objective of such processes is to recover water for reuse or disposal, lengthy pond residence times, often measured in years, can cripple process economics. Further, huge volumes of slurry can be environmentally and physically

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dangerous. Occasional dike failures of coal slurry ponds attest to both these dangers.

5 If the ponded slurry is predominantly composed of coarse minerals, the settling rate in tailings in such ponds is not generally an environmental or economic problem. In this instance, solids settle quickly and consolidate to disposable consistencies, and water is easily recovered. However, when the solid components of the ponded slurry are very fine, settling is often hindered and, in some instances, may take years to occur.

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A major undesired component of many mineral slurries is often clay. Clays have a variety of chemical compositions but a key determinant in how a clay behaves in a mineral slurry is whether it is predominantly in a monovalent (usually sodium) form or in a multivalent (usually calcium) form.
15 The effects of the varying chemical compositions of clays are well known to those in the industry. Monovalent clays tend to be water-swelling and dispersive, whereas multivalent clays generally are not.

Water-swelling and dispersive clays cause many of the problems in
20 mineral processing and tailings dewatering. These clays tend to be monovalent sodium clays, such as bentonite, which is largely composed of montmorillonite. These clays can be expressed as $\text{Na} \cdot \text{Al}_2 \cdot \text{SiO}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$.

Further, if the clays are very finely divided, the problem is often
25 magnified. If the clay particles are easily broken down to even finer particles through shearing in processing, problems can be compounded. Layered, platelet, or shale-like forms of clay are particularly sensitive to mechanical breakdown to even finer particles during processing.

30 In mineral processing, additives are often used to facilitate removal of specific components. Frothers used to separate and float ground coal particles are an example of this. In this instance, the desired component to be recovered is an organic material such as coal, but similar processes are used

for mineral recoveries. In almost all mining processes the remaining slurry must be separated to recover water and consolidated solids.

5 Since the late 1960s, a new mining industry has been operating in the northeast of the Canadian province of Alberta. The deposits being mined are referred to as the Athabasca oil sands. These deposits are formed from a heavy hydrocarbon oil (called bitumen), sand, clay, and water. In processing the deposit, the ore is slurried in warm or hot water with the objective of separating the bitumen from the sand and clay, recovering the bitumen by
10 flotation, recovering the water for reuse, and disposing of the dewatered residual mineral solids in site reclamation. Canada's oil sand deposits contain the second largest quantity of oil in the world, second only to Saudi Arabia's. Consequently, separation, water recovery, and solids disposal are carried out on an industrial scale never before seen.

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The first objective in oil sands processing is to maximize bitumen recovery. Slurrying in warm or hot water tends to release bitumen from the minerals in the ore, in a pipeline process called hydrotransport, while the slurry is transported via pipeline to a primary separation unit. Various
20 chemical additives, including caustic soda or sodium citrate, have been used to improve dispersion of the ore's components into the process water and to accelerate separation of the bitumen from the sand and clay for greater bitumen recovery. In the hydrotransport process, sand is relatively easily stripped of bitumen and readily drops out and is removed through the bottom
25 of the primary separation unit; the clays are the principal problem. Clays, associated with divalent or other multivalent cations, particularly calcium and magnesium, contributed by, for example, process waters are recognized to deter efficient separation and flotation of the bitumen. The use of additives such as caustic soda or sodium citrate aid in the dispersion to inhibit clay's
30 deleterious effects. Sodium citrate is a known dispersant and also acts as a water-softening agent, to sequester calcium and magnesium ions.

While improving recovery, these additives often have residual negative effects following bitumen separation by inhibiting subsequent water removal from the clay. A great deal of research has gone into studying the various types of clays found in the oil sands deposits. Different clays affect bitumen separation differently, often in ways not completely understood, and differences in the clays affect the clays' subsequent separation from the process water. Since ore is a natural deposit, the separation process is at the mercy of clay type and content, and the level of divalent ions. Pump and pipeline shear acting on the slurry also break down clay into finer clay particles, which further negatively affects the separation process. Various ore sources are often blended prior to hydrotransport in an attempt to mitigate the effects of clays. Compressed air may be introduced into the hydrotransport pipeline. The air dissolves under pressure and, as pressure is released ahead of the primary separation vessel, bubbles form to help float the bitumen.

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In the separation process, the floated bitumen overflows to further processing. Typically, the sand and any coarse clays settle quickly into the base of a conical primary separation unit. The withdrawal rate of this coarse segment can be controlled. The largest volumetric component, called middlings, is the middle stratum above the coarse layer and below the bitumen float. The middlings consist of a dispersion of the fine clays. The industry considers these fine clays to be any size less than 44 microns in diameter. These clays usually form a very stable dispersion. Any dispersive additives further increase the stability of the clay slurry. If the dispersant, or any other additive, increases middlings viscosity in the primary separation unit, then bitumen flotation and recovery may be hindered.

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In existing processes, the conditions that promote efficient dispersion and bitumen recovery appear to be diametrically opposed to the conditions that subsequently promote downstream fine clay separation, solids consolidation, and water recovery. The longer it takes to recover and reuse the process water, the more heat and evaporative losses occur. The tradeoff

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between efficient bitumen extraction and downstream disposal of mineral solids is an expensive problem for the oil sands industry.

5 In the extraction process, middlings are continuously withdrawn from the center of the primary separation unit. Both the heavy, easily settled sand/coarse clay component, withdrawn from the conical bottom of the primary separation unit, and the middlings component are usually subjected to additional cleaning and mechanical dewatering steps to recover any bitumen that is not floated off in the primary separation unit. The middlings
10 may be hydrocycloned to increase density. The middlings then generally report to a thickener, where high molecular weight sodium/potassium/ammonium-acrylate/acrylamide-based copolymers (called flocculants) are added to coagulate and flocculate the dispersed middling's fine clays. Four to five hours of residence time are generally required in the
15 thickener to produce a thickened underflow (to begin to increase clay solids for use in final solids consolidation) and to produce clarified overflow water for reuse in the process. Thickeners are immense, expensive mechanical separators with massive holding volumes.

20 The final objective of the oil sands process is to produce dense, trafficable solids for site reclamation and to recover water for process use. The two mineral process streams, sand/coarse clay from the primary separation unit, and middlings (often thickened as described above) are either pumped to separate containment areas (called ponds) or are combined and then sent to
25 ponds. Both approaches have created problems, with which the industry is grappling. The combined streams (called combined tailings, or CT) have produced a condition wherein the coarse sand and clays have settled relatively quickly in the ponds, but the fine clays have not. Instead of the desired settling and recovery of supernatant water, the upper layer in these- ponds forms an
30 almost permanent layer of suspended fine clays, referred to as mature fine tails (MFT). The clay content in this relatively fluid, almost permanent layer of MFT generally ranges from 30 wt% to 50 wt% solids. When the middlings are pumped separately to ponds, the same condition is immediately created. The

existence and size of these ponds threaten the very future of the industry. Government has ordered that these ponds of MFT must be reprocessed, water recovered for reuse, and dewatered solids consolidated to restore the mined sites.

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The oil sands industry has made a concerted effort to reprocess the MFT into what are called non-segregating tailings (NST). By this is meant sand and clay tailings of varying particle sizes that, when pumped to ponds, do not segregate by particle size upon settling but rather, settle in a non-segregating manner, more quickly releasing supernatant and/or underflow drainage waters, and ultimately producing a trafficable solid that can be used for mine site restoration. Heat is still lost after the NST slurry is pumped to ponds and the warm water still evaporates. Methods or procedure that can recover more warm water within the operating process, and that could produce easily-dewatered, non-segregating tailings immediately after the separation process, would be of great benefit to the oil sands industry.

Monovalent anionic polymer flocculants have been in use for several years for separating components within an aqueous slurry, recovering specific components within an aqueous slurry, and/or dewatering residual components of an aqueous slurry. Recently introduced calcium diacrylate / acrylamide copolymers have reached new performance levels in these applications. Nevertheless, given the concerns outlined above, further performance improvements are of interest to the oil sands and other industries.

SUMMARY:

We disclose anionic polymeric flocculants that combine monovalent and multivalent acrylate monomers in a single polymer or a mixture of polymers. In some applications, this may allow the ratio of monovalent and multivalent acrylate monomers in the polymer or polymer mixture to be tailored to match

substrate demand, particularly where the substrate in question consists of a mixture of materials.

We further disclose an anionic flocculant comprising a heteropolymer which includes: a monovalent acrylate monomer; a multivalent acrylate monomer; and an acrylamide monomer. This polymer may be a terpolymer of the aforementioned components. Thus, the monomer composition of the polymer may be varied by modifying the ratio of monomers included during catalysis.

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We further disclose an anionic flocculant comprising a mixture of a first copolymer and a second copolymer. The first copolymer includes a monovalent acrylate monomer and an acrylamide monomer. The second copolymer includes a multivalent acrylate monomer and an acrylamide monomer. Thus, the monomer composition of the mixture may be varied by changing the proportion of each copolymer added to the mixture.

Polymeric compounds, terpolymers, and copolymer mixtures as described herein may be used to treat bentonite/montmorillonite clay, which is prevalent in MFTs resulting from Athabasca oil sands processing. The following ratios of monomers may be used in a flocculant composition, wherein the respective compositions may comprise a mixture composed of distinct polymers or a single polymer that combines all three monomers:

25 Table 1. Exemplary Monomer Composition of the Flocculant

	Polymer Mixtures	Terpolymer
Monovalent acrylates	4-90 wt%	4-90 wt%
Multivalent acrylates	5-70 wt %	5-70 wt %
Acrylamide	10-90 wt %	10-90 wt %
Molecular Weight (kDa)	1,000 – 16,000	1,000 – 16,000

The monovalent acrylate monomer may be sodium acrylate, potassium acrylate, ammonium acrylate, or a combination thereof. Likewise, the multivalent acrylate may be calcium diacrylate, magnesium diacrylate, iron diacrylate, iron triacrylate, aluminum diacrylate, or a combination thereof.

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We further disclose a low-molecular weight copolymer (Copolymer L) for use as a pre-treatment prior to the addition of the terpolymer or polymer mixture described above. Copolymer L comprises a polymer of monovalent acrylate monomer and divalent acrylate monomer, at a 50/50 ratio. Copolymer L may have a molecular weight of between 80 to 250 kDa, 90 to 200 kDa, 100 kDa to 150 kDa, or about 100 kDa.

A terpolymer, copolymer mixture, and/or Copolymer L according to the present invention may be a water soluble gel, emulsion, or dry granular solid. Polymers may be manufactured by solution, emulsion, or dispersion polymerization.

We further disclose a method of water recovery or solids reclamation. The steps include: (a) providing an aqueous slurry of suspended particles; and (b) adding to said slurry a heteropolymer or copolymer mixture as described above, to flocculate the slurry. The heteropolymer or copolymer mixture may be added in solution at a dosage of between 100 and 2000 grams of polymer active per ton of solids in the slurry, between 700 and 1200 grams of polymer active per ton, or about 764 grams per ton.

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We further disclose a method in which the slurry in step (a) is first pre-treated with the Copolymer L described above. Copolymer L may be added during pre-treatment at a dosage of between 50 and 1200 grams of polymer active per ton of solids, such as 207 grams per ton.

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The aqueous slurry can be of various types. In some applications the slurry may comprise 30% to 50% solids by weight and/or particle sizes may be less than 50 microns or less than 44 microns. The slurry may be a mineral

slurry, such as a mineral slurry containing bitumen. The particles in the slurry may be sand or clay particles, which may include water-swelling sodium clays, non-water swelling calcium clays, bentonite/montmorillonite clays, and/or $\text{Na} \cdot \text{Al}_2 \cdot \text{SiO}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. In some cases, the slurry is derived from oil sands processing, such as MFT.

We further disclose the use of polymeric flocculants, or mixtures of polymeric flocculants, as described above for water recovery or solids reclamation from an aqueous slurry. We further disclose the use of the Copolymer L described above as a pre-treatment during water recovery or solids reclamation from an aqueous slurry.

DRAWINGS:

FIG 1 compares the amount of polymer required to treat the MFT sample (in grams per ton of solids) for Copolymer X alone, Copolymer Y alone, Mixture 1, and Terpolymer 1.

FIG 2 compares the drainage performance for MFT treated with Copolymer X alone, Copolymer Y alone, Mixture 1, and Terpolymer 1.

FIG 3 compares the dewatering performance (CST) for MFT treated with Copolymer X alone, Copolymer Y alone, Mixture 1, and Terpolymer 1.

FIG 4 compares the dewatering performance (CST) of Terpolymer 1 with and without pre-treatment with the Copolymer L.

DETAILED DESCRIPTION:**Definitions**

5 The terms identified below shall be defined in the specification and claims in accordance with the following definitions, unless otherwise specified or the context clearly requires otherwise.

10 Low molecular weight polymer: a polymer which is in the range of about 80-250 kDa.

High molecular weight polymer: a polymer which has a molecular weight which is above about 1,000 kDa.

15 Fines: Fine particle mine tailings waste (usually in an aqueous slurry) of less than 44 microns size.

Mature fine tailings (MFT): Poned fines, usually in concentrations from 30-50%.

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Monomer: A single reactable species.

Copolymer: A polymer from two monomers.

25 Terpolymer: A polymer comprising three or more monomers.

Polymer mixture: A physical blend of two or more polymers, either in solid form or in aqueous solution

30 Pretreatment: A treatment that is performed prior to flocculating the solids within a slurry to enhance to the performance of the flocculating agent.

The invention will now be described in further detail with reference to certain preferred embodiments set out in Examples 1 to 6 below. These embodiments are exemplary in nature and are not intended to limit the scope of the invention.

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EXAMPLE 1: Monovalent / Multivalent Acrylate Copolymers

Copolymers "X" and "Y" were obtained from commercial sources. In the present examples, copolymer "X" is A-3338™ (SNF Holding Co.) and copolymer "Y" is 1047™ (BASF-SE).

Copolymer "L" was prepared using 28 wt% stock solutions of each monomer. Monomer solutions were deoxygenated before catalysis. Catalysts were added separately to each monomer solution and the resulting solutions were combined instantly. Ammonium persulfate (0.06 wt%) was added to the sodium acrylate and calcium diacrylate solutions. Sodium bisulfite (0.06 wt%) and 2,2'-Azobis(2-amidinopropane) dihydrochloride (V50™ by Wako Chemical) (0.01 wt%) were added to the acrylamide monomer solution. The initiation temperature was 15°C. The final molecular weight was 100 kDa. All catalyst wt.%'s are based on total weight of monomer in the composition.

The molecular weight and monomer compositions of copolymers X, Y, and L are provided in Table 2 below.

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Table 2. Monomer Composition of Copolymers X, Y, and L

Monomer	Copolymer X (A-3338™ SNF Holding Co.)	Copolymer Y (1047™ BASF-SE)	Copolymer L
Sodium acrylate (wt%)	25%	0%	50%
Calcium diacrylate (wt%)	0%	40%	50%
Acrylamide (wt%)	75%	60%	0%
Molecular Weight (wt%)	12,500	10,000	100

EXAMPLE 2: Preparation of Copolymer Mixtures 1-5

- 5 Monovalent / multivalent acrylate mixtures were prepared for use with MFT containing bentonite/montmorillonite clay. Copolymers X and Y were combined to provide Mixtures 1-5, having the final monomer proportions shown in Table 3 below.

Table 3. Monomer Composition of Copolymer Mixtures 1-5

Monomer	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5
Copolymer X:Y Ratio (wt%)	1:1	2:1	5:1	1:2	1:5
Sodium Acrylate (wt%)	12%	17%	21%	8%	4%
Calcium Di Acrylate (wt%)	20%	13%	7%	27%	33%
Acrylamide (wt%)	68%	70%	72%	65%	63%
Molecular Weight (kDa)	11,500	11,600	12,100	10,800	10,400

**EXAMPLE 3: Preparation of Monovalent / Multivalent
Terpolymers 1-5**

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Terpolymers 1-5 were synthesized using the monomer proportions shown in Table 4 below.

Table 4. Monomer Composition of Terpolymers 1-5

Monomer	Ter- polymer 1	Ter- polymer 2	Ter- polymer 3	Ter- polymer 4	Ter- polymer 5
Sodium Acrylate wt%	12%	17%	21%	8%	4%
Calcium Di Acrylate wt%	20%	13%	7%	27%	33%
Acrylamide wt%	68%	70%	72%	65%	63%

As seen in Tables 3 and 4 above, the monomer composition of Mixtures 1-5 in Example 2 and Terpolymers 1-5 in this Example 3 were
5 substantially the same.

Mixtures 1-5 (table 3) provided monovalent and multivalent acrylate monomers using a mixture of two molecules. Terpolymers 1-5 (table 4) provided such monomers in a single polymeric compound
10 comprising the three monomers listed above within a single molecule.

Terpolymers 1-5 were prepared using the methods described for Copolymer L above in Example 1, with some amendments. The catalysis and reaction conditions for Terpolymers 1-5 are summarized
15 in Table 5 below.

Table 5. Catalysis of Terpolymers 1-5

Catalyst	Ter-polymer 1	Ter-polymer 2	Ter-polymer 3	Ter-polymer 4	Ter-polymer 5
Ammonium PerSulfate (wt%)	0.003571 %	0.003652 %	0.003652 %	0.00357 %	0.00357 %
Sodium BiSulfite (wt%)	0.001786 %	0.001799 %	0.001799 %	0.001786 %	0.0025 %
V50™ (wt%)	0.002143 %	0.002132 %	0.002052 %	0.002243 %	0.0024 %
Initiation Temperature	4 °C	4 °C	4 °C	4 °C	4 °C
Molecular Weight (kDa)	10,000	10,000	10,500	10,000	9,500

All catalyst wt.%'s are based on total weight of monomer in the composition.

5 **EXAMPLE 4: Performance of Copolymer Mixtures 1-5 and Terpolymers 1-5**

The Copolymer Mixtures 1-5 and Terpolymers 1-5 of Examples 2 and 3 were subjected to various performance tests using MFT containing
10 33.8% solids and having a methylene blue index (MBI) of 11.

Tests were performed at room temperature. MFT samples were mixed with Copolymers X, Y, Mixtures 1-5, and Terpolymers 1-5 after which performance tests were conducted.

Polymer solutions were reconstituted at 0.4% active polymer in process water. Prior to each performance test, a 40 ml sample of MFT was placed within a clear 300 ml tall plastic cup and then mixed by hand with an initial dose of the respective polymer mixture or terpolymers for about 10-20
5 seconds. The mixture was hand-stirred with a stainless steel spatula.

The initial dose of polymer was about 2 ml, which was about half of the expected total quantity. At this level of polymeric additive, the MFT mixture adhered to the spatula. Additional polymeric flocculant was added in 0.5 ml
10 doses and stirred until the spatula could be withdrawn without MFT adhering to the surface of the spatula.

In tests where a well-defined flocculate was formed, the MFT/polymer mixture solidified into a well-defined water breakout from the flocculate when
15 the cup was tipped wherein free-flowing water would flow out of solidified flocculate.

Free Drainage Test:

20 Free drainage tests were conducted in accordance with the following procedure:

1. 0.4 wt.% aqueous polymer solution was added to a 40 ml sample of homogenous MFT.
25
2. The polymer solution was added to the MFT in aliquots, with mixing, until the MFT formed a distinct flocculate and no longer adhered to the stainless steel spatula.
- 30 3. The treated 40ml MFT sample was dropped quickly onto a 4.4 cm diameter screen (having 0.18 cm openings).

4. Filtrate was collected over a period of 1 minute. This volume is reported as "Free Drainage".

Higher values indicate greater dewatering, and hence better performance.

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Capillary Suction Timer (CST) Test:

The Capillary suction timer (CST) test measures a combination of drainage and filtrate clarity. The test measures the time (in seconds) for filtrate to pass through a filter pad between two electrodes. The automatic timer starts when the filtrate touches the first electrode and the timer stops when the filtrate reaches the second electrode.

Filtrate quality is a key factor in rapid movement of the fluid front. A shorter time indicates better fine particulate retention within the flocculate structure (i.e. better flocculant performance).

CST tests were conducted in accordance with standard procedures using a FANN Model 440 CST apparatus (Fann Instrument Company, Houston, Texas). CST tests were conducted as follows:

1. 0.4 wt.% aqueous polymer solution was added to a 40 ml sample of homogenous MFT.
- 25 2. The polymer solution was added to the MFT in aliquots, with mixing, until the MFT formed a distinct flocculate and no longer adhered to the stainless steel spatula.
3. The treated 40 ml MFT sample was dropped immediately into the top of the transition tube of the CST apparatus and measurements were taken in accordance with standard techniques.

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Results:

The results of drainage and CST tests on MFT treated with Copolymers X-Y only, Mixtures 1-5, and Terpolymers 1-5 are provided in Table 6 below, along with the amount added (i.e. dosage) to the MFT to produce a flocculate, in grams of polymer per metric ton of solids.

Table 6. Performance of Copolymer Mixtures and Terpolymers

	Dosage (g/ton)	Free Drainage (mls)	CST (s)
Copolymer X	1035	8	163
Copolymer Y	962	11	129
Mixture 1	814	14	115
Terpolymer 1	764	16	75
Mixture 2	814	14	132
Terpolymer 2	764	16	79
Mixture 3	814	14	186
Terpolymer 3	764	19	119
Mixture 4	764	17	179
Terpolymer 4	764	17	134
Mixture 5	764	16	245
Terpolymer 5	764	17	189

As seen in Table 6, mixtures of monovalent and multivalent acrylamide co-polymers outperformed the individual components of the mixtures (i.e. Copolymers X and Y). Terpolymers having the same monomer ratios as the mixtures further improved flocculation and dewatering performance.

Both the mixtures and the terpolymers formed flocculates at lower dosages while also providing superior performance over the individual anionic copolymers X or Y alone. More specifically, mixtures 1-5 performed as well or better than either Copolymer X or Y alone, using less polymer.
5 Terpolymers 1-5 also outperformed Copolymers X or Y alone, using less polymer. Terpolymers also outperformed mixtures 1-5.

FIG 1 compares the amount of polymer required to treat the MFT sample for Copolymer X alone, Copolymer Y alone, Mixture 1, and
10 Terpolymer 1. As seen therein, the amount of polymer used progressively decreased.

FIG 2 compares the drainage from MFT treated with Copolymer X alone, Copolymer Y alone, Mixture 1, and Terpolymer 1. As seen therein,
15 the drainage progressively increased, with Terpolymer 1 providing the best performance despite using the least amount of polymer.

FIG 3 compares the CST values for MFT treated with Copolymer X alone, Copolymer Y alone, Mixture 1, and Terpolymer 1. As seen therein,
20 the CST values progressively decreased, with Terpolymer 1 providing the best performance despite using the least amount of polymer.

EXAMPLE 5: Performance of Terpolymers A-E

25 Terpolymers A-E were produced using the methods described in Example 3 above, with differing amounts of sodium acrylate and calcium diacrylate monomer solution, so as to achieve the monomer compositions shown in Table 7 below.

30 The resulting Terpolymers A-E contained higher levels of sodium acrylate and calcium acrylate monomers than can be produced from mixtures of copolymer X and copolymer Y.

Table 7. Monomer Composition of Terpolymers A-E

Monomer	Ter- polymer A	Ter- polymer B	Ter- polymer C	Ter- polymer D	Ter- polymer E
Sodium Acrylate wt%	55%	25%	40%	15%	35%
Calcium Di Acrylate wt%	15%	35%	25%	50%	15%
Acrylamide wt%	30%	40%	35%	35%	50%

Terpolymers A-E were subjected to the same tests described in
5 Example 4 above, using the same testing conditions. The results of such
testing are provided in Table 8 below.

Table 8. Performance of Copolymer Mixtures and Terpolymers

	Dosage (g/ton)	Free Drainage (mls)	CST (s)
Copolymer X	1035	8	163
Copolymer Y	962	11	129
Terpolymer A	764	17	92
Terpolymer B	764	18	79
Terpolymer C	764	15	121
Terpolymer D	764	16	115
Terpolymer E	764	18	84

EXAMPLE 6: Pretreatment with Low-Molecular Weight Copolymer L

Additional testing was performed by subjecting an MFT slurry to a pre-treatment, by contacting the slurry with Copolymer L of Example 1 prior to contacting the slurry with the high molecular weight anionic flocculants described herein.

Room temperature MFT samples were pre-treated with a 0.4% (w/v) solution of Copolymer L at 207 grams of polymer per ton of solids. Samples were hand stirred for 20-30 seconds during pre-treatment.

After pre-treatment, samples were treated with Terpolymer 1 and tested for performance, using the methods described in Example 4. The dosage, drainage, and CST values for such testing is provided in Table 9 below, which compares a control sample (Copolymer L only) versus terpolymer treated samples with and without pre-treatment.

Table 9. Performance of Terpolymer 1 With and Without Pre-Treatment

	Dosage (g/ton)	Free Drainage (mls)	CST (s)
Copolymer L Only	1108	0	∞
Terpolymer 1 (untreated)	764	17	71
Terpolymer 1 after pre-treatment with 207 g/ton Copolymer L	557	17	59

As seen in Table 9, pre-treatment with the Copolymer L improved dewatering (CST) performance of Terpolymer 1. Pre-treatment with

Copolymer L also reduced the amount of Terpolymer 1 required to form a stable flocculate, which was of higher quality.

5 These improvements could not be attributed to the Copolymer L, on its own, which provided no useful characteristics when used without the terpolymer. Indeed, dosages of Copolymer L up to 1108 grams of polymer per ton of solids did not generate a flocculate. Instead, a synergistic effect was observed between Copolymer L and the terpolymer flocculants.

10 FIG 4 compares the dewatering performance (CST) of Terpolymer 1 with and without pre-treatment with Copolymer L. As seen therein, pre-treatment improved dewatering performance.

15 The foregoing are examples only. The scope of the claims should not be limited by the preferred embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole. The claims are not to be limited to the preferred or exemplified embodiments of the invention as described herein, which may be combined or modified without departing from the scope of the present invention.

CLAIMS:

1. A polymeric anionic composition comprising at least one polymer, wherein the composition comprises:
 - a) a monovalent acrylate monomer;
 - b) a multivalent acrylate monomer; and
 - c) an acrylamide monomer.
2. The composition of claim 1 wherein the at least one polymer comprises a terpolymer comprising each of the monovalent acrylate monomer, the multivalent acrylate monomer and the acrylamide monomer.
3. The composition of claim 1 wherein the at least one polymer comprises a mixture of copolymers, wherein the copolymers comprise:
 - a first copolymer comprising the monovalent acrylate monomer and the acrylamide monomer; and
 - a second copolymer comprising the multivalent acrylate monomer and the acrylamide monomer.
4. The composition of any one of claims 1 to 3, wherein the monovalent acrylate monomer is sodium acrylate, potassium acrylate, ammonium acrylate, or a combination thereof.
5. The composition of claim 4, wherein the monovalent acrylate monomer is sodium acrylate.
6. The composition of any one of claims 1 to 5, wherein the multivalent acrylate monomer is calcium diacrylate, magnesium diacrylate, iron diacrylate, iron triacrylate, aluminum diacrylate, or a combination thereof.
7. The composition of claim 6, wherein the multivalent acrylate monomer is calcium diacrylate.

8. The composition of any one of claims 1 to 7, wherein the monovalent acrylate monomer comprises between 4 to 90% (w/w) of the composition.
9. The composition of claim 8, wherein the monovalent acrylate monomer comprises between 4 to 21% (w/w) of the composition.
10. The composition of claim 9, wherein the monovalent acrylate monomer comprises between 15 to 55% (w/w) of the composition.
11. The composition of any one of claims 1 to 10, wherein the multivalent acrylate monomer comprises between 5 to 70% (w/w) of the composition.
12. The composition of claim 11, wherein the multivalent acrylate monomer comprises between 7 to 33% (w/w) of the composition.
13. The composition of claim 11, wherein the multivalent acrylate monomer comprises between 15 to 50% (w/w) of the composition.
14. The composition of any one of claims 1 to 13, wherein the acrylamide monomer comprises between 10 to 90% (w/w) of the composition.
15. The composition of claim 14, wherein the acrylamide monomer comprises between 63 to 72% (w/w) of the composition.
16. The composition of claim 15, wherein the acrylamide comprises between 30 to 50% (w/w) of the composition.
17. The composition of any one of claims 1 to 7, wherein the total monomer ratio of the composition is about:
12% (w/w) monovalent acrylate monomer;

20% (w/w) multivalent acrylate monomer; and
68% (w/w) acrylamide monomer.

18. The composition of any one of claims 1 to 7, wherein the total monomer ratio of the composition is about:
 - 17% (w/w) monovalent acrylate monomer;
 - 13% (w/w) multivalent acrylate monomer; and
 - 70% (w/w) acrylamide monomer.
19. The composition of any one of claims 1 to 7, wherein the total monomer ratio of the composition is about:
 - 21% (w/w) monovalent acrylate monomer;
 - 7% (w/w) multivalent acrylate monomer; and
 - 72% (w/w) acrylamide monomer.
20. The composition of any one of claims 1 to 7, wherein the total monomer ratio of the composition is about:
 - 8% (w/w) monovalent acrylate monomer;
 - 27% (w/w) multivalent acrylate; and
 - 65% (w/w) acrylamide monomer.
21. The composition of any one of claims 1 to 7, wherein the total monomer ratio of the composition is about:
 - 4% (w/w) monovalent acrylate;
 - 33% (w/w) multivalent acrylate; and
 - 63% (w/w) acrylamide monomer.
22. The composition of any one of claims 1 to 7, wherein the total monomer ratio of the composition is about:
 - 55% (w/w) monovalent acrylate;
 - 15% (w/w) multivalent acrylate; and
 - 30% (w/w) acrylamide monomer.

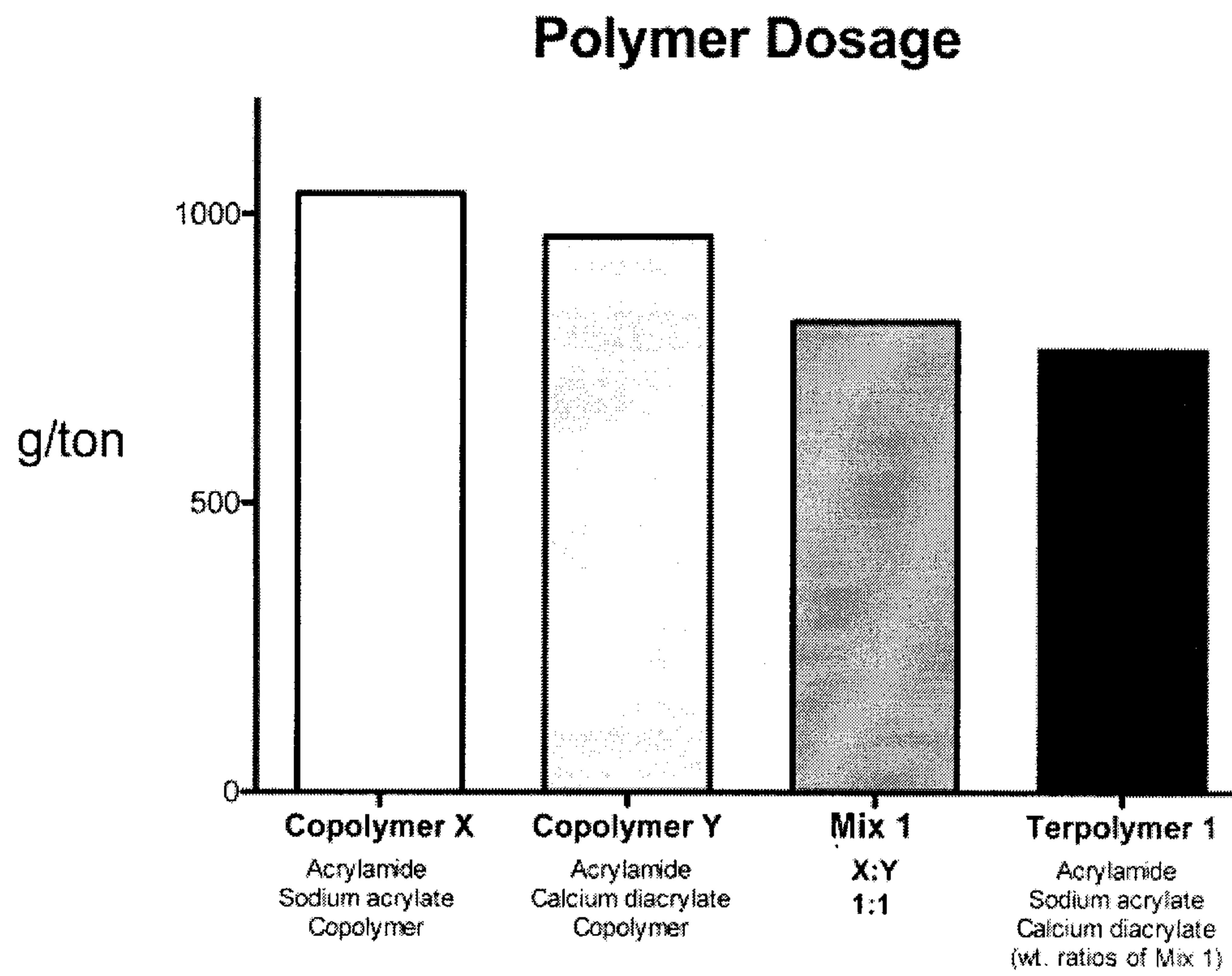
23. The composition of any one of claims 1 to 7, wherein the total monomer ratio of the composition is about:
- 25% (w/w) monovalent acrylate;
 - 35% (w/w) multivalent acrylate; and
 - 40% (w/w) acrylamide monomer.
24. The composition of any one of claims 1 to 7, wherein the total monomer ratio of the composition is about:
- 40% (w/w) monovalent acrylate;
 - 25% (w/w) multivalent acrylate; and
 - 35% (w/w) acrylamide monomer.
25. The composition of any one of claims 1 to 7, wherein the total monomer ratio of the composition is about:
- 15% (w/w) monovalent acrylate;
 - 50% (w/w) multivalent acrylate; and
 - 35% (w/w) acrylamide monomer.
26. The composition of any one of claims 1 to 7, wherein the total monomer ratio of the composition is about:
- 35% (w/w) monovalent acrylate;
 - 15% (w/w) multivalent acrylate; and
 - 50% (w/w) acrylamide monomer.
27. A copolymer comprising a monovalent acrylate monomer and a divalent acrylate monomer, the copolymer having a molecular weight between 80 to 250 kDa.
28. The copolymer of claim 27, having a molecular weight between 90 and 200 kDa, 100 and 150kDa, or about 100 kDa.
29. The copolymer of claim 27 or claim 28, wherein the monovalent acrylate monomer is sodium acrylate.

30. The copolymer of any one of claims 27 to 29, wherein the multivalent acrylate monomer is calcium diacrylate.
31. The copolymer of any one of claims 27 to 30, wherein the monomer ratio of the copolymer is about:
 - 50% (w/w) monovalent acrylate monomer; and
 - 50% (w/w) multivalent acrylate monomer.
32. A method of treating a slurry comprising solids suspended in an aqueous liquid, the method comprising the steps of:
 - contacting the slurry with the composition according to any one of claims 1 to 26 for a sufficient duration to allow clarification of liquid and/or flocculation of solids from the slurry; and
 - recovering the clarified liquid and/or flocculated solids.
33. The method of claim 32, wherein the composition is added at a dosage of between 100 and 2000 g per ton of solids in the slurry.
34. The method of claim 33, wherein the composition is added at a dosage of between 700 and 1200 g per ton.
35. The method of claim 34, wherein the the dosage is about 764 g per ton.
36. The method of any one of claims 32 to 35, comprising the further step of adding the copolymer of any one of claims 27 to 31 to the slurry prior to adding the composition.
37. The method of claim 36, wherein the copolymer of any one of claims 27 to 31 is added at a dosage of between 50 and 1200 g per ton of solids.
38. The method of claim 37, wherein the copolymer of any one of claims 27 to 31 is added at a dosage of about 207 g per ton of solids.

39. The method of any one of claims 32 to 38, wherein the slurry is a mineral slurry.
40. The method of claim 39 wherein the mineral slurry comprises $\text{Na} \cdot \text{Al}_2\text{SiO}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$.
41. The method of any one of claims 32 to 40, wherein the solids comprise sand or clay particles.
42. The method of claim 41, wherein the particles comprise water-swelling sodium clay.
43. The method of claim 41, wherein the particles comprise non-water-swelling calcium clay.
44. The method of claim 41, wherein the particles comprise bentonite/montmorillonite clay.
45. The method of claim 41, wherein the particles are less than 50 microns in size.
46. The method of any one of claims 32 to 45, wherein the slurry is 40-50 % (w/w) solids.
47. The method of any one of claims 32 to 46, wherein the slurry is mature fine tails (MFT).
48. The method of any one of claims 32 to 47, wherein the slurry is derived from an oil sands processing operation.
49. The use of a composition according to any one of claims 1 to 26 for treating an aqueous slurry.

50. The use of claim 49 wherein the slurry is derived from an oil sands processing operation.
51. The use of the copolymer of any one of claims 27 to 31 as a pre-treatment during water recovery or solids reclamation from an aqueous slurry.

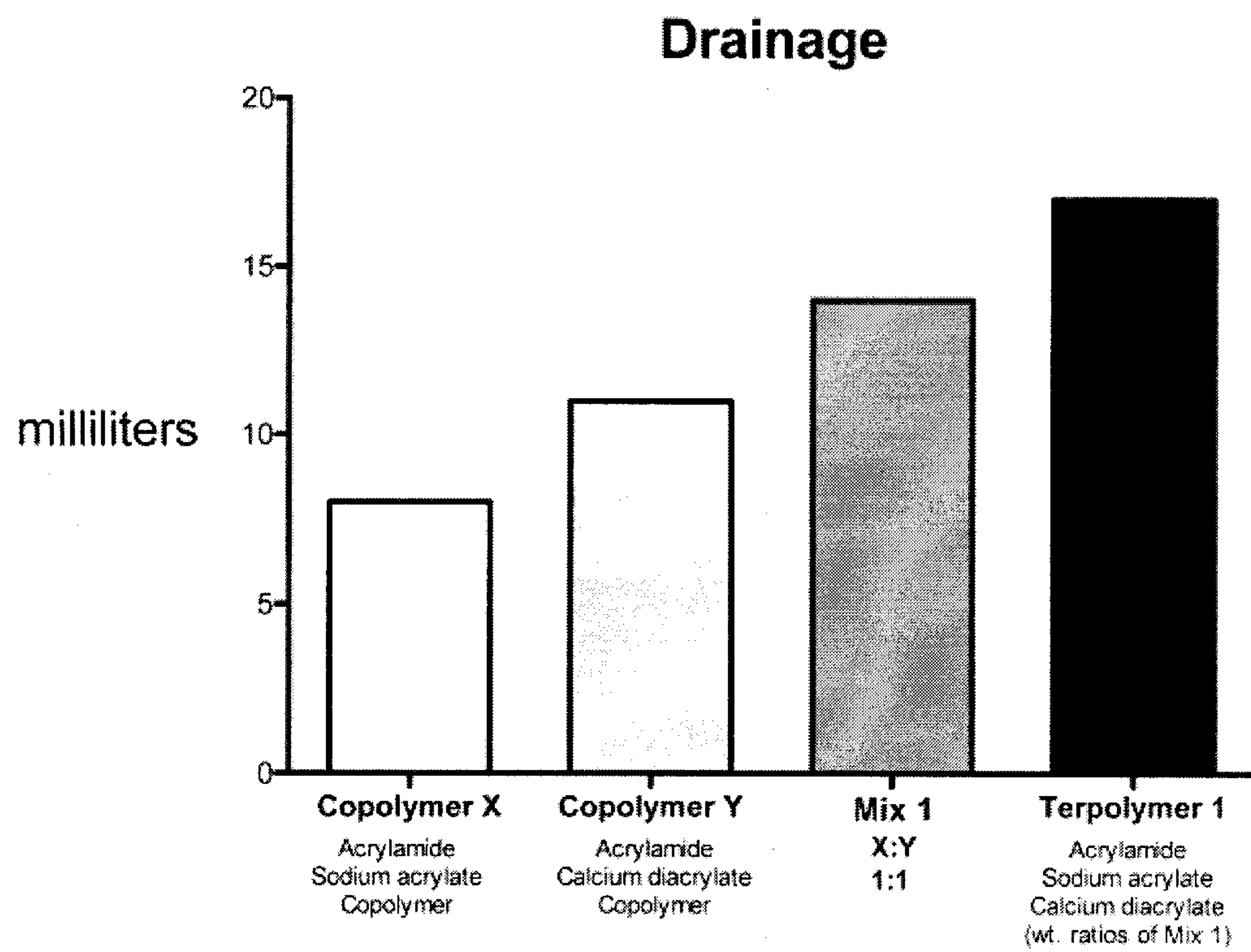
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FIG 1

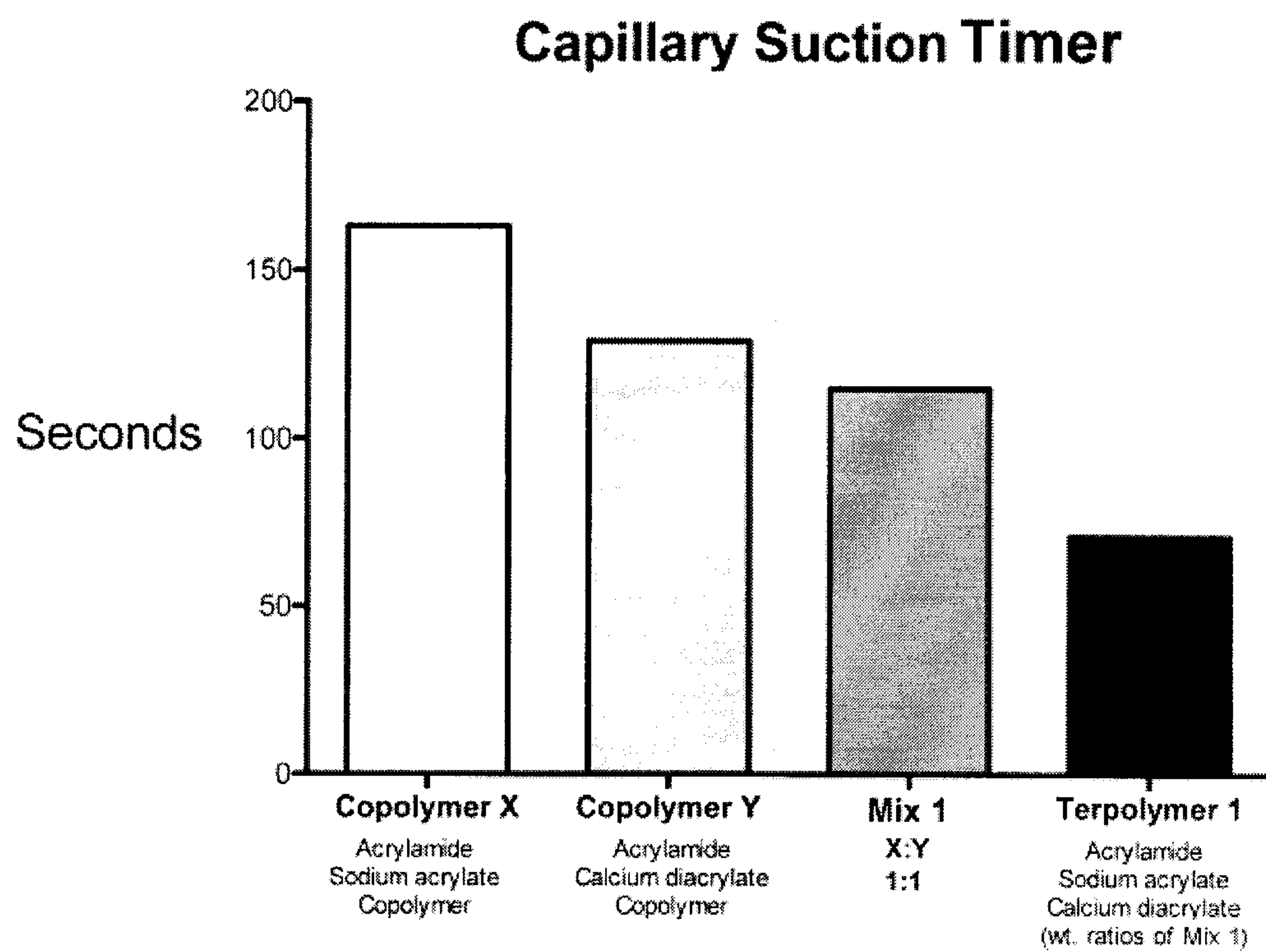
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FIG 2

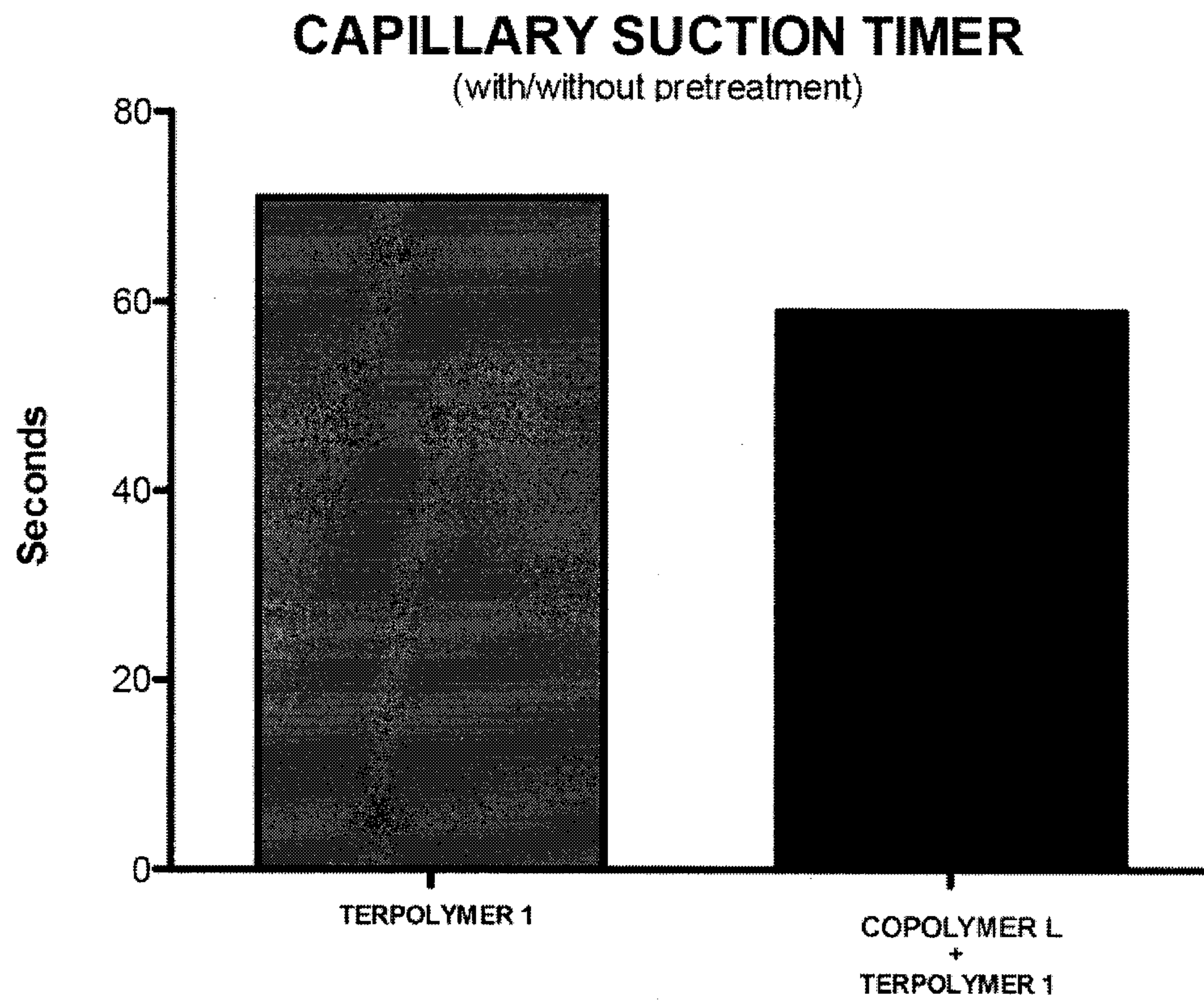
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FIG 3

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FIG 4