



(22) Date de dépôt/Filing Date: 2010/05/13

(41) Mise à la disp. pub./Open to Public Insp.: 2010/11/19

(45) Date de délivrance/Issue Date: 2013/03/26

(30) Priorité/Priority: 2009/05/19 (US61/179,652)

(51) Cl.Int./Int.Cl. *C09K 8/035* (2006.01),
C09K 8/12 (2006.01), *C09K 8/24* (2006.01),
C09K 8/524 (2006.01)

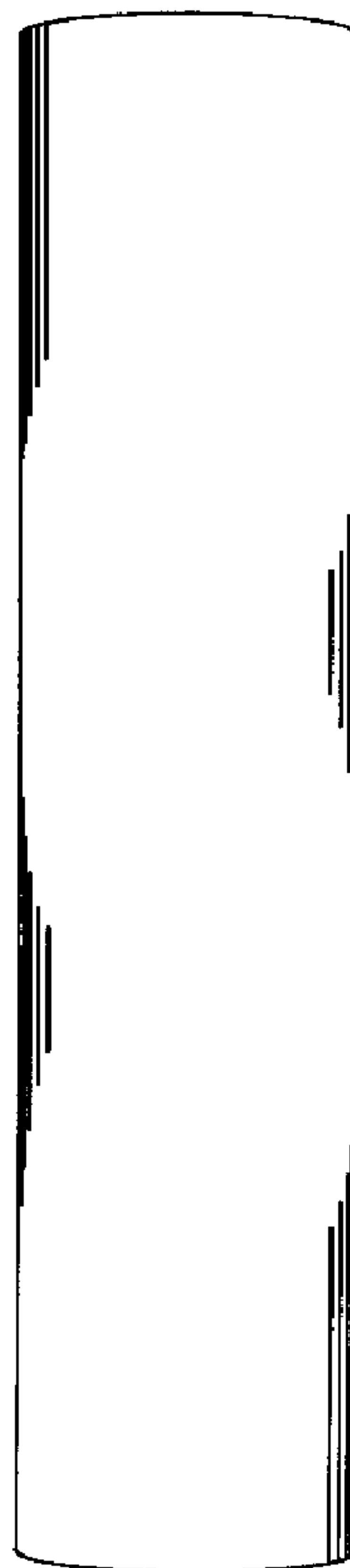
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(54) Titre : ADDITIF POUR EMPECHER L'ACCRETION DU BITUME

(54) Title: BITUMEN ANTI-ACCRETION ADDITIVE



BMP-1 + Xanthan at 400 psi

(57) Abrégé/Abstract:

Anti-accretion additives utilize silicone chemistry to prevent bituminous and heavy oil materials from sticking to metals surfaces such as drill bits, drillstring, casing and the like. Organopolysiloxanes and/or copolymers thereof are added directly to an aqueous

(57) **Abrégé(suite)/Abstract(continued):**

drilling fluid or are first diluted in a solvent for adding to the drilling fluid. Further, an alkyl polyalkylene oxide may also be added. If a silicone oil is used as the solvent, the anti-accretion additive has the increased functionality of minimizing the amount of bituminous or heavy oil material which is retained in the drilling fluid when returned to surface and permits removal of the bituminous or heavy oil materials with the solids using conventional solids control equipment.

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ABSTRACT

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Anti-accretion additives utilize silicone chemistry to prevent bituminous and heavy oil materials from sticking to metals surfaces such as drill bits, drillstring, casing and the like. Organopolysiloxanes and/or copolymers thereof are added directly to an aqueous drilling fluid or are first diluted in a solvent for adding to the drilling fluid. Further, an alkyl polyalkylene oxide may also be added. If a silicone oil is used as the solvent, the anti-accretion additive has the increased functionality of minimizing the amount of bituminous or heavy oil material which is retained in the drilling fluid when returned to surface and permits removal of the bituminous or heavy oil materials with the solids using conventional solids control equipment.

1 **“BITUMEN ANTI-ACCRETION ADDITIVE”**

2

3 **FIELD OF THE INVENTION**

4 Embodiments of the invention relate to anti-accretion additives for
5 addition to water-based drilling fluids to inhibit accretion of certain types of
6 hydrocarbons on the drilling apparatus and more particularly to inhibit accretion of
7 bitumen or heavy oil on drilling apparatus when drilling horizontal wellbores for
8 steam assisted gravity drainage (SAGD) operations.

9

10 **BACKGROUND OF THE INVENTION**

11 There are numerous deposits of heavy oil and bitumen across the
12 globe. Canada and Venezuela (Speight, 1990), in particular, have been estimated
13 to account for greater than 3 trillion barrels of oil with the major reserves being split
14 therebetween. The Canadian oil sand reserves play a significant role in the supply
15 of oil for both Canada and the US today, and will for many years to come.

16 Drilling efficiency, using water-based drilling fluids or muds, is
17 influenced to a large extent by the formations that are being drilled. Certain
18 formations like the McMurray formation found in Alberta, Canada and the Orinoco
19 Basin found in Venezuela are primarily made up of bitumen which can have a
20 significant effect on the drilling efficiency due to the naturally sticky nature of the
21 bitumen.

22 Bitumen is known to be a sticky, tar-like form of petroleum which can
23 be so thick and heavy that it must be heated or diluted to encourage it to flow. At

1 present there are two main methods that are used to recover bitumen from the oil
2 sands in Alberta, Canada. The two methods are truck and shovel surface mining for
3 subsequent extraction and steam assisted gravity drainage (SAGD). SAGD is used
4 when the depth of the bitumen formation, such as in the Fort McMurray formation in
5 Canada, is too deep to access and retrieve via the truck and shovel method. Two
6 horizontal wells are drilled, one on top of the other with approximately 5 meters
7 spacing therebetween. The shallower horizontal well is the injector well and is used
8 to pump steam into the formation in order to treat and soften the bitumen and allow
9 it to flow. The deeper horizontal well is the production well which collects the
10 heated bitumen for pumping to surface. Typically SAGD wells are not deep wells
11 and therefore water-based drilling muds do not require large volumes of weighting
12 agents, such as calcium chloride, to be added during drilling.

13 During drilling, the bitumen may stick to the drill bit, bottom-hole
14 assembly (BHA), drill-pipe and generally any of the drilling apparatus that has
15 contact with the drilling fluid, which can lead to significant delay to the drilling
16 operation. This delay may be due to trouble sliding the drilling apparatus and
17 drillstring when orientating the drill string for drilling horizontal sections of SAGD
18 wellbores as a result of the accretion of bitumen thereon, significantly affecting the
19 rate of penetration (ROP). Delays may also be attributed to time required to clean
20 the drill-pipe when tripping out of the hole. Further, delays are attributed to the need
21 to slow the mud pumps while shaker screens, coated with bitumen, are changed
22 and further to a slow down of the ROP with the slower mud pump speed.

1 SAGD drilling operations were initially plagued with severe issues due
2 to the sticky nature of bitumen. Drilling fluids used conventionally at the time
3 contained no additives to overcome the problems of drilling in bitumen and, as a
4 result, the bitumen stuck to everything including the drill-string, casing and surface
5 equipment which resulted in rig down-time and significant expenditure by the
6 operator.

7 As a result of the earlier experiences with drilling in bitumen-
8 containing formations, it became known to use additives within the fluid systems to
9 attempt to inhibit bitumen accretion and, as a result, improve ROP. In the last ten
10 years there have been a number of patents filed for drilling fluid systems or
11 additives to overcome the problems associated with drilling SAGD wells.

12 The prior art anti-accretion systems or additives used to prevent
13 bitumen from sticking are typically classed as either solvent and/or surfactant
14 chemistry or encapsulator-type chemistry.

15 The first generation of solvent/surfactant systems worked by
16 separating the bitumen from the sand and dissolving the bitumen so that it flowed
17 easily and did not stick. The solvent and/or surfactant systems used either a
18 solvent like D-limonene, as described in Canadian Patent 2,454,312 to McKenzie et
19 al., or a hydrocracked base oil, as described in Canadian Patent 2,481,543 to
20 Baltoiu et al, to solvate the bitumen. It was found however that by solvating the
21 bitumen, problems with odor and tank cleaning arose due to the fact that the
22 solvated bitumen floated on top of the returned drilling fluid in the mud pits.

1 A next generation of systems/additives utilized a surfactant, such as
2 taught in Canadian Patent 2,451,585 to Wu et al., to emulsify the free bitumen into
3 the returned drilling fluid therefore preventing it from separating and causing
4 problems with odor and cleaning.

5 In the solvent and/or surfactant systems described herein, the major
6 drawback is that the drilling fluids increasingly retain bitumen therein as the fluids
7 are used, limiting the number of wells that can be drilled before the drilling fluids
8 need to be stripped of the built-up bitumen. Further, each of the prior art solvent
9 and/or surfactant systems generate at least two waste streams: partially oil-coated
10 sand and solvated or emulsified bitumen.

11 The encapsulator-type chemistry system as described in Canadian
12 Patent 2,508,339 to Ewanek et al., utilizes a cationic polyacrylamide and works by
13 charge attraction to the anionic sites on the bitumen molecules. The cationic
14 polyacrylamide water-wets the bitumen with the polymer coating through ionic
15 attraction and keeps the bitumen and sand intact so that there is no dispersion.
16 Only one waste stream is produced and the returned drilling fluid can be reused
17 indefinitely as there is substantially no bitumen build-up in the system. The major
18 drawback to the use of cationic polyacrylamides is that the cationic polyacrylamides
19 make the drilling fluid extremely susceptible to flocculation of anionic polymers used
20 for viscosity control in the drilling fluids. The addition of relatively small amounts of
21 a cationic polyacrylamide reduce the effectiveness of Xanthan gum, a conventional
22 anionic viscosifier, and thus higher concentrations of the Xanthan gum are required.
23 If too high a concentration of cationic polyacrylamide is added, the drilling fluid

1 system will flocculate causing the anionic polymers and solids to precipitate from
2 the water phase which results in plugging or screen-out of the shale shakers. When
3 the shale shakers screen-out, fluid cascades over the shale shaker rather than
4 passing therethrough. The precipitation of polymers from the drilling fluid is
5 extremely costly to the operator as it results in a need to stop the drilling process
6 while a new fluid system is mixed. Additionally, cationic polyacrylamides are
7 available as solids and must be hydrated prior to use.

8 Further, cationic polyacrylamides have a propensity to oil-wet
9 sandstone which can cause formation damage.

10 Ideally, what is required is a drilling fluid or additive for drilling fluid
11 which prevents bitumen from sticking to metal surfaces, which would solve many of
12 the known problems related to the drilling of SAGD wells. Preferably, the drilling
13 fluid would be easily mixed without detrimental effects or only minimal detrimental
14 effects to the properties of the drilling fluid. Further, there is great interest in the
15 industry to provide a fluid that not only prevents sticking, but which would also allow
16 bitumen to be removed from returned drilling fluid, preferably using conventional
17 solids control equipment.

18

19

1 BRIEF DESCRIPTION OF THE DRAWINGS

2 Figure 1 is a side view of a drill bit which is affected by accretion,
3 cutting elements of the drill bit being substantially coated with bituminous material;

4 Figure 2 is a perspective view of a drill bit affected by accretion,
5 cutting elements of the drill bit being substantially coated with bituminous material;

6 Figure 3 is a side view of a metal surface evidencing some accretion
7 thereon using a drilling fluid using Xanthan as a viscosifier at ambient pressure and
8 without the addition of an anti-accretion additive according to Example 1 described
9 herein;

10 Figure 4 illustrates the metal surface being substantially coated with
11 accretion thereon using the drilling fluid as described for Fig. 3 at a pressure of 400
12 psi and according to Example 1 described herein;

13 Figure 5 illustrates significant inhibition of accretion with the addition of
14 an anti-accretion additive according to an embodiment of the invention, according to
15 Example 1 described herein, the metal surface being substantially free of any
16 accretion thereon; and

17 Figure 6 represents a visual comparison of a test simulating a
18 returned drilling fluid containing an anti-accretion additive according to an
19 embodiment of the invention diluted in a silicone solvent, compared to a returned
20 drilling mud having a conventional solvent surfactant and according to Example 7
21 described herein, the anti-accretion additive comprising the silicone surfactant
22 showing substantially less retained bitumen therein.

23

1 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

2 Figs. 1 and 2, published in "Balling in Water-Based Muds" by Ron
3 Bland, Rolf Pessier and Matt Isbell at the AADE National Drilling Technical
4 Conference 2001 (AADE 01-NC-HO-56), illustrate bit balling or accretion on a drill
5 bit. Further, Figs. 3 and 4 illustrate accretion of bitumen to metal surfaces when in
6 contact with aqueous drilling fluids in the absence of embodiments of the invention.

7 Embodiments of the invention relate to an anti-accretion additive for
8 mixing with water-based drilling fluids to prevent bitumen or heavy oil from sticking
9 to metal surfaces. Further, embodiments of the invention permit easy separation of
10 the bitumen and bitumen/sand from returned drilling fluid using conventional solids
11 control equipment. Embodiments of the invention, when added to drilling fluids, do
12 not substantially adversely affect the drilling fluid properties.

13 Anti-accretion additives according to embodiments of the invention are
14 based on silicone chemistry which prevents bitumen from sticking to surfaces,
15 particularly metal surfaces, and which can be easily mixed into a drilling fluid. More
16 particularly, embodiments of the invention comprise a polysiloxane or a copolymer
17 thereof and further may comprise an alkyl polyalkylene oxide.

18 Applicant believes that the embodiments of the invention prevent the
19 bitumen from sticking to the metal surfaces because of the surface-active nature of
20 silicone-containing compounds. The silicone-based additives are surface active
21 because they are neither water nor oil soluble and therefore migrate to the interface
22 between oil, water and solids and affect both surface and interfacial tension forces.
23 Thus, the silicone-based additive acts like a non-stick coating, which allows the

1 bitumen to encounter the metal surfaces without sticking thereto. Further, the
2 silicone-based additives prevent the bitumen from becoming substantially dispersed
3 in the drilling fluid which permits easy separation using conventional solids control
4 equipment.

5 Embodiments of the invention are primarily applicable to drilling SAGD
6 wells for the recovery of bitumen however embodiments of the invention are also
7 useful in heavy oil applications.

8 In embodiments of the invention, the anti-accretion additive comprises
9 an organopolysiloxane or a co-polymer of organopolysiloxanes such as a copolymer
10 with a polyalkylene oxide or mixtures thereof and further may comprise alkyl
11 polyalkylene oxide.

12 In other words, the active ingredient in an anti-accretion additive blend
13 comprises either of an organopolysiloxane or a co-polymer of organopolysiloxanes
14 and polyalkylene oxides alone or a blend thereof, and may include alkyl
15 polyalkylene oxide. As appreciated by those skilled in the art, preparations of
16 polyalkylene oxide copolymers of organopolysiloxanes typically comprise some
17 unreacted polyalkylene oxide.

18 It is believed that alkyl polyalkylene oxide cannot be used alone.

19 In embodiments of the invention, the anti-accretion additive blend
20 contains 0-100wt%, 0-90wt% or 0-80wt% of organopolysiloxane component,
21 provided that the sum of the concentrations of an organopolysiloxane and a co-
22 polymer of organopolysiloxanes and polyalkylene oxides is larger than zero. That is

1 to say there must be at least the organosiloxane or the co-polymer thereof and not
2 the alkyl polyalkylene oxide alone.

3 In embodiments of the invention, the anti-accretion additive blend
4 contains 0-100wt%, 1-90wt% or 5-80wt% of a co-polymer of organopolysiloxanes
5 and polyalkylene oxides provided the sum of the concentrations of the co-polymer
6 of organopolysiloxanes and polyalkylene oxides components and an
7 organopolysiloxane is larger than zero.

8 In embodiments of the invention, the anti-accretion additive blend
9 contains 0-50wt%, 0-40wt% and or 0-30wt% of the alkyl polyalkylene oxide
10 component. In other words, the anti-accretion additive comprises less than 50wt%
11 of the alkyl polyalkylene oxide and in embodiments, may contain no alkyl
12 polyalkylene oxide at all.

13

14 ORGANOPOLYSILOXANE

15 In embodiments of the invention, the organopolysiloxane component
16 is selected from polyalkylsiloxanes, polyalkylsiloxane polyols, aminosiloxanes, and
17 polyalkylsiloxanes containing fine particles, typically silica.

18 In embodiments of the invention using polyalkylsiloxanes as the
19 organopolysiloxane component, the polyalkylsiloxanes are poly-dimethylsiloxanes
20 having a viscosity in the ranges of about 10 centistokes (cSt) to about 10,000,000
21 cSt, about 50 cSt to about 1,000,000 cSt, or about 100 cSt to about 100,000 cSt.

22 In embodiments of the invention, using polyalkylsiloxane polyols as
23 the organopolysiloxane component, the polyalkylsiloxane polyols are polyols of

1 poly-dimethylsiloxane, having a viscosity in the range of about 10 cSt to about
2 10,000,000 cSt, about 50 cSt to about 1,000,000 cSt, or about 100 cSt to about
3 100,000 cSt. Silanols are one embodiment of such polyalkylsiloxane polyols.

4 In embodiments of the invention using aminosiloxanes as the
5 organopolysiloxane component, the aminosiloxanes are amino-modified poly-
6 dimethylsiloxanes, (poly-dimethylsiloxanes substituted with one or more amino or
7 alkylamino groups) having a viscosity in the range of about 10 cSt to about
8 10,000,000 cSt, about 50 cSt to about 1000,000 cSt, or about 100 cSt to about
9 100,000 cSt.

10 In embodiments of the invention using polyalkylsiloxanes containing
11 silica particles as the organopolysiloxane component, the polyalkylsiloxanes
12 containing silica particles are typically blends of poly-dimethylsiloxanes and
13 hydrophilic and/or hydrophobic silica, having a viscosity in the range of about 10cSt
14 to about 10,000,000 cSt, about 50 cSt to about 1000,000 cSt, or about 100 cSt to
15 about 100,000 cSt.

16 In embodiments of the invention, the blend of polyalkylsiloxanes filled
17 with fine particles contains from about 0.01wt% to about 30wt%, about 0.05 wt% to
18 about 20 wt% or from about 0.1 wt% to about 15 wt% fine particles.

19

20 CO-POLYMERS OF ORGANOPOLYSILOXANES AND POLYALKYLENE OXIDES

21 In embodiments of the invention the co-polymer of
22 organopolysiloxanes and polyalkylane oxides is selected from co-polymers of poly-
23 dimethylsiloxanes and polyethyleneoxides, polypropyleneoxides and

1 polyethyleneoxide-polypropyleneoxide copolymers. The siloxanes and the
2 polyalkyleneoxides are connected either via alkylene (Si-C linkage) or oxy-alkyl (Si-
3 O-C linkage) bridges. Polyethyleneoxides, polypropylene oxides and polyethylene
4 oxide-polypropylene oxides are derived from 1-50 ethyleneoxide and 1-50
5 propyleneoxide units or 1-25 ethyleneoxide and 1-25 propyleneoxide units or
6 combinations thereof and have a viscosity in the range of about 1 cSt to about
7 100,000 cSt, about 5 cSt to about 50,000 cSt, or about 10 cSt to about 30,000 cSt.

8

9 ALKYL POLYALKYLENE OXIDE

10 In embodiments of the invention, the alkyl polyalkylene oxide is
11 selected from alkyl-polyethyleneoxides, alkyl-polypropyleneoxides and alkyl-
12 polyethyleneoxide-polypropyleneoxide copolymers. The alkyl groups contain 1-30,
13 1-15 or 1-10 carbon atoms. The polyethyleneoxides, polypropyleneoxides and
14 polyethyleneoxide-polypropyleneoxide section of the alkyl polyalkylene oxide is
15 derived from 1-50 ethyleneoxide and 1-50 propyleneoxide units, or from 1-25
16 ethyleneoxide and 1-25 propyleneoxide units having a viscosity in the range of
17 about 1 cSt to about 100,000 cSt, about 5 cSt to about 50,000 cSt or about 10 cSt
18 to about 30,000 cSt.

19

20 IN USE

21 In embodiments of the invention the active ingredients may be added
22 to the aqueous drilling fluid diluted in a solvent for ease of handling or the active
23 ingredients may be added separately to the aqueous drilling fluid. The active

1 ingredients of the anti-accretion additive, as identified herein, are present in a
2 volume from about about 1 vol% to about 100 vol% of the total volume of the anti-
3 accretion additive.

4 In embodiments of the invention, wherein the active ingredients are
5 diluted in a solvent for forming the anti-accretion additive, the active ingredients are
6 present in a volume from about 5 vol% to about 30 vol% of the total volume of the
7 anti-accretion additive. In embodiments of the invention, the active ingredients are
8 added from about 5 vol% to about 15 vol% or from about 10 vol% to about 15 vol%
9 of the total volume of the anti-accretion additive. Additionally, the anti-accretion
10 additive may comprise minor amounts of water and emulsifiers. Preparation of the
11 anti-accretion additive by diluting in a solvent facilitates ease of handling of the
12 active ingredients when preparing the drilling fluid on site.

13 In a case where the active ingredients are added directly to the
14 aqueous drilling fluid, no solvent is required.

15 As previously noted, components of the anti-accretion additives are
16 neither soluble in water nor in oil and typically migrate to an interface therebetween.
17 Applicant believes that these properties are largely responsible for the surface and
18 interfacial behavior of the anti-accretion additives between the aqueous drilling fluid
19 and the surface of the bitumen. The components of the anti-accretion additive,
20 regardless whether they are added to the drilling fluid separately or in a solvent,
21 form an emulsion of fine droplets which are dispersed within the drilling fluid.

22 Emulsion stability is largely dictated by the droplet size of the
23 discontinuous phase in either oil-in-water or water-in-oil emulsions. Generally, the

1 smaller the droplet size the greater the stability of the emulsion. The anti-accretion
2 additives according to embodiments of the invention when added to an aqueous
3 drilling mud form a droplet size which is sufficiently small so as to effectively
4 disperse the anti-accretion additive in the aqueous phase, but which is not so large
5 as to cause coalescence of the droplets which would adversely affect the dispersion
6 thereof. Typically shear, which results from pumping of the fluids downhole through
7 the drill bit, further acts to maintain the small droplet size within the drilling fluid.

8 Anti-accretion additives, according to embodiments of the invention
9 are added at a minimum of about 0.05 L/m^3 of the active ingredients to the total
10 volume of the aqueous drilling mud. Applicant believes that as much as 6 L/m^3 or
11 more of active ingredients may be added to the total volume of the aqueous drilling
12 mud. Applicant believes that the amount of active ingredient required is largely
13 dependent upon the amount and type of bituminous and heavy oil materials which
14 are encountered in the formation.

15 An exemplary anti-accretion additive according to an embodiment of
16 the invention, referred to herein as BMP-1, comprises a polysiloxane emulsion.
17 BMP-1 is delivered to the drilling mud as an emulsion having a sufficiently small
18 droplet size so as to be stable when dispersed within an aqueous drilling fluid.

19 In an embodiment, BMP-1 comprises 25.5% organopolysiloxane,
20 0.15% alkyl polyalkylene oxide and 4.35% of a co-polymer of organopolysiloxanes
21 and polyalkylene oxides in a solvent, such as a blend of a refined hydrotreated
22 hydrocarbon, for example ENVIRODRILL® (available from Innovative Chemical

1 Technologies Canada, Calgary, Alberta, Canada) and glycol ether EB. BMP-1 may
2 also comprise a minor amount of water and emulsifiers.

3 It is to be noted that the refined hydrotreated hydrocarbon solvents,
4 such as ENVIRODRILL®, have a tendency to dissolve bitumen from the bitumen-
5 coated solids and therefore, while these embodiments of the invention prevent
6 accretion of bitumen to metal surfaces, there is a reduced ability to recycle the
7 drilling mud when returned to surface. The bitumen, once dissolved in the drilling
8 mud, is not readily removed with the solids using conventional solids control
9 equipment.

10 For greater recyclability of the drilling mud, solvents such as refined
11 hydrotreated hydrocarbons are to be avoided. In embodiments of the invention,
12 BMP-1 is prepared and diluted in a silicone oil, such as an organopolysiloxane oil,
13 which has no affinity for either the water or the bitumen. One such exemplary
14 organopolysiloxane oil is polydimethylsiloxane oil. Using the silicone oil, bitumen
15 does not dissolve in the returned drilling mud and remains with the returned solids.
16 Thus, the bitumen can be removed from the drilling mud using conventional solids
17 control equipment. Further, the addition of a silicone oil further aids in preventing
18 accretion of bitumen.

19 It is generally understood in the prior art that calcium ions destabilize
20 oil-in-water emulsions because of the effect of divalent cations on surfactant
21 function. Surfactants are meant to facilitate dispersion and stability of droplets in the
22 emulsion. When calcium is introduced, many calcium-surfactant-non-aqueous
23 phase interactions occur, such as the formation of calcium soaps, which thereafter

1 partition a larger amount of the surfactant to the non-aqueous phase thereby
2 disrupting the stability of the emulsion. Thus, it is generally thought that droplet size
3 would be increased with the addition of calcium ions.

4 Contrary to the conventional wisdom however, embodiments of the
5 invention have an enhanced performance in the presence of calcium ions and the
6 small droplet size is maintained. Detrimental effects resulting from bitumen
7 accretion are dramatically reduced using embodiments of the invention, even in the
8 presence of calcium ions. The enhanced performance has been observed in as little
9 as 200 mg/L calcium and as high as 1500 mg/L calcium. Applicant believes that an
10 upper limit for calcium may be reached when the calcium becomes so high as to
11 interfere with anionic polymers added to the drilling fluid, causing the anionic
12 polymers to coil up and lose effectiveness for the purpose for which they were
13 added.

14 Aqueous drilling fluids for use in drilling through subterranean
15 formations having at least bituminous or heavy oil materials therein comprise a
16 polysiloxane, a copolymer of polysiloxane or mixtures thereof as active ingredients
17 for preventing accretion of the bituminous or heavy oil materials to at least metal
18 surfaces. Further, wherein the active ingredients are diluted in a silicone oil prior to
19 addition to the aqueous drilling fluid, retention of the bituminous or heavy oil
20 materials in the aqueous drilling fluid are minimized permitting the bituminous or
21 heavy oil materials to be removed from the aqueous drilling fluid with conventional
22 solids control equipment. The active ingredients are added at a minimum of
23 0.05L/m³ to the total volume of the drilling fluid.

1 In a method for drilling through subterranean formations having
2 bituminous or heavy oil materials therein, an anti-accretion additive is added to the
3 aqueous drilling fluid. For greater recyclability of the drilling fluid, the active
4 ingredients of the additive are first diluted in a silicone solvent before addition to the
5 aqueous drilling fluid.

6

7 EXAMPLES

8 BMP-1 – polysiloxane emulsions

9 A variety of formulations of polysiloxane emulsions (BMP-1), were
10 prepared as follows:

11 Formulation 1:

12 85wt% of a blend of poly-dimethylsiloxane with 350 cSt viscosity and
13 5% hydrophobic silica;

14 14.5wt% of a copolymer from poly-dimethylsiloxane and
15 polyethyleneoxide-polypropyleneoxide copolymers, with a viscosity of 13,750
16 cSt at ambient temperature; and

17 0.5wt% of butyl-polypropyleneoxide, with a viscosity of 165 cSt at
18 100°F.

19

20

1 Formulation 2:

2 85wt% of a blend of poly-dimethylsiloxane with 350 cSt viscosity and

3 10% of hydrophobic silica;

4 14.5wt% of a copolymer from poly-dimethylsiloxane and

5 polyethyleneoxide-polypropyleneoxide copolymers, with a viscosity of 13,750

6 cSt at ambient temperature; and

7 0.5wt% of butyl-polypropyleneoxide, with a viscosity of 165 cSt at

8 100°F.

9 Formulation 3:

10 85wt% of poly-dimethylsiloxane with 350 cSt viscosity;

11 14.5wt% of a copolymer from poly-dimethylsiloxane and

12 polyethyleneoxide-polypropyleneoxide copolymers, with a viscosity of

13 13,750cSt at ambient temperature; and

14 0.5wt% of butyl-polypropyleneoxide, with a viscosity of 165 cSt at

15 100°F.

16 Formulation 4:

17 80wt% of poly-dimethylsiloxane with 350 cSt viscosity;

18 19.4wt% of a copolymer from poly-dimethylsiloxane and

19 polyethyleneoxide-polypropyleneoxide copolymers, with a viscosity of 13,750

20 cSt at ambient temperature; and

21 0.6wt% of butyl-polypropyleneoxide, with a viscosity of 165 cSt at

22 100°F.

23

1 Formulation 5:

2 85wt% of silanol with 500-800 cSt viscosity;

3 14.5wt% of a copolymer from poly-dimethylsiloxane and
4 polyethyleneoxide-polypropyleneoxide copolymers, with a viscosity of 13,750
5 cSt at ambient temperature; and

6 0.5wt% of butyl-polypropyleneoxide, with a viscosity of 165 cSt at
7 100°F.

8

9 Formulation 6:

10 85wt% of silanol with 2500-3500 cSt viscosity;

11 14.5wt% of a copolymer from poly-dimethylsiloxane and
12 polyethyleneoxide-polypropyleneoxide copolymers, with a viscosity of 13,750
13 cSt at ambient temperature; and

14 0.5wt% of butyl-polypropyleneoxide, with a viscosity of 165 cSt at
15 100°F.

16

17 Formulation 7:

18 85wt% of poly-dimethylsiloxane with 12,500 cSt viscosity;

19 14.5wt% of a copolymer from poly-dimethylsiloxane and
20 polyethyleneoxide-polypropyleneoxide copolymers, with a viscosity of 13,750
21 cSt at ambient temperature; and

22 0.5wt% of butyl-polypropyleneoxide, with a viscosity of 165 cSt at
23 100°F.

1 **Formulation 8:**

2 95wt% of poly-dimethylsiloxane with 350 cSt viscosity;

3 4.85wt% of a copolymer from poly-dimethylsiloxane and
4 polyethyleneoxide-polypropyleneoxide copolymers, with a viscosity of 13,750
5 cSt at ambient temperature ;and

6 0.15wt% of butyl-polypropyleneoxide, with a viscosity of 165 cSt at
7 100°F.

8 **Formulation 9:**

9 50wt% of poly-dimethylsiloxane with 350 cSt viscosity;

10 35wt% of silanol with 500-800 cSt viscosity;

11 14.5wt% of a copolymer from poly-dimethylsiloxane and
12 polyethyleneoxide-polypropyleneoxide copolymers, with a viscosity of 13,750
13 cSt at ambient temperature; and

14 0.5wt% of butyl-polypropyleneoxide, with a viscosity of 165 cSt at
15 100°F.

16 **Formulation 10:**

17 90wt% of poly-dimethylsiloxane with 350 cSt viscosity;

18 9.7wt% of a copolymer from poly-dimethylsiloxane and
19 polyethyleneoxide-polypropyleneoxide copolymers, with a viscosity of 13,750
20 cSt at ambient temperature; and

21 0.3wt% of butyl-polypropyleneoxide, with a viscosity of 165 cSt at
22 100°F.

23

1 Testing of formulations of BMP-1

2 Testing of the various BMP-1 formulations was performed by rolling a
3 steel bar (115mm x 25mm) in 350 ml drilling fluid with 50 grams of bitumen (sourced
4 from core samples) in an OFI Testing Equipment (OFITE) aging cell.

5 The drilling fluid comprised:

- 6 • 2 kg/m³ Xanthan Gum (Viscosifier);
- 7 • 5 L/m³ Aminodrill (Clay Stabilizer);
- 8 • 1 kg/m³ CaCl₂; and
- 9 • 0.05 L/m³ anti-accretion additive.

10

11 Each of the anti-accretion additive formulations was formulated so as
12 to contain 30 vol% active ingredients in the total additive volume. The BMP-1 was
13 diluted in ENVIRODRILL® prior to addition to the drilling fluid. The formulations
14 were rolled in the OFITE cell with the steel bar for one hour at 400 psi at 40°C to
15 simulate any heat generated at the bit.

16

17 Results – Table A

18 Table A shows the maximum number of rolls for each example before
19 failure was observed. Failure was determined when bitumen adhered to the bar.
20 Further, the stability of the anti-accretion additive was observed.

21

Results -Table A

Formulation	# of Rolls	Formulation Stability			
		1-Day Stability	3-Day Stability	4-Day Stability	6-Day Stability
1	4	Stable		Stable	Stable
2	4	Stable		Stable	Stable
3	4	Separated			
4	4	Separated			
5	3	Separated			
6	3	Trace separation	2mm separation		Lots of separation
7	2	Stable	Trace separation		2-3 mm separation
8	3	Separated			
9	2	Separated			
10	2	Separated			

Conclusions:

While all of the formulations tested showed an ability to prevent accretion of bitumen at the levels tested, many of the additive formulations showed varying degrees of instability over time.

Formulations 1 and 2 showed excellent anti-accretion properties and were stable over 6 days.

Formulation 1 was utilized for further testing as an exemplary anti-accretion additive according to an embodiment of the invention.

Examples – Formulation 1

The examples presented below are provided to illustrate the invention and are not meant to limit the scope of the invention as will be apparent to those skilled in the art.

1 All testing was performed by rolling a steel bar (115mm x 25mm) in 350
2 ml of a conventional drilling fluid matrix, and 50 grams of bitumen (sourced from
3 core samples) in an OFI Testing Equipment (OFITE) aging cell. Rolling times were
4 for one hour and the test was performed at 40°C to simulate heat generated at the
5 bit.

6 BMP-1, according to formulation 1, was used as the anti-accretion
7 additive.

8

9 Example 1 – Effect of Pressure

10 Testing was performed to assess the effect of pressure on the test
11 results to simulate pressure conditions of the fluid when circulated down-hole. A
12 minimal amount of Xanthan, a conventional viscosifier, was added to the brine
13 matrix, with and without the further addition of anti-accretion additive BMP-1.

14

15 Results - Table B

	Ambient Pressure	400 psi Pressure
2 kg/m ³ Xanthan	Bitumen sticking to bar and cell.	Bitumen sticking to bar and cell.
2 kg/m ³ Xanthan + 2 L/m ³ BMP-1	Bar and cell clean	Bar and cell clean

16

17

1 Conclusions:

2 As seen in the results in Table B and in Fig. 3, some accretion or
3 sticking of bitumen to the steel bar is observed at ambient pressure without the
4 addition of BMP-1. As shown in Fig. 4, when elevated pressure (400psi) equivalent
5 to that of the hydrostatic pressure in a true vertical depth of approximately 300m is
6 applied to the OFITE cell, severe accretion occurs in the brine without the addition
7 of BMP-1. The steel bar is substantially coated with bitumen.

8 Fig. 5 illustrates that the addition of the anti-accretion additive (BMP-1)
9 according to an embodiment of the invention effectively inhibits accretion of the
10 bitumen, even at the elevated pressure. The steel bar is substantially free of any
11 bitumen sticking thereto.

12

13 Example 2 – Effect of Other Drilling Fluid Additives

14 Various drilling fluid additives are typically added to conventional
15 drilling fluid systems. Thus, testing was performed adding a variety of common
16 conventional additives to a brine base fluid to determine whether negative
17 interactions were observed between the additives and the anti-accretion additive
18 BMP-1 and whether there was any negative effect of the ability of the anti-accretion
19 additive to prevent sticking.

20

1 The following additives are commonly used in the oil industry to
2 formulate a drilling fluid:

- 3 1. Xanthan Gum (Viscosifier)
- 4 2. Polyanionic Cellulose [PAC] (Fluid Loss Additive)
- 5 3. Aminodril* NPH (Clay Control) (* available from ICTC)

6 Each additive was mixed individually and in combination with BMP-1
7 and was rolled with the steel bar in the OFITE aging cell at 400 psi.

8 The steel bar was observed following rolling to determine any adverse
9 effects in the presence of the anti-accretion additive.

10 Results – Table C

Formulation	Observation
3 kg/m ³ Xanthan + 2 L/m ³ BMP-1	Bar and cell clean
3 kg/m ³ PAC + 2 L/m ³ BMP-1	Bar and cell clean
5 L/m ³ Aminodril NPH + 2 L/m ³ BMP-1	Bar and cell clean
3 kg/m ³ Xanthan + 2 L/m ³ BMP-1 + 2 kg/m ³ PAC + 5 L/m ³ Aminodril NPH	Bar and cell clean

11

12 Conclusions:

13 It is clear from the results in Table C that none of the conventional
14 additives tested had a negative impact on the anti-accretion properties of BMP-1.

15 Further, when combined in a single fluid, the combination did not have
16 a negative impact on the anti-accretion additive.

17

18

1 Example 3 – Effect of Drilled Solids

2 During a drilling operation, it is expected that the drilling fluid would be
3 exposed to formations that not only contain bitumen, but also to formations that
4 contain swellable clay, such as in the Clearwater formation in Cold Lake Alberta,
5 Canada.

6 For the purposes of the testing, the drilling fluid containing brine, some
7 conventional additives and BMP-1 as the anti-accretion additive was contaminated
8 with 30 kg/m³ Wyoming bentonite, a highly swellable clay similar to the clays found
9 in the Clearwater formation, prior to rolling in the OFITE aging cell at 400 psi.

10 Results – Table D

Formulation	Observation
3 kg/m ³ Xanthan + 2 L/m ³ BMP-1 + 2 kg/m ³ PAC + 5 L/m ³ Aminodril NPH + 30 kg/m ³ Wyoming Bentonite	Bar and cell clean

11
12 Conclusions:

13 Despite the addition of highly swellable clay, BMP-1 effectively
14 prevented sticking of the bitumen to the OFITE cell or steel bar therein.

15
16 Example 4 – Effect of Calcium

17 During a drilling operation, there is a chance that the drilling fluid could
18 be contaminated with significant amounts of calcium which is known to have
19 detrimental effects on the rheology of the mud system. The significant amounts of
20 calcium typically result either from the natural composition of the formation drilled or
21 from residual calcium present as a result of other operations, such as cementing.

1 Testing was performed in fluids contaminated with 200, 400, 700 and
 2 1000 ppm calcium, over and above the amount of calcium present in the brine, prior
 3 to rolling in an OFITE aging cell at 400 psi.

4

5 Results– Table E

Formulation	Observation
3 kg/m ³ Xanthan + 2 L/m ³ BMP-1 + 200ppm Calcium	Bar and cell clean
3 kg/m ³ Xanthan + 2 L/m ³ BMP-1 + 400ppm Calcium	Bar and cell clean
3 kg/m ³ Xanthan + 2 L/m ³ BMP-1 + 700ppm Calcium	Bar and cell clean
3 kg/m ³ Xanthan + 2 L/m ³ BMP-1 + 1000ppm Calcium	Bar and cell clean

6

7 Conclusions:

8 As shown in the results in Table E, calcium had no detrimental effect
 9 on the anti-accretion properties of BMP-1 when present from 200ppm to 1000ppm.

10 Further, it was observed that BMP-1 showed enhanced anti-accretion
 11 performance in the presence of additional amounts of calcium.

12

13 Example 5 – Effect on Fluid Properties

14 Testing using a Model 900 rheometer was performed in order to
 15 ascertain whether the addition of BMP-1 to a drilling fluid had any adverse affects
 16 on fluid rheology.

17 Mixing of the drilling mud, bitumen and conventional additives was
 18 performed for 20 minutes on a Hamilton Beach mixer with and without the addition
 19 of BMP-1 and further, in the presence of calcium. A drop in fluid properties would
 20 be indicative of a negative impact on the fluid properties.

21

1 Results – Table F

	Plastic Viscosity (m.Pa.s)	Yield Point (Pa)	Low Shear Rate Viscosity – 0.3 rpm (cP)
3 kg/m ³ Xanthan + 2 kg/m ³ PAC	16	10	1500
3 kg/m ³ Xanthan + 2 L/m ³ BMP-1 + 2 kg/m ³ PAC	17	17	2500
3 kg/m ³ Xanthan + 2 L/m ³ BMP-1 + 2 kg/m ³ PAC + 300 ppm Calcium	13	10	1500

2

3 Conclusions:

4 It is clear from the results in Table F, that the presence of BMP-1 or
5 the combination of BMP-1 and calcium at about 300ppm had no adverse effects on
6 the rheology of the fluids tested.

7

8 Example 6 – Efficiency of the System

9 In order to measure the efficiency of the anti-accretion additive on a
10 drilling fluid system, the same drilling fluid was rolled with the steel bar multiple
11 times to simulate repeated use of the same drilling fluid. The rolling was repeated
12 until bitumen accretion was observed which was deemed a failure of the anti-
13 accretion additive.

14 The fluid was rolled for one hour with 50 grams of bitumen. The
15 bitumen was then screened out and another 50 grams of bitumen was added. The
16 process was repeated without the addition of any additional BMP-1 until failure of
17 the anti-accretion additive was observed. Failure was determined to be the
18 presence of any bitumen stuck to the metal bar or cell.

1 The effect of the anti-accretion additive according to an embodiment
 2 of the invention, BMP-1, was compared to a commercially available anti-accretion
 3 additive employing encapsulation technology (CP905H available from Hychem,
 4 Canada).

5

6 Results-Table G

Formulation	Concentration of Bitumen	Number of Rolls Before Failure
3 kg/m ³ Xanthan + 1 L/m ³ BMP-1	286 kg/m ³	2
3 kg/m ³ Xanthan + 1 L/m ³ BMP-1 + 200ppm Calcium	1430 kg/m ³	>10
3 kg/m ³ Xanthan + 1 L/m ³ BMP-1 + 400ppm Calcium	1430 kg/m ³	>10
3 kg/m ³ Xanthan + 1 L/m ³ BMP-1 + 1000 ppm Calcium	1430 kg/m ³	>10
2 kg/m ³ CP 905H** (Cationic Polyacrylamide)	286 kg/m ³	1
2 kg/m ³ CP 905H** + 200 ppm Calcium	143 kg/m ³	0

7

8 Conclusions:

9 It is clear from the results in Table G that BMP-1 outperforms the
 10 current encapsulation technology in the absence of additional calcium.

11 Further, at additional amounts of calcium of about 200 ppm present,
 12 the efficiency of BMP-1 is increased by an order of magnitude over that of the
 13 conventional additive.

14

15

1 Example 7 – Recyclability of Drilling Mud containing an anti-accretion additive
2 according to an embodiment of the invention
3

4 Testing was performed to simulate the performance of drilling fluids,
5 with and without the addition of anti-accretion additives according to embodiment of
6 the invention when subjected to high shear, such as when the drilling fluid passes
7 through the drill bit and is returned to surface through the annulus. The drilling fluids
8 were observed, following testing, to determine whether bitumen was retained in the
9 drilling fluid or if it remained with the solids.

10 A drilling fluid (Sample 1) containing a conventional solvent/surfactant
11 system was compared to a drilling fluid (Sample 2) containing an anti-accretion
12 additive according to Formulation 1, diluted in a silicone oil, such as
13 polydimethylsiloxane, for addition to the drilling mud.

14 The drilling fluid, according to an embodiment of the invention,
15 comprised 2kg/m^3 Xanthan, 1 kg/m^3 PAC, 1 kg/m^3 CaCl_2 and 5 L/m^3 BMP-1, the
16 balance being water, for forming an aqueous drilling fluid. The drilling fluid, absent
17 the BMP-1 and CaCl_2 , was first mixed on a Hamilton Beach mixer to fully hydrate
18 the polymers contained therein. After 20 minutes, the BMP-1 was added to the
19 drilling fluid and about 1 minute later the CaCl_2 was added to the mixture.

20 To test the recyclability of the drilling mud, 70g of bitumen-laden sand
21 was added to each of the conventional drilling fluid and the fluid prepared according
22 to an embodiment of the invention, as described. The drilling fluids were then
23 subjected to high shear by mixing at about 13,000 rpm for 1 hour.

24

1 Results

2 As shown in Fig. 6, after 1 hour a visual comparison was made
3 between the conventional drilling fluid and the drilling fluid containing BMP-1 diluted
4 in silicone oil.

5 The conventional fluid (Sample 1) appeared to have dissolved
6 bitumen from the sand into the fluid. Sample 1 appears significantly darker than
7 Sample 2.

8 The fluid containing BMP-1 diluted in polydimethylsiloxane oil (Sample
9 2) appeared to have little or no bitumen dissolved within the fluid.

10

11 Conclusions:

12 Drilling fluids containing an anti-accretion additive according to an
13 embodiment of the invention, does not appear to dissolve bitumen. The bitumen
14 remains with the sand, and thus, the drilling fluid can be recycled by removal of the
15 sand and bitumen using conventional solids control equipment.

16

1 **THE EMBODIMENTS OF THE INVENTION IN WHICH AN**
2 **EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS**
3 **FOLLOWS:**
4

5 1. A bitumen anti-accretion additive for addition to an aqueous
6 drilling fluid comprising a polysiloxane and a copolymer of polysiloxane as active
7 ingredients therein, wherein

8 when in contact with bitumen or a bitumen-containing sand in the
9 aqueous drilling fluid, the additive minimizes sticking of the bitumen to metal
10 surfaces and minimizes dispersion of the bitumen to the aqueous drilling fluid.
11

12 2. The anti-accretion additive of claim 1 wherein the co-polymer of
13 polysiloxane is a polyalkylene oxide co-polymer thereof comprising the
14 polysiloxane-polyalkylene oxide co-polymer and polyalkylene oxide.
15

16 3. The anti-accretion additive of claim 1 or 2 further comprising an
17 alkyl polyalkylene oxide.
18

19 4. The anti-accretion additive of claim 3 wherein the alkyl
20 polyalkylene oxide comprises less than about 50% of the additive.
21

22 5. The anti-accretion additive of any one of claims 1 to 4 wherein
23 the polysiloxane is an organopolysiloxane.
24

1 6. The anti-accretion additive of claim 5 wherein the
2 organopolysiloxane is selected from the group comprising polyalkylsiloxanes,
3 polyalkylsiloxane polyols, aminosiloxanes, polyalkylsiloxanes containing fine
4 particles and mixtures thereof.

5

6 7. The anti-accretion additive of any one of claims 1 to 6 wherein
7 the co-polymer of polysiloxane is selected from the group comprising co-polymers
8 of poly-dimethylsiloxanes and polyethyleneoxides, polypropyleneoxides and
9 polyethyleneoxide-polypropyleneoxide copolymers, the siloxanes and the
10 polyalkyleneoxides being connected by alkylene or oxy-alkyl bridges and the
11 polyethyleneoxides, polypropylene oxides and polyethylene oxide-polypropylene
12 oxides being derived from 1-50 ethyleneoxide and 1-50 propyleneoxide units or 1-
13 25 ethyleneoxide and 1-25 propyleneoxide units and mixtures thereof.

14

15 8. The anti-accretion additive of claim 3 or 4 wherein the alkyl
16 polyalkylene oxide is selected from the group comprising alkyl-polyethyleneoxides,
17 alkyl-polypropyleneoxides and alkyl-polyethyleneoxide-polypropyleneoxide
18 copolymers, the alkyl groups having from 1 to about 30 carbon atoms, the
19 polyethyleneoxides, polypropyleneoxides and polyethyleneoxide-
20 polypropyleneoxide portions being derived from 1-50 ethyleneoxide and 1-50
21 propyleneoxide units, or from 1-25 ethyleneoxide and 1-25 propyleneoxide units
22 and mixtures thereof.

23

1 9. The anti-accretion additive of any one of claims 1 to 8 further
2 comprising a solvent.

3

4 10. The anti-accretion additive of claim 9 wherein the solvent is a
5 hydrotreated hydrocarbon solvent and glycol ether EB.

6

7 11. The anti-accretion additive of claim 9 wherein the solvent is an
8 organopolysiloxane solvent, the anti-accretion further minimizing retention of the
9 bitumen in the aqueous drilling fluid.

10

11 12. The anti-accretion additive of claim 9, 10 or 11 wherein the
12 active ingredients comprise from about 5 vol% to about 30 vol% of the total volume
13 of the additive and the solvent comprises from about 95 vol% to about 70 vol% of
14 the total volume of the additive.

15

16 13. The anti-accretion additive of claim 12 wherein the 30 vol%
17 active ingredients comprise:

18 from about 50wt% to about 95wt% organopolysiloxane;

19 from about 4.85 wt% to about 14.5wt% organopolysiloxane-
20 polyalkylene oxide co-polymers; and

21 from about 0.15wt% to about 0.5wt% alkyl polyalkylene oxide; and

22 wherein

23 the 95 vol% to 70 vol% solvent is an organopolysiloxane solvent.

1 14. An aqueous drilling fluid for use in subterranean formations
2 having at least bituminous or heavy oil materials therein, the aqueous drilling fluid
3 comprising an anti-accretion additive according to any one of claims 1 to 13.

4

5 15. The aqueous drilling fluid of claim 14 wherein the drilling fluid
6 comprises at a minimum about 0.05L of the active ingredients per cubic meter of the
7 aqueous drilling fluid.

8

9 16. A method for minimizing bitumen accretion to metal surfaces
10 and for minimizing bitumen retention in an aqueous drilling fluid returned to surface
11 from a subterranean formation comprising:

12 adding to the aqueous drilling fluid, an additive according to any one
13 of claims 1 to 13.

14

1/6

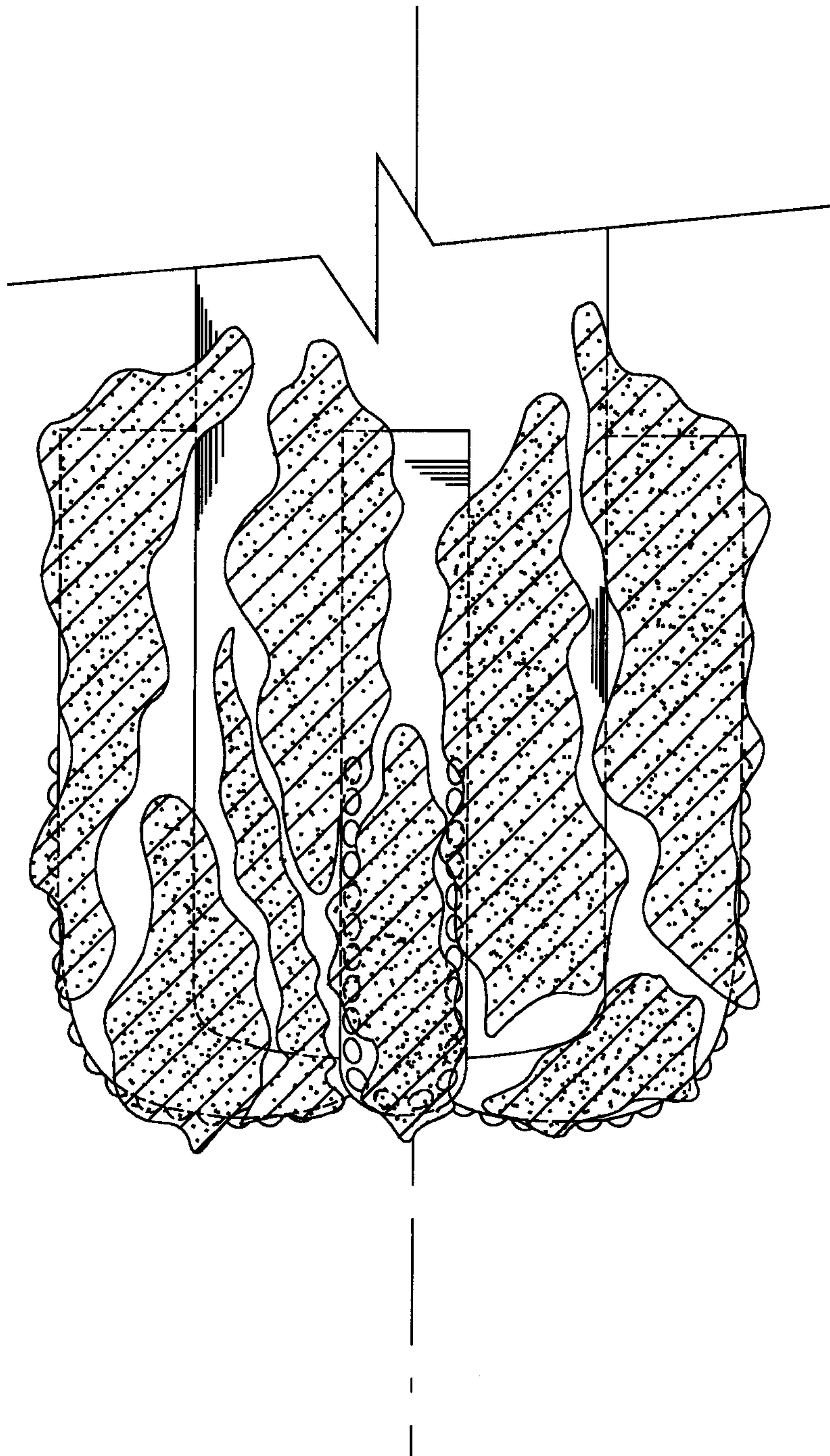


Fig. 1
PRIOR ART

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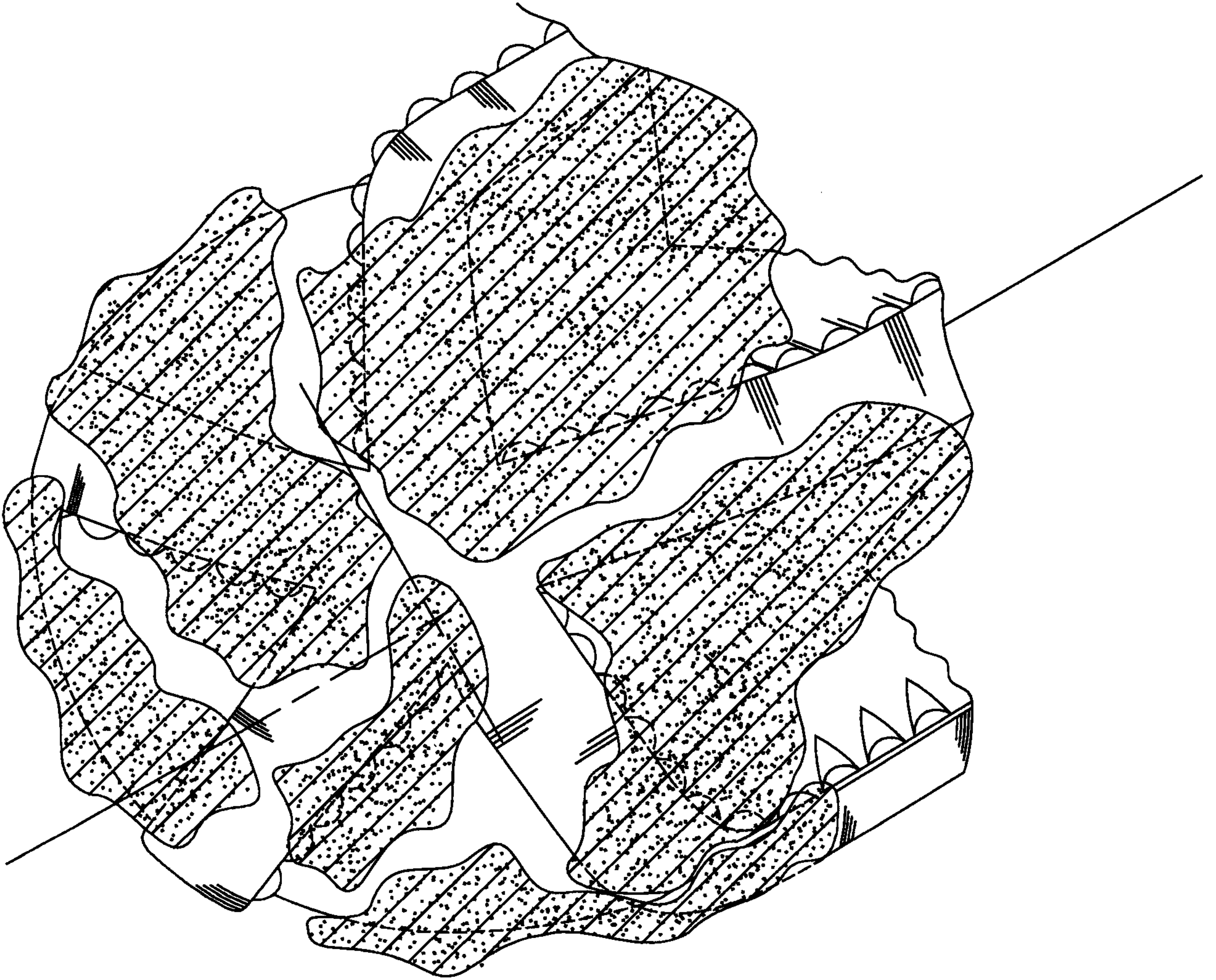
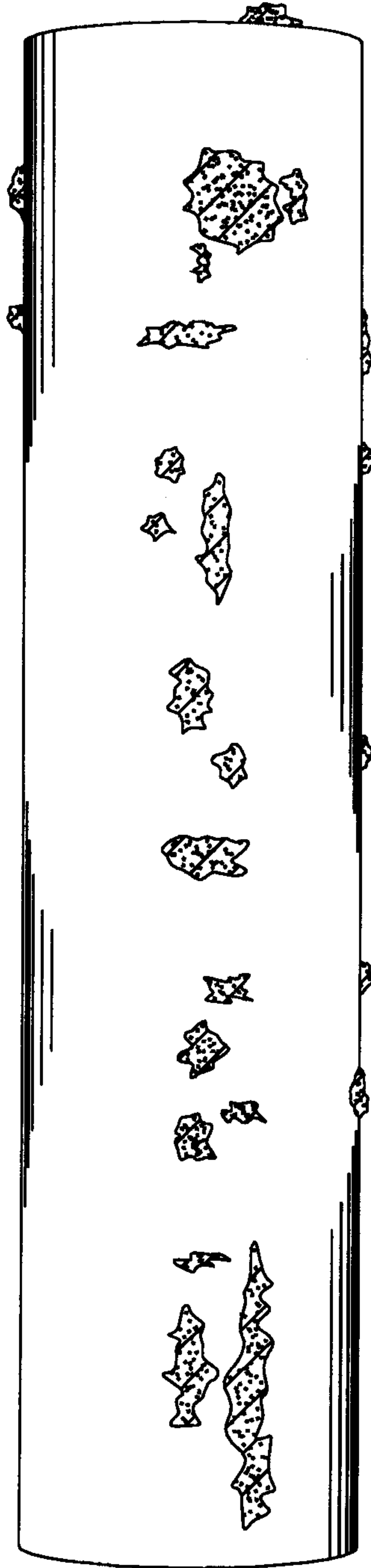


Fig. 2
PRIOR ART

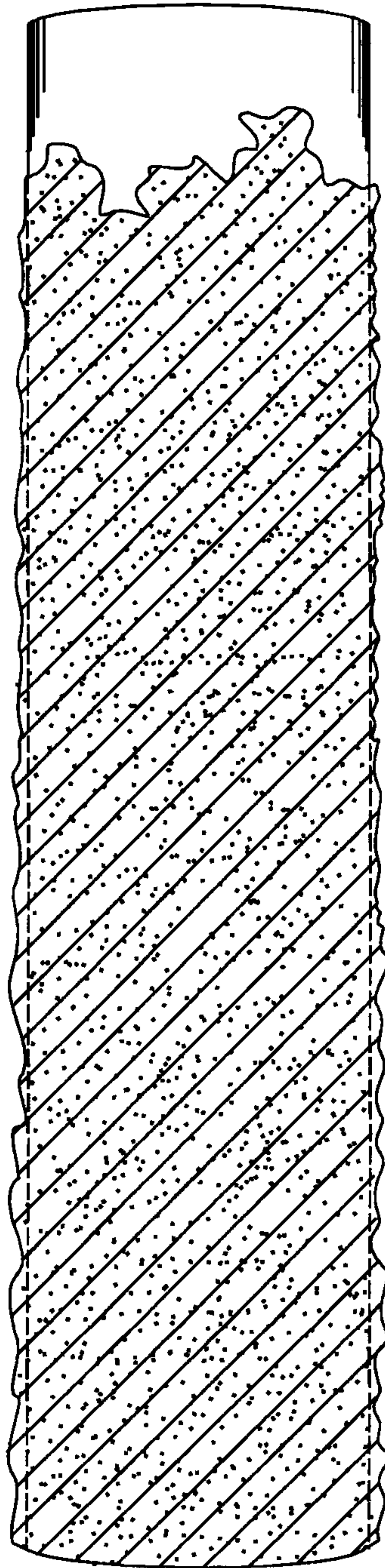
3/6



Xanthan at Ambient Pressure

Fig. 3

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Xanthan at 400 psi

Fig. 4

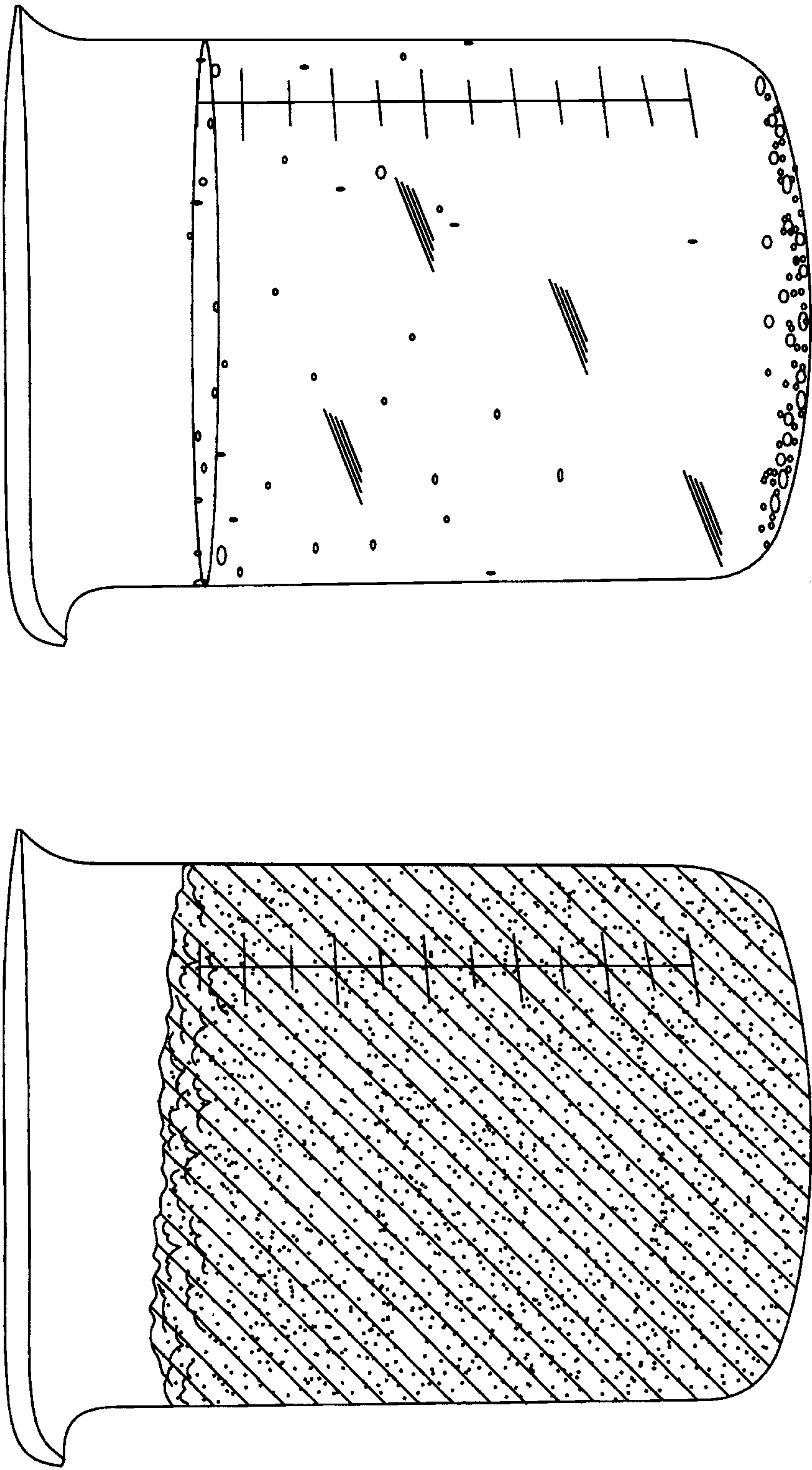
5/6



BMP-1 + Xanthan at 400 psi

Fig. 5

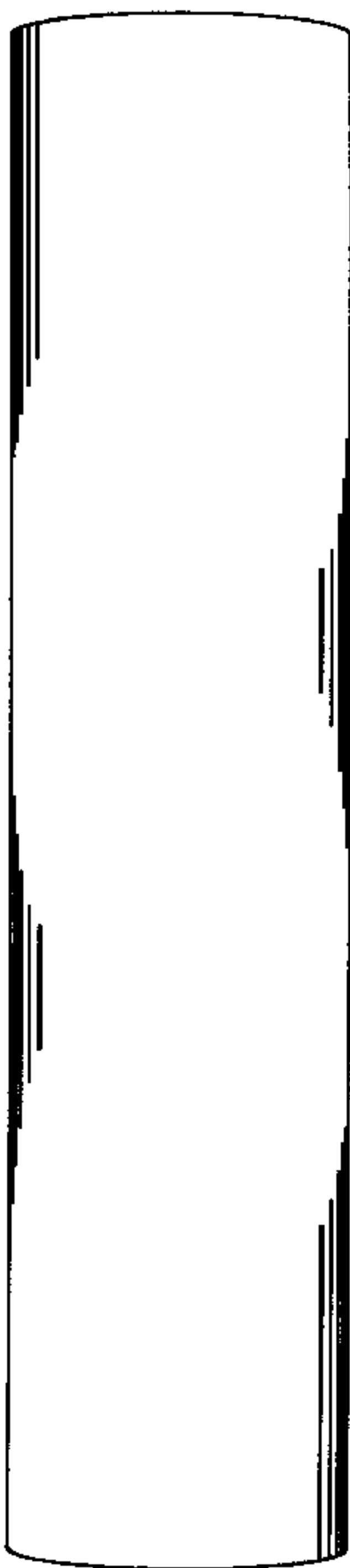
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Sample #2

Sample #1

Fig. 6



BMP-1 + Xanthan at 400 psi