

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 May 2003 (08.05.2003)

PCT

(10) International Publication Number
WO 03/038008 A1

- (51) International Patent Classification⁷: **C09K 7/06**, (74) Agent: **TRIPP, Karen, B.**; Attorney at Law, P.O. Box 1301, Houston, TX 77251-1301 (US).
B01F 17/00
- (21) International Application Number: PCT/US02/34667 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 29 October 2002 (29.10.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 09/999,799 31 October 2001 (31.10.2001) US (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
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- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: ADDITIVE FOR OIL-BASED DRILLING FLUIDS

(57) Abstract: A method and product is disclosed which provides emulsion stability and filtration control to invert emulsion drilling fluids. The product comprises a blend of a carboxylic acid terminated polyamide and a mixture produced by the Diels-Alder reaction of dienophiles, preferably carboxylic acids, polycarboxylic acids, acid anhydrides, or combinations or mixes thereof, with a mixture of fatty acids and resin acids. The product is extremely effective, decreasing by about two-thirds the amount of emulsifier generally required to formulate an effective drilling fluid. The product also greatly reduces and in many cases eliminates the need for conventional fluid loss additives, and additionally provides electrical stability. Moreover, the product has a pour point as low as about 20 degrees Fahrenheit with minimal solvents, thereby eliminating the need to ship large amounts of inert material for use, and may be transported in a highly active state.



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ADDITIVE FOR OIL-BASED DRILLING FLUIDS**BACKGROUND OF THE INVENTION****1. Field of the Invention**

5 The present invention relates to methods for drilling boreholes in subterranean formations, particularly hydrocarbon bearing formations, and to drilling fluids for use in such drilling operations. More particularly, the present invention relates to oil or synthetic based drilling fluids, fluids comprising invert emulsions, and more particularly drilling fluid additives that facilitate or enhance emulsification, electrical stability or filtration properties of the drilling fluid.

2. Description of Relevant Art

10 A drilling fluid or mud is a specially designed fluid that is circulated through a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid include removing drill cuttings from the wellbore, cooling and lubricating the drill bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain
15 the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation.

 Oil or synthetic-based muds, or invert emulsions, are normally used to drill swelling or sloughing shales, salt, gypsum, anhydrite or other evaporite formations, hydrogen sulfide-
20 containing formations, and hot (greater than about 300 degrees Fahrenheit) holes, but may be used in other holes penetrating a subterranean formation as well. These non-aqueous based drilling fluids typically contain oil or a synthetic oil or other synthetic material or synthetic fluid ("synthetic") as the continuous phase and may also contain water which is dispersed in the continuous phase by emulsification so that there is no distinct layer of water in the fluid. The
25 term "oil mud" or "oil or synthetic-based mud" typically means an invert oil mud emulsion or invert emulsion. An all oil mud simply comprises 100% oil by volume as the liquid phase; that is, there is no aqueous internal phase. An invert emulsion drilling fluid may commonly comprise between about 50:50 to 95:5 by volume oil phase to water phase.

 Most commonly, invert emulsions used in drilling typically comprise: a base oil or
30 synthetic fluid for the external phase; a saline, aqueous solution for the internal phase (typically a solution comprising about 30% calcium chloride); and other agents or additives for suspension, fluid loss, density, oil-wetting, emulsification, filtration, and rheology control. With space at some well sites limited, such as on offshore platforms, and with increasing costs of transport of materials to a wellsite, there is industry-wide interest in, and on-going need for, more efficient and

concentrated drilling fluid additives and for drilling fluids which can be formulated and maintained with minimal or fewer additives than common with prior art drilling fluids.

SUMMARY OF THE INVENTION

An improved and more efficient material or product and method is disclosed for providing emulsion stability and filtration control to invert emulsions and other oil or synthetic based drilling fluids for use in drilling boreholes in subterranean formations, particularly hydrocarbon bearing formations.

The product of the invention has the advantage of a pour point at temperatures as low as about 20 degrees Fahrenheit with minimal solvent. Thus, the product of the invention may be transported in a highly (about 90% to about 100%) active state, which reduces the need to inventory products containing different solvents for compatibility with the drilling fluid. This advantage further eliminates the need for shipping large amounts of inert material. Moreover, the product of the invention has the further advantage of providing high levels of filtration control to a drilling fluid made with conventional emulsifiers, especially at temperatures up to about 250°F. Still further, the product of this invention, when added to drilling fluids, reduces or eliminates the need for conventional fluid loss additives.

The product of this invention comprises two primary components or parts. One part is a carboxylic acid-terminated polyamide and the other part is itself a mixture produced by the Diels-Alder reaction of dienophiles, preferably carboxylic acids, polycarboxylic acids, acid anhydrides, or combinations or mixes thereof, with a mixture of fatty acids and resin acids. These two components or parts are blended or mixed and further reacted with cations to form soaps. This saponification reaction may be achieved in the manufacturing process or it may be effected "in situ" by the presence of or addition of cations to the drilling fluid. As used herein, the term "in situ" shall be understood to mean in the drilling fluid. Typically, such saponification reaction will occur in the drilling fluid when the drilling fluid is being prepared for use as a drilling fluid or when the drilling fluid is in use as a drilling fluid in drilling a borehole in a subterranean formation. Drilling fluids commonly comprise cations. Sources of such cations include, without limitation, lime, quicklime, and calcium chloride, among others. Further, drilling fluids may incorporate cations contacted in or available from the subterranean formation itself. The method of the invention employs the product of the invention for improved drilling fluids and improved drilling of boreholes in subterranean formations.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph comparing the electrical stability of a synthetic based drilling fluid

containing the product of the invention with the same synthetic based drilling fluid containing conventional emulsifiers instead of the product of the invention, using data from Tables 1 and 2.

Figure 2 is a graph comparing HTHP filtration of a synthetic based drilling fluid containing the product of the invention with the same synthetic based drilling fluid containing conventional emulsifiers instead of the product of the invention, using data from Tables 3 and 4.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS.

The product of the invention comprises a blend, mixture, or a combination (hereinafter "blend") of a carboxylic acid-terminated polyamide ("Component 'A'") and a mixture ("Component 'B'") produced by the Diels-Alder reaction of dienophiles, preferably carboxylic acids, polycarboxylic acids, and anhydrides, or combinations or mixes thereof, with a mixture of fatty acids and resin acids. Component B has a ratio of fatty acids to resin acids preferably ranging from about 4:1 to about 1:1 and a most preferred ratio of about 2:1 and is preferably comprised of fatty acids and resin acids derived from the distillation of crude tall oil.

Component A is preferably concentrated (i.e., about 90 % active), and typically made from the condensation reaction between fatty acids and polyamines. The fatty acids and polyamines are reacted in such proportion as to create a "partial amide" intermediate product having a mole ratio of the reactive acid sites to amine sites ranges from about 0.5:1 to about 0.75:1 and most preferably about 0.6:1. This partial amide intermediate product is diluted with a minimum amount of solvent, as needed for further processing, and the remaining amine sites are further reacted with an acid anhydride or polycarboxylic acid to produce the carboxylic acid-terminated polyamide.

A most preferred carboxylic acid-terminated fatty polyamide for use in the invention is EZ-MUL® NT CONCENTRATE, the active constituent of EZ-MUL® NT available from Halliburton Energy Services, Inc. in Houston, Texas, although other carboxylic acid terminated fatty polyamides are believed to be useable.

In comprising the product of the invention, the preferred ratio of Component A to Component B is about 1:5 to about 1:1. Ratios of Component A to Component B of about 1:2 to about 1:3 are most preferred. The exact ratio of these two components or parts may vary greatly depending on the exact desired characteristics of the product. Preferably, however, the quantity of Component B will exceed the quantity of Component A.

The blend comprising the product of the invention is preferably made by blending, mixing, or combining these two components-the polyamide and the modified fatty acid/resin acid mixture-together. After blending, the polyamide and fatty acid/resin acid components are reacted with cations to form soaps. Such reaction or saponification may be achieved as part of the manufacturing process of the product of the invention or may be effected in situ the drilling fluid

by the presence or addition of cations to the drilling fluid. Calcium cations are preferred and may be obtained, for example, by reacting the polyamide and modified fatty acid/resin acid components with lime, quicklime, or calcium chloride.

5 Tall oil is a commonly known product made from acid treatment of alkaline liquors obtained from the manufacture of wood pulp, and tall oil and its derivatives have previously been used in oil-well drilling muds. However, the modified fatty acid/resin acid component of the blend of the product of the invention alone is not effective for achieving the advantages of the invention. EZ-MUL® is known to have utility as an emulsifier for oil based drilling fluids. However, carboxylic acid- terminated fatty polyamides alone cannot achieve all of the advantages of the
10 invention. In the combination disclosed, however, the blend (or mixture) comprising the product of the invention provides a marked advance in the art.

The product of the invention is a powerfully efficient additive for oil or synthetic based drilling fluids, affording or effecting enhanced emulsification, and improved electrical stability and fluid loss control, with significantly less volume of additive than previously known or
15 available with prior art drilling fluid additives. The product effects or helps facilitate emulsification typically in amounts of about one-third the quantity commonly needed for emulsification of oil or synthetic based fluids with prior art emulsifiers. That is, amounts of about three pounds to about five pounds of the product of the invention per barrel of drilling fluid can be effective for emulsification. Even lower quantities can improve the electrical stability and
20 filtration control of drilling fluids, even if already emulsified with other emulsifiers.

The product of the invention does not rely on a carrier. The material comprising the product is highly active and is believed to be useful with all or substantially all synthetic and oil-based systems known to be effective for drilling fluids. The product of the invention may also add viscosity to the drilling fluid and thus is preferably added to the base drilling fluid before any
25 weighting agents such as barite, for example, are added.

The product of this invention is stable even at temperatures up to (and including) about 250 degrees Fahrenheit without filtration additives and up to about 300 to about 350 degrees Fahrenheit with filtration additives. Adding wetting agents along with the product of the invention in an emulsifier package may improve the oil-wetting nature of the drilling fluid in some base oils
30 but will not be needed in others. Wetting agents may also improve the rheological stability at temperatures up to about 300°F. The addition of wetting agents to drilling fluids comprising the product of the invention may also further enhance performance of some fluid systems.

The product of the invention has a high acid value. Consequently, improved results may be seen when a neutralizer or neutralizing agent is added to the drilling fluid. For example, a

minimum of about eight pounds of lime (or similar saponifying agent) might favorably be added per barrel of drilling fluid when about three pounds per barrel of the product of the invention are used in the drilling fluid. Additional lime (or similar saponifying agent) may be helpful or needed with larger quantities of product of the invention for optimum results, although satisfactory results might also be obtained with less.

Care is recommended when using the product of this invention to avoid over-treating. Excess emulsifiers (i.e., more than needed to effect emulsification) in drilling fluids can contribute to high fluid viscosity at cold temperatures (i.e., temperatures less than about 45 degrees Fahrenheit). For deepwater operations (i.e., use of drilling fluids at depths of water greater than about 500 feet and at temperatures less than about 45 degrees Fahrenheit), wetting agents may preferably be added to help maintain low riser viscosities as drill solids are incorporated in or become carried by the drilling fluid.

The method of the invention comprises adding the product of the invention to an oil or synthetic based drilling fluid or employing a drilling fluid comprising the product of the invention in drilling a borehole in a subterranean formation. In another embodiment, the method of the invention comprises adding the product of the invention to an oil or synthetic based drilling fluid to facilitate emulsification of the drilling fluid or the formation of invert emulsions.

Experiments were conducted that demonstrate or exemplify the invention. Several formulations of synthetic or oil-based drilling fluids were prepared, typical of those used in the field, and all of which comprised invert emulsions. Specifically, samples of drilling fluids were prepared comprising a synthetic or diesel oil base, to which additives were added, including the product of the invention or a known emulsifier for comparison, as indicated in Tables 1-12 below. The different samples were subjected to different conditions, such as high temperatures or hot rolling, or further additives or contaminants, for example, simulated drill solids or salt water, for comparison of performance and properties. The results of tests tabulated in Tables 1-4 are graphed in Figures 1 and 2.

As used in the tables, the following compounds or products have the meanings indicated below:

SF BASE™ is a synthetic oil base for drilling fluids typically used in drilling mud systems such as PETROFREE®SF, available from Halliburton Energy Services, Inc. in Houston Texas; LE BASE™ is a synthetic oil base for drilling fluids typically used in drilling mud systems such as PETROFREE® LE; GELTONE® II, is an organoclay for improving viscosity characteristics;

SUSPENTONE® is an organoclay for improving the ability of a drilling fluid to suspend drill cuttings;

INVERMUL® is an emulsifier;

EZ MUL® is an emulsifier;

5 LE SUPERMUL® is an emulsifier;

LE MUL® is an emulsifier;

DRILTREAT™ is a wetting agent;

DEEP-TREAT™ is a wetting agent;

BAROID® is barite, a weighting agent;

10 DURATONE® HT is a filtration control agent; and

BDF-258™ is the product of the invention.

All trademarks are the property of Halliburton Energy Services, Inc. and the products are available from Halliburton Energy Services, Inc. in Houston, Texas.

TABLE 1

PETROFREE® SF
14 lb/gal; 75/25 OWR with 250,000 ppm WPS

Sample Mark	A (7.33 lb/bbl Active emulsifier content)						
SF BASE, bbl	0.516						
Freshwater, bbl	0.181						
GELTONE® II, lb	3						
SUSPENTONE™, lb	1						
LE™ MUL, lb	4						
LE™ SUPERMUL, lb	6						
Lime, lb	5						
DURATONE® HT, lb	7						
BAROID®, lb	330						
Calcium chloride, lb	21.9						
DEEP-TREAT™, lb	3						
Mixed 15 minutes at 7000 rpm on a Silverson L4RT before testing; mixed 10 minutes after rolling							
Rev Dust, lb	—			45		—	
15% NaCl Brine Added, % vol	—			—		33	
Hot rolled @250°F, hr	—	16		16		16	
Temperature, °F	120	40	120	40	120	40	120
Plastic viscosity, cP	23	80	24	112	37	108	38
Yield point, lb/100 ft²	15	18	8	19	8	26	11
10 Sec gel, lb/100 ft²	8	7	6	10	7	9	6
10 Min gel, lb/100 ft²	9	11	8	18	10	12	10
Electrical stability, v	690	235		488		77	
HTHP filtrate @250°F, ml	2.4	2.4		10.4		7.6 (0.5 water)	
Fann 35 dial readings							
600 rpm	61	178	56	243	82	242	87
300 rpm	38	98	32	131	45	134	49
200 rpm	29	69	24	91	33	94	36
100 rpm	20	38	15	51	20	53	23
6 rpm	7	7	5	10	5	10	7
3 rpm	6	6	4	9	4	8	6

Note: Contaminated samples were made up with mud already hot rolled 16 hr.@250°F

TABLE 2

PETROFREE® SF
14 lb/gal; 75/25 OWR with 250,000 ppm WPS

Sample Mark	H3										
SF BASE, bbl	0.516										
Freshwater, bbl	0.181										
GELTONE® II, lb	3										
SUSPENTONE™, lb	1										
BDF-258, lb	3										
Lime, lb	8										
DURATONE® HT, lb	7										
BAROID®, lb	330										
Calcium chloride, lb	21.9										
DEEP-TREAT™, lb	3										
Mixed 15 minutes at 7000 rpm on a Silverson L4RT before testing; mixed 10 minutes after rolling											
Rev Dust, lb	—					45					—
15% NaCl Brine Added, % vol	—					—					33
Hot rolled @250°F, hr	—		—		16		16		16		
Temperature, °F	120	40	120	40	120	40	120	40	120	40	
Plastic viscosity, cP	29	78	27	72	26	N/A	49	113	43	43	
Yield point, lb/100 ft²	16	33	14	24	12	N/A	24	43	20	20	
10 Sec gel, lb/100 ft²	8	15	7	13	7	27	16	19	13	13	
10 Min gel, lb/100 ft²	10	17	9	15	9	57	36	20	13	13	
Electrical stability, v	638	669		630		884		393		393	
HTHP filtrate @250°F, ml	2.0		1.6		5.2		2.4		2.4		
Fann 35 dial readings											
600 rpm	74	189	68	168	64	O/S	122	269	106	106	
300 rpm	45	111	41	96	38	186	73	156	63	63	
200 rpm	35	82	32	72	30	139	56	116	48	48	
100 rpm	24	53	22	45	20	88	38	72	32	32	
6 rpm	9	17	8	14	8	29	15	21	12	12	
3 rpm	8	15	7	12	7	26	14	19	11	11	

Note: O/S indicates an off-scale reading, or >300. Contaminated samples were made up with mud already rolled 16 hr @250°F

TABLE 3

PETROFREE® LE
14 lb/gal; 75/25 OWR with 250,000 ppm WPS

Sample Mark	C									
LE BASE, bbl	0.5094									
Freshwater, bbl	0.1793									
GELTONE® II, lb	3.5									
SUSPENTONE™, lb	2									
LE™ MUL, lb	7									
LE™ SUPERMUL, lb	4									
Lime, lb	7									
DURATONE® HT, lb	6									
Calcium chloride, lb	21.8									
BAROID®, lb	332.3									
DEEP-TREAT™, lb	3.5									
Mixed 15 minutes at 7000 rpm on a Silverson L4RT before testing; mixed 10 minutes after rolling										
Rev Dust, lb	—				45		—			
15% NaCl Brine Added, % vol	—				—		33			
Hot rolled @250°F, hr	—		—		16		16		16	
Temperature, °F	120	40	120	40	120	40	120	40	120	120
Plastic viscosity, cP	23	94	22	77	23	82	32	87	35	35
Yield point, lb/100 ft²	12	51	9	18	6	12	5	14	4	4
10 Sec gel, lb/100 ft²	6	17	6	9	5	8	5	7	5	5
10 Min gel, lb/100 ft²	9	21	8	15	7	15	8	10	6	6
Electrical stability, v	737	676		474		545		230		
HTHP filtrate @250°F, ml	4.4			2.0			10.0			12.0–1.1 emul.
Fann 35 dial readings										
600 rpm	58	239	53	172	52	176	69	188	74	
300 rpm	35	145	31	95	29	94	37	101	39	
200 rpm	26	108	24	67	22	66	28	70	29	
100 rpm	17	66	16	38	13	37	17	38	17	
6 rpm	6	19	5	9	4	8	4	7	5	
3 rpm	5	17	4	8	3	7	3	6	4	

Note: O/S indicates an off-scale reading, or >300. Contaminated samples were made up with mud already hot rolled 16 hr @250°F

TABLE 4

PETROFREE® LE
14 lb/gal; 75/25 OWR with 250,000 ppm WPS

Sample Mark	B2									
LE BASE, bbl	0.5163									
Freshwater, bbl	0.1796									
GELTONE® II, lb	3									
SUSPENTONE™, lb	2									
BDF-258, lb	3									
Lime, lb	7									
DURATONE® HT, lb	6									
Calcium chloride, lb	21.8									
BAROID®, lb	333.2									
DEEP-TREAT™, lb	3.3									
Mixed 15 minutes at 7000 rpm on a Silverson L4RT before testing; mixed 10 minutes after rolling										
Rev Dust, lb	45									
15% NaCl Brine Added, % vol	33									
Hot rolled @250°F, hr	16									
Temperature, °F	120	40	120	40	120	40	120	40	120	120
Plastic viscosity, cP	26	72	23	64	23	98	34	96	36	36
Yield point, lb/100 ft²	12	29	9	16	7	26	6	32	11	11
10 Sec gel, lb/100 ft²	7	14	6	12	6	13	6	16	10	10
10 Min gel, lb/100 ft²	9	18	8	16	9	28	8	21	9	9
Electrical stability, v	554	615		568		574		269		
HTHP filtrate @250°F, ml		2.2		2.2		3.0		1.8		
Fann 35 dial readings										
600 rpm	64	173	55	144	53	222	74	224	83	
300 rpm	38	101	32	80	30	124	40	128	47	
200 rpm	29	75	25	58	23	89	29	94	36	
100 rpm	20	47	17	35	15	52	18	58	23	
6 rpm	7	15	6	10	6	13	4	16	8	
3 rpm	6	14	5	9	5	11	3	14	7	

Note: O/S indicates an off-scale reading, or >300. Contaminated samples were made up with mud already hot rolled 16 hr @250°F

TABLE 5

PETROFREE® SF
14 lb/gal; 75/25 OWR with 250,000 ppm WPS

Sample Mark	H2										
SF BASE, bbl	0.516										
Freshwater, bbl	0.181										
GELTONE® II, lb	3										
SUSPENTONE™, lb	1										
BDF-258, lb	3										
Lime, lb	8										
DURATONE® HT, lb	7										
BAROID®, lb	330										
Calcium chloride, lb	21.9										
DEEP-TREAT™, lb	3										
DRILTREAT®, lb	1										
Mixed 15 minutes at 7000 rpm on a Silverson L4RT before testing; mixed 10 minutes after rolling											
Rev Dust, lb	—										
15% NaCl Brine Added, % vol	—										
Hot rolled @250°F, hr	—										
Temperature, °F	120	40	120	40	120	40	120	40	120	40	120
Plastic viscosity, cP	28	82	25	86	25	86	N/A	46	116	41	41
Yield point, lb/100 ft²	14	36	16	29	14	29	N/A	22	45	22	22
10 Sec gel, lb/100 ft²	7	17	7	14	8	28	18	19	12	12	12
10 Min gel, lb/100 ft²	10	20	9	18	10	60	31	21	12	12	12
Electrical stability, v	603	694		684		846		409		409	
HTHP filtrate @250°F, ml	1.2		1.6		4.0		1.6				
Fann 35 dial readings											
600 rpm	70	200	66	201	64	O/S	114	277	104	104	104
300 rpm	42	118	41	115	39	201	68	161	63	63	63
200 rpm	33	89	32	84	30	149	52	119	48	48	48
100 rpm	22	57	22	51	21	93	34	74	33	33	33
6 rpm	8	19	8	15	8	28	13	22	13	13	13
3 rpm	7	17	7	14	7	24	12	19	12	12	12

Note: O/S indicates an off-scale reading, or >300. Contaminated samples were made up with mud already rolled 16 hr @250°F

TABLE 6

PETROFREE® SF
14 lb/gal; 75/25 OWR with 250,000 ppm WPS
NO DURATONE® HT

Sample Mark	O											
SF BASE, lb	0.516											
Freshwater, bbl	0.181											
GELTONE® II, lb	4											
SUSPENTONE™, lb	1											
BDF-258, lb	3											
Lime, lb	9											
Calcium chloride, lb	21.9											
BAROID®, lb	330											
DRILTREAT®, lb	1											
DEEP-TREAT™, lb	3											
Mixed 15 minutes at 7000 rpm on a Silverson L4RT before testing; mixed 10 minutes after rolling												
Hot rolled @250°F, hr	—	—	—	16	16	16	16	16	16	16	16	16
Rev Dust, lb	—	—	—	—	—	—	—	—	—	—	—	—
15% NaCl brine, % vol	—	—	—	—	—	—	—	—	—	—	—	33
Temperature, °F	120	40	120	40	120	40	120	40	120	40	120	120
Plastic viscosity, cP	28	88	33	85	29	N/A	50	N/A	50	N/A	69	69
Yield point, lb/100 ft²	5	19	8	20	8	N/A	5	N/A	5	N/A	45	45
10 Sec gel, lb/100 ft²	5	10	7	9	5	5	3	48	25	25	25	25
10 Min gel, lb/100 ft²	8	14	9	13	7	14	10	> 60	62	62	62	62
Electrical stability @120°F, v	471	519	496 / 230	218	4.0	285	285	285	285	285	285	285
HTHP filtrate @250°F, ml	0.2		1.6		4.0		3.4 – 0.4 H₂O		3.4 – 0.4 H₂O		3.4 – 0.4 H₂O	
Fann 35 dial readings												
600 rpm	61	195	74	190	66	O/S	105	O/S	183	O/S	183	183
300 rpm	33	107	41	105	37	173	55	O/S	114	O/S	114	114
200 rpm	25	75	31	75	27	123	39	256	87	256	87	87
100 rpm	16	43	20	44	17	68	21	163	57	163	57	57
6 rpm	5	10	7	10	5	7	3	45	26	45	26	26
3 rpm	4	8	6	8	4	5	2	40	24	40	24	24

Note: O/S indicates an off-scale reading, or >300. Contaminated samples were made up with mud already rolled 16 hr @250°F

TABLE 7

INVERMUL®
14 lb/gal; 250,000 WPS

Sample Mark	1	2	3	4	5			
Diesel, bbl	0.5395	0.5234	0.5679	0.5743	0.5608			
Fresh water, bbl	0.1814	0.1815	0.1449	0.1453	0.1454			
<i>Oil-to-Water Ratio</i>	<i>75/25</i>	<i>75/25</i>	<i>80/20</i>	<i>80/20</i>	<i>80/20</i>			
GELTONE® II, lb	2	2	2	2	2			
SUSPENTONE™, lb	1	1	—	—	—			
BDF-258, lb	3.5	-	6	3	—			
INVERMUL® NT, lb	—	3	—	—	3			
Lime, lb	8	8	12	8	8			
DURATONE® HT, lb	6	6	6	6	6			
EZ MUL® NT, lb	—	6	—	—	6			
Calcium chloride, lb	22.0	22.1	17.6	17.7	17.7			
BAROID®, lb	302	301	307	310	309			
Rev Dust, lb	20	20	20	20	20			
DRILTREAT®, lb	—	—	—	1.5	—			
Hot rolled @300°F, hr	—	—	—	16	—	16	—	16
Plastic viscosity @150°F, cP	25	26	21	23	22	19	20	22
Yield point, lb/100 ft ²	31	53	17	11	13	9	30	8
10 Sec gel, lb/100 ft ²	26	32	12	14	8	8	16	8
10 Min gel, lb/100 ft ²	34	34	23	29	15	16	16	9
Electrical stability, v	593	1140	923	1302	697	783	1404	766
HTHP filtrate @300°F, ml	11.6*	3.8	6.2	16.4	5.6	10.0	5.4	7.6
Fann 35 dial readings								
600 rpm	81	105	59	57	57	47	70	52
300 rpm	56	79	38	34	35	28	50	30
200 rpm	46	69	30	26	28	21	42	23
100 rpm	36	56	22	17	19	14	32	16
6 rpm	21	33	10	8	8	7	17	7
3 rpm	20	32	9	7	7	6	16	6

*Trace of water/emulsion was seen in the filtrate.

TABLE 8

INVERMUL®
14 lb/gal; 80/20 OWR with 250,000 WPS

Sample Mark	10	11
Diesel, bbl	0.577	0.577
Fresh water, bbl	0.145	0.145
GELTONE® II, lb	6	6
BDF-258, lb	3	3
Lime, lb	8	8
Calcium chloride, lb	17.6	17.6
DEEP-TREAT™, lb	1.5	1
BAROID®, lb	312	312
Rev Dust, lb	20	20
DRILTREAT®, lb	—	1

Hot rolled @150°F, hr	16	—	16	—
Hot rolled @250°F, hr	—	16	—	16
Plastic viscosity @150°F, cP	23	24	23	24
Yield point, lb/100 ft ²	28	10	25	12
10 Sec gel, lb/100 ft ²	17	10	18	11
10 Min gel, lb/100 ft ²	22	16	20	20
Electrical stability, v	686	783	561	723
HTHP filtrate @250°F, ml	5.6	6.8	6.6	9.4
HTHP filt.cake thickness, 1/32"	4	3	5	5
Fann 35 dial readings				
600 rpm	74	58	71	60
300 rpm	51	34	48	36
200 rpm	42	26	39	28
100 rpm	32	17	30	19
6 rpm	17	7	17	8
3 rpm	16	6	17	8

Note: 0.4 lb/bbl DEEP-TREAT™ was sufficient to wet in the barite and Rev Dust in mud 11. Additional product was added after the Rev Dust to total 1 lb/bbl.

TABLE 9

PETROFREE® SF
14 lb/gal; 75/25 OWR with 250,000 ppm WPS
NO DURATONE® HT

Sample Mark	I										
SF BASE, bbl	0.516										
Freshwater, bbl	0.181										
GELTONE® II, lb	4										
SUSPENTONE™, lb	1										
BDF-258, lb	3.5										
Lime, lb	9										
DURATONE® HT, lb	-										
Calcium chloride, lb	21.9										
DEEP-TREAT™, lb	3										
BAROID®, lb	330										
Mixed 15 minutes at 7000 rpm on a Silverson L4RT before testing; mixed 10 minutes after rolling											
Hot rolled @250°F, hr	—	—	—	—	16	16	16	16	16	16	16
Rev Dust, lb	45										
15% NaCl Brine Added, % vol	—										
Temperature, °F	120	40	120	40	120	40	120	40	120	58	120
Plastic viscosity, cP	29	85	32	76	31	N/A	54	N/A	71	N/A	71
Yield point, lb/100 ft²	9	17	9	15	6	N/A	7	N/A	53	N/A	53
10 Sec gel, lb/100 ft²	7	10	8	9	7	6	4	55	34	55	34
10 Min gel, lb/100 ft²	8	15	11	10	7	13	8	-	65	-	65
Electrical stability, v	482	529		241		234		293		293	
HTHP filtrate @250°F, ml		1.6		2.8*		6.0		5.0 - 1.0 H₂O		5.0 - 1.0 H₂O	
Fann 35 dial readings											
600 rpm	67	187	73	167	68	O/S	115	O/S	195	O/S	195
300 rpm	38	102	41	91	37	186	61	278	124	278	124
200 rpm	29	73	31	65	28	130	43	220	97	220	97
100 rpm	19	42	20	38	18	71	23	151	67	151	67
6 rpm	6	10	7	9	6	8	3	53	29	53	29
3 rpm	5	8	6	7	5	5	2	50	28	50	28

Note: O/S indicates an off-scale reading, or >300. Contaminated samples were made up with mud already rolled 16 hr @250°F

*Some small water droplets were observed in the filtrate

TABLE 10

PETROFREE® SF
 14 lb/gal; 75/25 OWR with 250,000 ppm WPS
 NO DURATONE® HT

Sample Mark	N										
SF BASE, lb	0.516										
Freshwater, bbl	0.181										
GELTONE® II, lb	4										
SUSPENTONE™, lb	1										
BDF-258, lb	3.5										
Lime, lb	9										
Calcium chloride, lb	21.9										
DEEP-TREAT™, lb	4										
BAROID®, lb	330										
Mixed 15 minutes at 7000 rpm on a Silverson L4RT before testing; mixed 10 minutes after rolling											
Hot rolled @250°F, hrs	—	—	—	16	16	16	16	16	16	16	
Rev Dust, lb					45				—		
15% NaCl brine, % vol					—				—		
DEEP-TREAT™, lb					—				2		
Temperature, °F	120	40	120	40	120	40	120	40	120	40	
Plastic viscosity, cP	35	103	38	80	31	124	44	N/A	53	53	
Yield point, lb/100 ft²	11	18	11	16	6	22	5	N/A	10	10	
10 Sec gel, lb/100 ft²	8	10	7	8	6	5	5	8	6	6	
10 Min gel, lb/100 ft²	14	16	11	9	7	8	7	10	7	7	
Electrical stability @120°F, v	503	527	209		275		156				
HTHP filtrate @250°F, ml		0.6	1.2		1.6		1.0 — trace emul				
Fann 35 dial readings											
600 rpm	81	224	87	176	68	270	93	O/S	116		
300 rpm	46	121	49	96	37	146	49	189	63		
200 rpm	35	85	37	68	29	101	35	134	44		
100 rpm	22	49	24	39	18	55	20	74	25		
6 rpm	7	10	7	8	6	6	4	10	5		
3 rpm	6	8	6	7	5	4	3	7	4		

Note: O/S indicates an off-scale reading, or >300. Contaminated samples were made up with mud already rolled 16 hr @250°F

TABLE 11

PETROFREE® SF
14 lb/gal; 75/25 OWR with 250,000 ppm WPS

Sample Mark	BB										
SF BASE, lb	0.516										
Freshwater, bbl	0.181										
GELTONE® II, lb	4										
SUSPENTONE™, lb	1										
BDF-258, lb	3.5										
Lime, lb	9										
Calcium chloride, lb	21.9										
BD QUAT 2HT, lb	1										
BAROID®, lb	330										
DEEP-TREAT™, lb	3										
Mixed 15 minutes at 7000 rpm on a Silverson L4RT before testing; mixed 10 minutes after rolling											
Hot rolled @250°F, hr	—	—	—	16	16	16	16	16	16	16	16
Rev Dust, lb	—	—	—	—	—	45	—	—	—	—	—
15% NaCl brine, % vol	—	—	—	—	—	—	—	—	—	25	—
Temperature, °F	120	40	120	40	120	40	120	40	120	40	120
Plastic viscosity, cP	29	76	30	75	28	119	40	119	40	119	43
Yield point, lb/100 ft²	15	32	17	24	10	16	6	35	14	35	14
10 Sec gel, lb/100 ft²	8	14	8	11	7	7	5	15	8	15	8
10 Min gel, lb/100 ft²	13	17	9	12	8	11	10	15	9	15	9
Electrical stability @120°F, v	633	*486 average		333	576		223				
HTHP filtrate @250°F, ml		2.2		5.4	4.0		3.0 – 0.2 emul.				
Fann 35 dial readings											
600 rpm	73	184	77	174	66	254	86	273	100	273	100
300 rpm	44	108	47	99	38	135	46	154	57	154	57
200 rpm	34	81	36	73	30	93	33	111	42	111	42
100 rpm	23	52	24	45	19	50	19	65	26	65	26
6 rpm	8	16	8	13	7	7	4	15	8	15	8
3 rpm	7	14	7	11	6	5	3	13	7	13	7

Note: Contaminated samples were made up with mud already hot rolled 16 hr. @250°F

*ES readings ranged from 347 to 656 volts.

TABLE 12

14.0 lb/gal PETROFREE® SF
70/30 OWR; 250,000 ppm WPS

Sample Mark	Base - D. Carbajal FLC Evaluation Data					
SF BASE, bbl	0.505					
Freshwater, bbl	0.220					
GELTONE® II, lb	3					
LE™ MUL, lb	3					
LE™ SUPERMUL, lb	3					
Lime, lb	5					
BAROID®, lb	330					
Calcium chloride, lb	27					
<i>A 3-gal. batch was mixed at low shear; then 30 min on a Silverson L4RT</i>						
BDF-258, lb	—		1.5		3	
<i>Samples were mixed, then hot rolled 16 hours at 150°F</i>						
<i>Temperature, °F</i>	<i>40</i>	<i>120</i>	<i>40</i>	<i>120</i>	<i>40</i>	<i>120</i>
Plastic viscosity, cP	75	26	90	30	97	32
Yield point, lb/100 ft ²	26	16	37	30	39	33
10 Sec gel, lb/100 ft ²	17	10	30	17	32	19
10 Min gel, lb/100 ft ²	18	12	30	20	33	24
Electrical stability, volts	259		650		679	
HTHP filtrate @250°F, ml oil	11.8		3.2		Trace	
HTHP filtrate @250°F, ml H ₂ O	5.6		—		—	
Fann 35 dial readings						
600 rpm	176	68	217	90	233	97
300 rpm	101	42	127	60	136	65
200 rpm	74	33	94	49	101	54
100 rpm	47	27	61	36	66	40
6 rpm	16	10	23	17	26	20
3 rpm	16	9	20	15	23	18

These experimental results show that the product of the invention has emulsion-forming capabilities comparable to or exceeding prior art emulsifiers at only about one-third the concentration and that the product of the invention improves the electrical stability of the drilling fluid, even after heat stress. These results also show that the product of the invention imparts very low filtration properties to the drilling fluids. Further, the product of the invention provides significantly better filtration control than conventional emulsifiers, especially when used with a wetting agent, even after solids and brine contamination. Still further, the tests showed that no fluid loss control additives were needed for the same filtration properties as prior art emulsifiers when the product of the invention was used. The tests also indicate that the product of the invention performs well with other emulsifying products, which should allow simpler maintenance treatments in oil or synthetic based fluids when using the product of the invention.

In the method of the invention, the product of the invention is added to an oil or synthetic based drilling fluid or a drilling fluid comprising an invert emulsion to improve or facilitate the emulsification of the oil or synthetic base fluid.

The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described product and method can be made without departing from the intended scope of this invention as defined by the appended claims.

1 We claim:

- 2 1. A drilling fluid comprising an oil or synthetic base and further comprising a blend of a
3 carboxylic acid terminated polyamide and a mixture produced by the Diels-Alder reaction
4 of dienophiles with a mixture of fatty acids and resin acids.
- 5 2. The drilling fluid of claim 1 wherein said dienophiles are selected from the group
6 comprising carboxylic acids, polycarboxylic acids, acid anhydrides, and mixes thereof.
- 7 3. The drilling fluid of claim 1 wherein said mixture of fatty acids and resin acids are derived
8 from the distillation of tall oil.
- 9 4. The drilling fluid of claim 1 wherein said dienophiles are maleic anhydrides.
- 10 5. The drilling fluid of claim 1 wherein said mixture has a ratio of fatty acids to resins acids
11 ranging from about 4:1 to about 1:1.
- 12 6. The drilling fluid of claim 1 wherein said mixture has a ratio of fatty acids to resin acids
13 of about 2:1.
- 14 7. The drilling fluid of claim 1 wherein the ratio of polyamide to said mixture is about 1:5
15 to about 1:1.
- 16 8. The drilling fluid of claim 1 wherein the ratio of said polyamide to said mixture is about
17 1:2 to about 1:3.
- 18 9. The drilling fluid of claim 1 wherein said blend is saponified.
- 19 10. The drilling fluid of claim 9 wherein said saponification is effected with calcium chloride,
20 lime, quicklime, or other sources of calcium cations.
- 21 11. The drilling fluid of claim 9 wherein said saponification occurs in situ.
- 22 12. The drilling fluid of claim 9 wherein said saponification occurs before said blend is added
23 to said drilling fluid.
- 24 13. The drilling fluid of claim 1 further comprising lime, calcium chlorides, quicklime, or
25 other saponifying agents.
- 26 14. The drilling fluid of claim 1 further comprising wetting agents.
- 27 15. The drilling fluid of claim 1 wherein said blend provides filtration control.
- 28 16. The drilling fluid of claim 1 wherein said blend provides emulsification.
- 29 17. The drilling fluid of claim 1 wherein said blend provides electrical stability.
- 30 18. An emulsifier comprising a blend of a carboxylic acid terminated polyamide and a mixture
31 produced by the Diels-Alder reaction of dienophiles selected from the group comprising
32 carboxylic acids, polycarboxylic acids, and acid anhydrides, and combinations or mixes
33 thereof, with a mixture of fatty acids and resin acids derived from the distillation of crude
34 tall oil, wherein said mixture comprises a ratio of fatty acids to resin acids ranging from

about 4:1 to about 1:1, and wherein the ratio of said polyamide to said mixture in said blend ranges from about 1:5 to about 1:1.

19. The emulsifier of claim 18 wherein said blend is saponified.

20. The emulsifier of claim 19 wherein said saponification is effected by reaction of said blend with calcium cations.

21. An additive for improving the properties of an invert emulsion comprising water or brine in an oil or synthetic based drilling fluid for use in drilling a borehole in a subterranean formation, said additive comprising a blend of a carboxylic acid terminated polyamide and a mixture produced by the Diels-Alder reaction of dienophiles, selected from compounds or reagents selected from the group comprising carboxylic acids, polycarboxylic acids, acid anhydrides, and combinations or mixes thereof, with a mixture of fatty acids and resin acids derived from the distillation of crude tall oil, wherein said acid mixture comprises a ratio of fatty acids to resin acids ranging from about 4:1 to about 1:1, and wherein the ratio of said polyamide to said mixture in said blend ranges from about 1:5 to about 1:1.

22. The additive of claim 21 wherein said additive is saponified.

23. The additive of claim 22 wherein said properties comprise emulsification.

24. The additive of claim 22 wherein said properties comprise filtration control.

25. The additive of claim 22 wherein said properties comprise electrical stability.

26. A method for drilling a borehole in a subterranean formation, said method comprising employing an oil or synthetic based drilling fluid comprising an invert emulsion and an additive comprising a blend of a carboxylic acid terminated polyamide and a mixture produced by the Diels-Alder reaction of compounds or reagents with a mixture of fatty acids and resin acids wherein said compounds or reagents are selected from the group comprising carboxylic acids, polycarboxylic acids, acid anhydrides and combinations or mixes thereof.

27. The method of claim 26 wherein said acid mixture is comprised of fatty acids and resin acids derived from the distillation of tall oil.

28. The method of claim 26 wherein said mixture has a ratio of fatty acids to resin acids ranging from about 4:1 to about 1:1.

29. The method of claim 26 wherein said mixture has a ratio of fatty acids to resin acids of about 2:1.

30. The method of claim 26 wherein the ratio of said polyamide to said mixture is about 1:5 to about 1:1.

- 1 31. The method of claim 26 wherein the ratio of said polyamide to said mixture is about 1:2
2 to about 1:3.
- 3 32. The method of claim 26 wherein said blend is saponified.
- 4 33. The method of claim 32 wherein said blend is saponified with calcium chloride, lime,
5 quicklime, or other sources of calcium cations.
- 6 34. The method of claim 32 wherein said saponification occurs in situ.
- 7 35. The method of claim 32 wherein said saponification occurs before said blend is added to
8 said drilling fluid.
- 9 36. A method for improving or facilitating the emulsification of an oil or synthetic based
10 drilling fluid or a drilling fluid comprising an invert emulsion, said method comprising
11 adding to said drilling fluid a blend of a carboxylic acid terminated polyamide and a
12 mixture produced by the Diels-Alder reaction of dienophiles with a mixture of fatty acids
13 and resin acids.
- 14 37. The method of claim 36 wherein said dienophiles are selected from the group comprising
15 carboxylic acids, polycarboxylic acids, acid anhydrides, and combinations or mixes
16 thereof.
- 17 38. A method for improving the filtration properties of an oil or synthetic based drilling fluid
18 or a drilling fluid comprising an invert emulsion, said method employing adding to said
19 drilling fluid a blend of a carboxylic acid terminated polyamide and a mixture produced
20 by the Diels-Alder reaction of dienophiles with a mixture of fatty acids and resin acids.
- 21 39. The method of claim 38 wherein said dienophiles are selected from the group comprising
22 carboxylic acids, polycarboxylic acids, acid anhydrides, and combinations or mixes
23 thereof.
- 24 40. A method for improving the electrical stability of an oil or synthetic based drilling fluid,
25 or a drilling fluid comprising an invert emulsion, said method comprising adding to said
26 fluid a blend of a carboxylic acid terminated polyamide and a mixture produced by the
27 Diels-Alder reaction of dienophiles with a mixture of fatty acids and resin acids.
- 28 41. The method of claim 40 wherein said dienophiles are selected from the group comprising
29 carboxylic acids, polycarboxylic acids, acid anhydrides, and combinations or mixes
30 thereof.

1/1

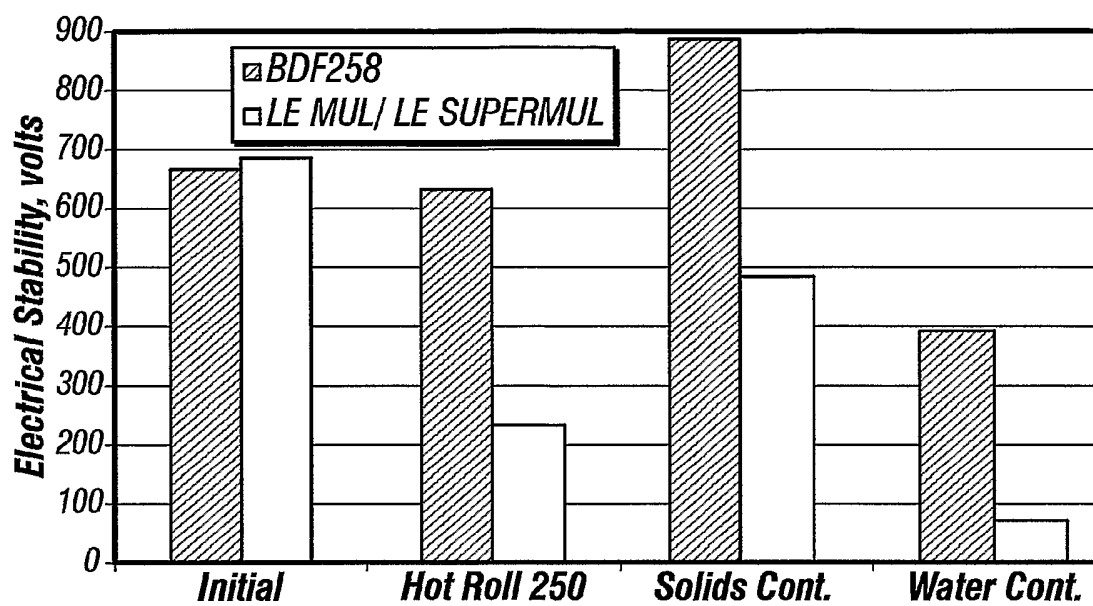


FIG. 1

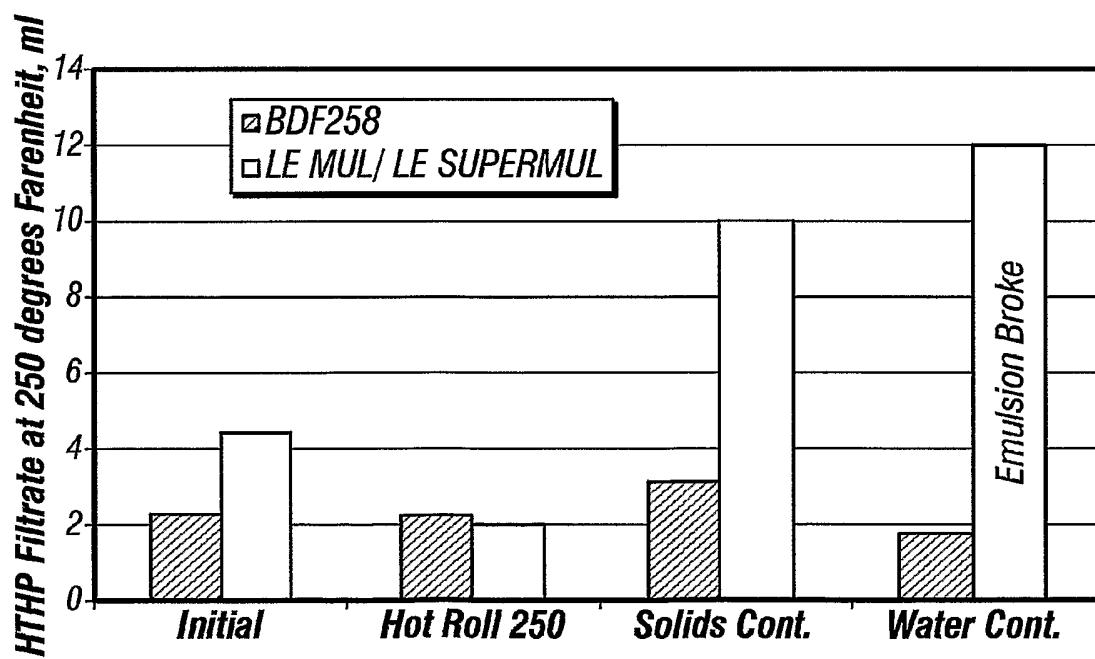


FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/34667

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K7/06 B01F17/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K B01F

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- * & * document member of the same patent family

Date of the actual completion of the international search

5 February 2003

Date of mailing of the international search report

11/02/2003

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/34667

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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