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(54) Title: ETHOXYLATED RAW COTTON LINTERS FOR COMPLETION AND WORKOVER FLUIDS

(57) Abstract: A completion and workover fluid composition comprising, water and at least one rheology modifier and/or fluid loss control agent, and at least one other ingredient selected from the group consisting of inorganic salts, shale inhibitors, corrosion inhibitor, biocide, defoamers and finely divided solids particles (e.g., bentonite, attapulgite, sepiolite, calcium carbonate, etc.), depending upon the desired attributes, wherein the rheology modifier and/or the fluid loss control agent is an ethoxylated raw cotton linters or a modified ethoxylated raw cotton linters. The ethoxylated raw cotton linters provides comparable or better rheology and viscosity properties compared to high molecular weight commercial HECs made from purified cotton linters. These ethoxylated raw cotton linters derivatives are suitable for applications in oil-well servicing fluids, particularly to enhance functional properties of completion and workover fluids used during oil-well drilling operations.



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**ETHOXYLATED RAW COTTON LINTERS
FOR COMPLETION AND WORKOVER FLUIDS**

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 60/778,040, filed on February 23, 2006, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention relates to the use of non-ionic polymers in oil-well servicing fluids. More specifically, this invention relates to the use of ethoxylated raw cotton linters as an effective additive to control the rheology and/or reduce fluid loss of completion and workover fluids.

BACKGROUND OF THE INVENTION

[0003] Completion fluids are composed of a variety of brines of different salinity characterized by a density ranging from 8.5 pounds per gallon (ppg) for seawater to 19.2 ppg for heavy brines containing zinc bromide and calcium bromide. Currently, high viscosity grade hydroxyethylcelluloses (HECs), such as Natrosol® HEC 250 HHR-P, Natrosol® HEC HI-VIS and Natrosol® HEC 210 HHW (available from Hercules Incorporated) are used as thickeners for brines having density from 9-13 ppg. These Natrosol® HECs are presently manufactured using purified cotton linters and are characterized by a 1% aqueous solution having a Brookfield viscosity exceeding 5,000 cPs. For lower density, non-calcium based brines, xanthan gum is the polymer of choice for its high carrying capacity and gel strength.

[0004] Currently, there is no efficient viscosifier for heavy brines with a density ranging from 14 ppg (CaBr_2) to 19.2 ppg ($\text{ZnBr}_2/\text{CaBr}_2$). These brines have a very low level of free water, and therefore, do not promote optimum hydration of standard HECs. As the salt content in the brine solution is increased, the hydration rate of the HEC dramatically decreases, and it takes longer time to build

the desired viscosity. Furthermore, these brines are characterized by a very low pH (pH < 1 for ZnBr₂/CaBr₂).

[0005] Obviously, there is a need to develop an HEC or an analogous polymer that has very high solution viscosity and dissolves rapidly in high density brines. While technically it is possible to increase the viscosity of the HECs by reducing their average oxyethylene molar substitution (MS), the manufacture of such low MS HECs is difficult.

SUMMARY OF THE INVENTION

[0006] The present invention is directed to a completion and workover fluid composition. The completion and workover fluid composition comprises water and at least one rheology modifier and/or fluid loss control agent, and at least one other ingredient selected from the group consisting of polymeric additive, inorganic salts, shale stabilizers, corrosion inhibitors, weighting agents, and finely divided solid particles (e.g., bentonite, attapulgite, sepiolite, calcium carbonate, etc.), the selection of which is dependent upon the desired attributes of the completion and workover fluids composition. The rheology modifier and/or the fluid loss control agent is an ethoxylated raw cotton linters (EO-RCL). The EO-RCL of use in the completion and workover fluids compositions of the present invention may be an unmodified EO-RCL or a modified EO-RCL. The EO-RCL is made by grafting ethylene oxide (EO) onto RCL. Modified EO-RCLs contain an additional substituent such as carboxymethyl groups and/or hydrocarbyl groups containing 1-30 carbon atoms. The EO-RCLs provide better viscosifying properties and rheology than the HECs made from purified cotton linters. The EO-RCLs provide improved functional properties in completion and workover fluids.

BRIEF DESCRIPTION OF THE FIGURES

[0007] Figure 1 is a line graph depicting the rheological profiles of a fluid of Example 1 and a fluid containing a currently available high viscosity grade hydroxyethylcellulose (Comparative Example 2) in various low density brines.

[0008] Figure 2 is a line graph depicting the rheological profiles of a fluid of Example 1 and a fluid containing a currently available high viscosity grade hydroxyethylcellulose (Comparative Example 2) in various high density brines.

[0009] Figure 3 is a line graph depicting the viscosity profiles of a fluid of Example 1 and a fluid containing a currently available high viscosity grade hydroxyethylcellulose (Comparative Example 2) at a high sheer rate of 510s^{-1} .

[0010] Figure 4 is a line graph depicting the viscosity profiles of a fluid of Example 1 and a fluid containing a currently available high viscosity grade hydroxyethylcellulose (Comparative Example 2) at a low sheer rate of 5.1s^{-1} .

DETAILED DESCRIPTION OF THE INVENTION

[0011] Raw cotton linters ("RCL") are an excellent source of high molecular weight cellulose. Raw cotton linters, also commonly referred to as "linters", are short fiber residues which are left on the cottonseed after the longer staple ("lint") fibers are removed by ginning and which have not been subjected to chemical cleaning steps which are typically performed to yield high purity furnish. Linters are shorter, thicker, and more colored fibers than lint. They, also, adhere more strongly to the cotton-seed relative to lint. Raw cotton linters are removed from cottonseeds using a number of technologies including linter saws and abrasive grinding methods, both of which yield suitable materials. The amount of hemicellulose, lignin or colored impurities and foreign matter in the various types of raw cotton linters increases with the number of passes or "cuts" used in removing the linter from the cottonseed. The first-cut linters typically contain the least amount of impurities and foreign matter and subsequent cuts contain more impurities and foreign matter. Typically, the cellulose content of RCL is about 69-78 wt % as measured by the American Oil Chemists' Society (AOCS) "bB 3-47: Cellulose Yield Pressure-Cook Method". The balance of noncellulosic materials found in the RCL consists primarily of seed hulls, dirt, field trash, lignin, hemicellulose, wax, fat, protein, moisture and traces of other organic impurities.

[0012] The ether derivatives of RCL may be produced by processes known in the art such as those disclosed in German Patent Application No. 4,034,709 A1

which describes the preparation of high molecular weight methylcellulose, ethylcellulose and hydroxyalkyl alkyl celluloses from RCL, or U.S. Pat. No. 5,028,342 which describes the use of a mixture of 20 to 80% by weight of a crude (technical grade) carboxymethyl cellulose obtained from RCL and/or wood cellulose by a slurry process and 20 to 80% of a polycarboxylic acid in making drilling fluids.

[0013] One process for producing EO-RCL is more fully described in US Patent Application 20050228174 (US Serial No. 10/822, 926) to Gillette, et al. which is incorporated herein by reference in its entirety. In this patent, a process is disclosed for making an EO-RCL using RCL as a starting material includes a) treating the RCL with a base in a slurry or high solids process at a cellulose concentration of greater than 9 wt % to form an activated cellulose slurry, b) reacting the activated cellulose slurry with an etherifying agent (ethylene oxide) to form an EO-RCL, and c) recovering the EO-RCL.

[0014] Alternatively, the order of treatment of the RCL with a base solution (step a) and etherifying agent (step b) can be reversed. It is also possible to perform steps a) and b) simultaneously.

[0015] In this process for preparing ether derivatives, the base can be either organic or inorganic or mixtures thereof. The inorganic bases include sodium hydroxide, potassium hydroxide, calcium hydroxide, barium hydroxide, ammonium hydroxide, lithium hydroxide, and mixtures thereof. The organic bases must be strong and include, but are not limited to, amines and quaternary ammonium hydroxides.

[0016] In the preparation of the ether derivatives, the etherifying agent includes alkyl halides (e.g., methyl and ethyl chloride), alkenyl halides (e.g., ethylene and propylene halide), alkylene oxides (e.g. ethylene oxide, propylene oxide, and butylene oxide), alkyl glycidyl ethers, metal salts of alpha-halogenoalkanoates, vinyl sulfonates, and mixtures thereof. Other etherifying agents are monochloroacetic acid and salts thereof, butyl glycidyl ether, and glycidyl silane (e.g., 3-glycidoxypropyltrimethoxysilane and 3-

glycidoxypopylmethyldimethoxysilane). For use in the present invention, the preferred ether derivative is EO-RCL.

[0017] In US Patent Application 20050228174, an example is provided which sets forth a process for producing EO-RCL is described as follows:

[0018] To a Chemco reactor containing a mixture of t-butyl alcohol (611.2 g), isopropanol (28.8 g), acetone (21.6 g), and water (59.07 g) were charged cut second-cut raw cotton linters (80 g on a dry basis). After sealing the reactor, the atmosphere in the reactor was rendered inert by five cycles of evacuation and nitrogen purging. Then, under agitation, 50% caustic solution (44.8 g) was added slowly to the raw cotton linters slurry. The resulting slurry was mixed at 20°C for 45 minutes and then ethylene oxide (76 g) was added. The resulting mixture was heated at 55°C for 25 minutes and then at 95°C for 30 minutes. Following this, the reaction mixture was cooled to 50°C and treated with 70% nitric acid (50.4 g). The reaction mixture was subsequently cooled to room temperature and filtered under vacuum. The residue was washed three times with 80:20 (w/w) acetone/water mixture and the purified polymer was dehydrated with acetone. The dehydrated polymer was dried in a fluid bed dryer at 70°C for 0.5 hour.

[0019] The hydroxyethyl molar substitution (MS), which is defined as the average number of moles of ethylene oxide grafted per mole of anhydroglucose unit of the cellulose, of the product was 2.67. The 1% aqueous solution Brookfield viscosity of the EO-RCL was 5620 cPs at 30 rpm at 25°C.

[0020] To practice the present invention, EO-RCL can be made from "as supplied" RCL, such as first-cut, second-cut, third-cut and "mill run" RCL. If needed, seed hulls and other impurities that are physically held to the fibers could be substantially removed by mechanical means, such as sieving and centrifugation or a combination thereof prior to ethoxylation. The separation of impurities from RCL can be done in the dry or wet condition.

[0021] To prepare the EO-RCL, the RCL can be used "as is" or pulverized or comminuted to shorten the fiber length. The pulverization can be carried out

separately or it can be done simultaneously as the RCL is being treated with the base and/or the ethoxylating agent. It is important that no substantial molecular degradation of the polymeric species present in RCL occurs during the pulverization step. To prevent this from happening, the pulverization should be conducted in an inert atmosphere, such as in nitrogen, and at low temperatures.

[0022] It has been surprising to find that EO-RCLs are efficient thickeners of completion and workover fluids in conjunction with a wide range of brines. Particularly, they provide more efficient thickening capacity in high density brines relative to existing HECs

[0023] To practice the utilization of the EO-RCL in completion and workover fluids as a thickener and/or fluid loss control agent, the oxyethylene molar substitution (MS) of the EO-RCL should have a lower limit of about 0.5, preferably a lower limit of about 1.5, more preferably a lower limit of about 1.8. To practice the utilization of the EO-RCL in completion and workover fluids as a thickener and/or fluid loss control agent, the oxyethylene MS of the EO-RCL should have an upper limit of about 3.5, more preferably an upper limit of about 2.5, still more preferably an upper limit of about 2.2. The oxyethylene MS of the EO-RCL should be in a range of from about 0.5 to about 3.5, preferably, the MS should be in a range of from about 1.5 to 2.5 and most preferably the MS should be in a range of from about 1.8 to 2.2.

[0024] The EO-RCL can be used as an additive in completion and workover fluids with or without purification. The term "purification" is defined as the removal of the low molecular weight by-products formed during the ethoxylation of the RCL. These by-products can be removed partially or completely. The use level of the EO-RCL in the drilling fluid will be dictated by the purity of the EO-RCL. The purer the EO-RCL the lesser the amount of EO-RCL that needs to be used in the completion and workover fluids.

[0025] To meet the desired application properties, such as rheology and/or fluid loss control of various types of completion and workover fluids, the MS and molecular weight of the EO-RCL could be tailored. The molecular weight of the

EO-RCL can be lowered by treating the EO-RCL with degradation agents, such as an acid, a mixture of caustic and oxygen, peroxides, hypochlorites, chlorites, cellulolytic enzymes or radiation. The molecular degradation of EO-RCL can be carried out in situ or after its isolation in a slurry process or solution.

[0026] The completion and workover fluid compositions of the present invention comprising EO-RCL may also contain other polymeric additives which are used in completion and workover fluid compositions. These other polymeric additives may be selected from the group consisting of starch and its derivatives, guar gum and its derivatives, xanthan gum, welan gum, diutan gum, cellulose ethers, polyacrylates, polyacrylamides and mixtures thereof.

[0027] The completion and workover fluid compositions of the present invention comprising EO-RCL may also contain inorganic salts selected from the group consisting of calcium carbonate, calcium chloride, potassium chloride, sodium chloride, magnesium chloride, sodium bromide, potassium bromide, calcium bromide, zinc bromide, sodium formate, potassium formate, cesium formate and mixtures thereof.

[0028] The completion and workover fluid compositions of the present invention comprising EO-RCL may also contain shale stabilizers or corrosion inhibitors. These shale stabilizers or corrosion inhibitors may be selected from the group consisting of partially hydrolyzed polyacrylamides (PHPA), potassium chloride, potassium acetate, potassium carbonate, potassium hydroxide, sulfonated asphalt, blown asphalt, gilsonite, polyglycols, polyamino acids, surfactants, cationic polymers, mixed metal hydroxides (MMH), and mixtures thereof.

[0029] The completion and workover fluid compositions of the present invention comprising EO-RCL may also contain weighting agents. These weighting agents may be selected from the group consisting of barite, hematite, manganese oxide, sized calcium carbonate made from ground limestone or marble, and mixtures thereof.

[0030] The completion and workover fluid compositions of the present invention comprising EO-RCL may also contain finely divided clay particles. These finely divided clay particles may be selected from the group consisting of bentonite, attapulgite, sepiolite, saponite, and mixtures thereof.

[0031] The completion and workover fluid compositions of the present invention comprising EO-RCL may also contain a lubricant. This lubricant may be selected from the group consisting of glycol, asphalt, and mixtures thereof.

[0032] The completion and workover fluid compositions of the present invention comprising EO-RCL may also contain a biocide and/or defoamer.

[0033] The following examples illustrate the usefulness and applicability of EO-RCL in brines used as clear, solids-free completion and workover fluids. The examples are merely set forth for illustrative purposes, but it is to be understood that other modifications of the present invention can be made by skilled artisans in the related industry without departing from the spirit and scope of the invention.

Examples

[0034] An EO-RCL of Example 1 was evaluated in different brine systems (freshwater, NaCl saturated water, CaBr_2 and $\text{ZnBr}_2/\text{CaBr}_2$) at 2 pounds per barrel (ppb), corresponding to 0.57 wt%. Its performance was compared against that of standard high molecular weight HECs widely used in completion and workover fluids. Comparative Example 1 is a standard high molecular weight HEC (Natrosol® HI-VIS HEC, available from Hercules Incorporated). Comparative Example 2 is also a standard high molecular weight HEC (Natrosol® 210HHW HEC, available from Hercules Incorporated). The viscosity and fluid loss properties were measured after static aging overnight at room temperature the results of this testing are found in Table 1.

Table 1: Comparative Rheology/Fluid Loss (FL) Performance of Various HECs and EO-RCL in Completion Fluids

Fluid system			Sample		Final	Aging	Final	OFITE Viscometer								A.V.	P.V.	Yv	F.L.	
Brine	S.G.	Density	Ref.	ppb	MgO	pH	Temp.	pH	600	300	200	100	60	30	6	3	cPs	cPs	lb/100ft2	(ml)
							(16 hrs)	Aft. Ag.	rpm	rpm	rpm	rpm	rpm	rpm	rpm	rpm				
			Comp. Ex. 1	2	1	9.98	24.2	10.07	90	71	61	47	38	28.5	12	8	45	19	52	31
			Comp Ex. 2	2	1	10.84	24.4	10.36	87	68	58	44	35	25	9.5	6.5	43.5	19	49	89
			Ex 1	2	1	10.55	24.6	10.35	88	71	61.5	48.5	40	30	13	9	44	17	54	67.2
			Comp. Ex. 1	2	1	9.73	24	10.18	109.5	83.5	71	52	41	28.5	10.5	7	54.75	26	57.5	31.2
			Comp Ex. 2	2	1	9.98	24.3	9.93	108.5	82.5	69	50	38.5	26	8.5	5.5	54.25	26	56.5	29
			Ex 1	2	1	9.91	24.5	9.78	103	80	68	51	41	29	11	7.5	51.5	23	57	30.2
			Comp Ex. 2	2	1	8.09	24.2	7.84	241.5	181	154	118	97	73.5	35.5	24.5	120.75	60.5	120.5	32
			Ex 1	2	1	8.23	24.2	7.88	237	179	153.5	121	102	82	48	37	118.5	58	121	64.2
			Comp. Ex. 1	2	1	7.36	24	7.65	97	65	52	35.5	26.5	18	7	4.5	48.5	32	33	13
			Comp Ex. 2	2	1	7.13	24.9	7.02	140	96.5	78	54	41	27.5	10.5	6.5	70	43.5	53	12.8
			Ex 1	2	1	7.09	24.8	6.96	244	184	156.5	121	99	76	36.5	25	122	60	124	17.7
Did not go in solution																				
			Comp. Ex. 1																	
			Comp Ex. 2	2	1	0.93	23.5	0.85	>330	267	222	166	136.5	107	63	49.5	-	-	-	79.8
			Ex 1	2	1	0.83	24.2	0.92	>330	275	230	175.5	146	117.5	74	60	-	-	-	105.4

[0035] It was found that the EO-RCL was more efficient than high molecular weight commercial HECs in viscosifying high density (heavy) brines as evident by the high apparent viscosities (A.V.) and yield values (Yv) developed in these systems (Figure 2). In the $\text{ZnBr}_2/\text{CaBr}_2$ brine, characterized by an extremely low pH, Comparative Example 1 (Natrosol® HI-VIS HEC) did not simply go into solution.

[0036] In low to medium density brines, the performances of EO-RCL were equivalent to those of high molecular weight commercial HECs (Figure 1).

[0037] Data in Figure 3 indicate that fluid of Example 1 containing EO-RCL develops a more regular viscosity profile at high shear rate (510 s^{-1}) than the fluid of Comparative Example 2 containing an commercial HEC with a significant improvement of viscosity for brine densities exceeding 12 ppg.

[0038] Interestingly, the fluid of Example 1 containing EO-RCL develops much higher low shear viscosity than fluid containing commercial HECs (Figure 4). This feature is highly desired because it would provide greater carrying capacity during the completion and workover operations.

[0039] Although the invention has been described with reference to preferred embodiments, it is to be understood that variations and modifications in form and detail thereof may be made without departing from the spirit and scope of the claimed invention. Such variations and modifications are to be considered within the purview and scope of the claims appended hereto.

WHAT IS CLAIMED:

1. A completion and workover fluid composition comprising water and at least one rheology modifier and/or fluid loss control agent, and at least one other ingredient selected from the group consisting of polymeric additive, inorganic salts, shale stabilizers, corrosion inhibitors, weighting agents, and finely divided clay particles wherein the rheology modifier and/or the fluid loss control agent is ethoxylated raw cotton linters (EO-RCL).
2. The composition of claim 1, wherein the EO-RCL contains an additional substituent.
3. The composition of claim 2 wherein the additional substituent comprises alkyl groups.
4. The composition of claim 3 wherein the alkyl groups contain 1 to 30 carbon atoms.
5. The composition of claim 3 wherein the additional substituent comprises carboxymethyl groups.
6. The completion and workover fluid composition of claim 1, wherein the EO-RCL has an oxyethylene molar substitution (MS) with a lower limit of about 0.5.
7. The completion and workover fluid composition of claim 6, wherein the EO-RCL has an oxyethylene molar substitution (MS) with a lower limit of about 1.5.
8. The completion and workover fluid composition of claim 7, wherein the EO-RCL has an oxyethylene molar substitution (MS) with a lower limit of about 1.8.

9. The completion and workover fluid composition of claim 1, wherein the EO-RCL has an oxyethylene molar substitution (MS) with an upper limit of about 3.5.
10. The completion and workover fluid composition of claim 9, wherein the EO-RCL has an oxyethylene molar substitution (MS) with an upper limit of about 2.5.
11. The completion and workover fluid composition of claim 10, wherein the EO-RCL has an oxyethylene molar substitution (MS) with an upper limit of about 2.2.
12. The completion and workover fluid composition of claim 1, wherein the EO-RCL has an oxyethylene molar substitution (MS) in a range of from about 0.5 to about 3.5,
13. The completion and workover fluid composition of claim 12, wherein the EO-RCL has an oxyethylene molar substitution (MS) in a range of from about 1.5 to 2.5.
14. The completion and workover fluid composition of claim 13, wherein the EO-RCL has an oxyethylene molar substitution (MS) in a range of from about 1.8 to 2.2.
15. The completion and workover fluid composition of claim 1, wherein the at least one other ingredient comprises a polymeric additive and wherein the polymeric additive is selected from the group consisting of starch and its derivatives, guar gum and its derivatives, xanthan gum, welan gum, diutan gum, cellulose ethers, polyacrylates, polyacrylamides and mixtures thereof.
16. The completion and workover fluid composition of claim 1, wherein the at least one other ingredient comprises an inorganic salt and wherein the inorganic salt is selected from the group consisting of calcium carbonate, calcium chloride, potassium chloride, sodium chloride, magnesium chloride, sodium

bromide, potassium bromide, calcium bromide, zinc bromide, sodium formate, potassium formate, cesium formate and mixtures thereof.

17. The completion and workover fluid composition of claim 1, wherein the at least one other ingredient comprises a shale stabilizer or corrosion inhibitor and wherein the shale stabilizer or corrosion inhibitor is selected from the group consisting of partially hydrolyzed polyacrylamides (PHPA), potassium chloride, potassium acetate, potassium carbonate, potassium hydroxide, sulfonated asphalt, blown asphalt, gilsonite, polyglycols, polyamino acids, surfactants, cationic polymers, mixed metal hydroxides (MMH), and mixtures thereof.

18. The completion and workover fluid composition of claim 1, wherein the at least one other ingredient comprises a weighting agent and wherein the weighting agent is selected from the group consisting of barite, hematite, manganese oxide, sized calcium carbonate made from ground limestone or marble, and mixtures thereof.

19. The completion and workover fluid composition of claim 1, wherein the at least one other ingredient comprises finely divided clay particles and wherein the finely divided clay particles are selected from the group consisting of bentonite, attapulgite, sepiolite, saponite, and mixtures thereof.

20. The completion and workover fluid composition of claim 1, wherein the at least one other ingredient comprises a lubricant and wherein the lubricant is selected from the group consisting of glycol, asphalt, and mixtures thereof.

21. The completion and workover fluid composition of claim 1, further comprising a biocide.

22. The completion and workover fluid composition of claim 1, further comprising a defoamer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/004460

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/04 C09K8/08 C09K8/20

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)

C09K C04B E21B

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006/019834 A1 (MELBOUCI MOHAND [US] ET AL) 26 January 2006 (2006-01-26) the whole document	1-22
Y	WO 2006/014717 A (HERCULES INC [US]) 9 February 2006 (2006-02-09) the whole document	1-22
Y	US 2005/056424 A1 (HANES ROBERT E [US] ET AL HANES JR ROBERT E [US] ET AL) 17 March 2005 (2005-03-17) paragraph [0014]	1-22
A	US 2005/235878 A1 (PODLAS THOMAS J [US]) 27 October 2005 (2005-10-27) paragraph [0011] - paragraph [0012]	1-22

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Further documents are listed in the continuation of Box C.

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See patent family annex.

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Date of the actual completion of the international search

2 July 2007

Date of mailing of the international search report

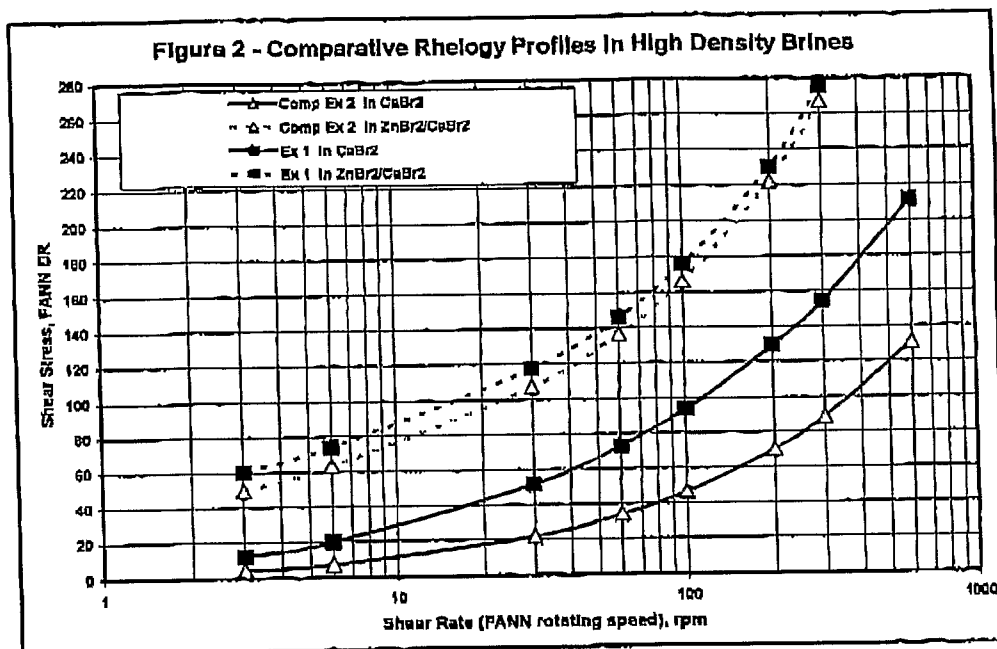
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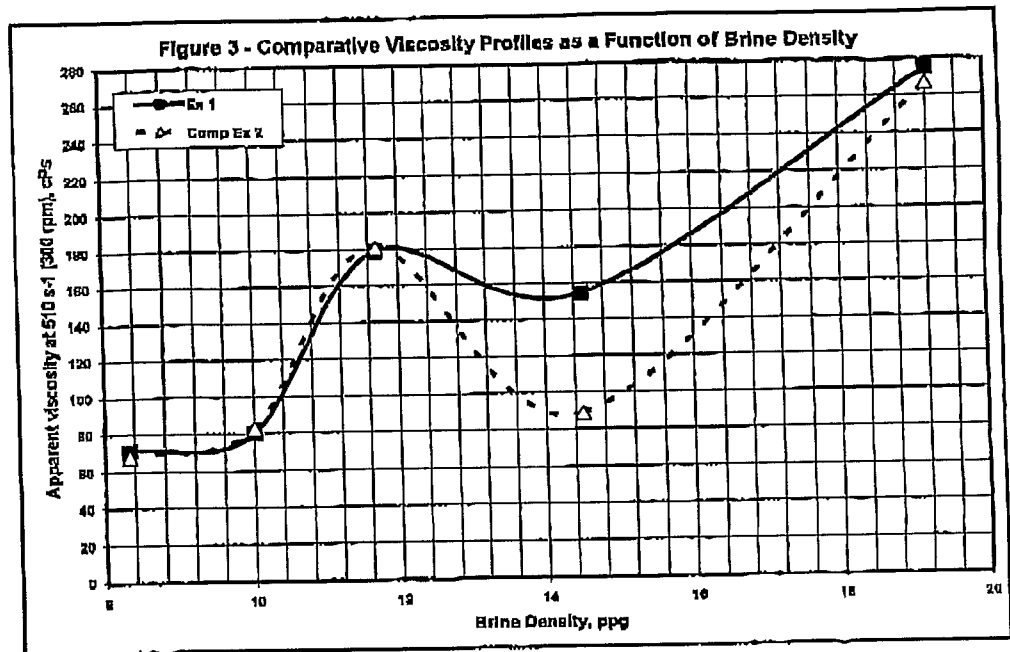
Name and mailing address of the ISA/

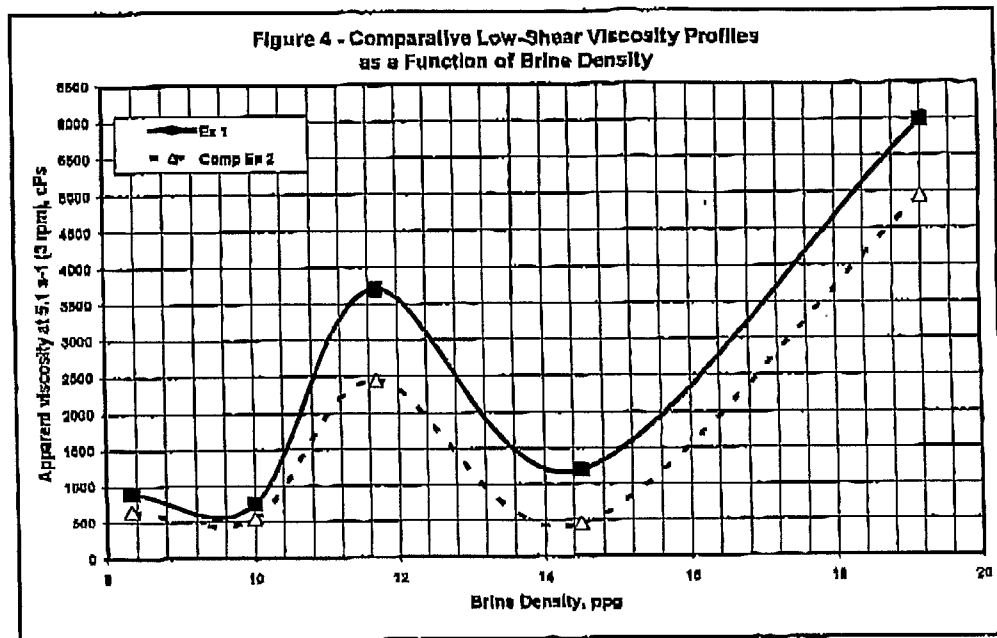
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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2007/004460

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/04 C09K8/08 C09K8/20

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)

C09K C04B E21B

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)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006/019834 A1 (MELBOUCI MOHAND [US] ET AL) 26 January 2006 (2006-01-26) the whole document	1-22
Y	WO 2006/014717 A (HERCULES INC [US]) 9 February 2006 (2006-02-09) the whole document	1-22
Y	US 2005/056424 A1 (HANES ROBERT E [US] ET AL HANES JR ROBERT E [US] ET AL) 17 March 2005 (2005-03-17) paragraph [0014]	1-22
A	US 2005/235878 A1 (PODLAS THOMAS J [US]) 27 October 2005 (2005-10-27) paragraph [0011] - paragraph [0012]	1-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* & * document member of the same patent family

Date of the actual completion of the international search

2 July 2007

Date of mailing of the international search report

09/07/2007

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2007/004460

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WO 2006014717 A	09-02-2006	AR 051365 A1 CA 2574498 A1 EP 1769046 A1 US 2006019834 A1	10-01-2007 09-02-2006 04-04-2007 26-01-2006
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