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Señor
SUPERINTENDENTE DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES
E. S. D.

REF: Expediente No.: **04-010.426**
Patente de Invención: **"LODO CONDUCTOR BASADO ELÉCTRICAMENTE EN ACEITE"**
Titular: **HALLIBURTON ENERGY SERVICES, INC.**

Publicada en la Gaceta de la Propiedad Industrial No. 555 de 31 de agosto de 2.005

SOLICITUD DE EXAMEN DE PATENTABILIDAD

HUMBERTO RUBIO CAMACHO, mayor de edad, domiciliado en Bogotá, D.C., identificado con la cédula de ciudadanía número 17.192.062 de Bogotá, abogado Titulado con Tarjeta Profesional No. 50.007 del Consejo Superior de la Judicatura, actuando en carácter de **APODERADO** de la Sociedad **HALLIBURTON ENERGY SERVICES, INC.**; domiciliada en Duncan, Oklahoma, Estados Unidos de América; respetuosamente solicito a esa Dependencia:

1.- De conformidad con lo establecido en el Artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina y estando dentro del termino legal de seis meses contados desde la fecha de publicación en la Gaceta No. 555 de 31 de agosto de 2.005, de la solicitud de la patente de la referencia, solicito se sirvan proceder a efectuar el examen de patentabilidad de la Invención.

2.- Para que la presente petición sea viable, estoy anexando el siguiente documento:

2.1. Recibo de pago No. 05-76,781 de 05 de octubre de 2.005; por un valor de $ 186.000,oo, de acuerdo con la Resolución No. 31980 de 24 de diciembre de 2.004.

3.- Por lo anterior solicito se continúe con el trámite correspondiente.

Del Señor Superintendente,

HUMBERTO RUBIO CAMACHO
C.C. 17.192.062 de Bogotá
T.P. 50.007 Consejo Superior de la Judicatura.
COD. 4134

04/448-013/pi

cpfm.-

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PARA USO EXCLUSIVO DE
HUMBERTO RUBIO & CIA. LTDA

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

EXAMEN DE PATENTABILIDAD
PATENTE DE INVENCION: LODO
CONDUCTOR BASADO ELÉCTRICAMENTE
EN ACEITE

RECIBO OFICIAL DE CAJA : 05 - 76,781
FECHA : OCTUBRE 5 DE 2005

SUPERINTENDENCIA Y COMERCIO
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C O N S I G N A C I O N

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
HUMBERTO RUBIO ABOGADOS L	CONSIGNACION	BANCO POPULAR	050-00110-6	41400445	05/10/2005	10,313,000.00

C O N C E P T O

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	114 PTC CAP-II EXAMEN DE PATENTIBILID	186,000.00
		TOTAL : $	186,000.00

SON: CIENTO OCHENTA Y SEIS MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No._____

Industria y Comercio
SUPERINTENDENCIA

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No **04-10426**

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**

– PCT, FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No

555, DE FECHA **31** DE **AGOSTO** DE **2005**, EL TERMINO HABIL SEÑALADO

POR LA LEY EXPIRA EL **28** DE **NOVIEMBRE** DE **2005**

NOTA Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, debera solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Articulo 44 de la Decisión 486/2000

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS

SI ___ _____ NO ___ X ____

Carrera 13 No. 27-00 Piso 5 y 10
Conmutador 334 12 21-2-3-4
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United States Patent Office 2,739,120 Patented Mar 20, 1956

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2,739,120

ELECTRICALLY CONDUCTIVE DRILLING FLUIDS

Paul W Fischer, Whittier, Calif assignor to Union Oil Company of California, Los Angeles, Calif a corporation of California

No Drawing. Application May 18, 1953, Serial No. 355,259

18 Claims. (Cl. 252—8.5)

This invention relates to oil-base drilling fluids, and in particular concerns oil-base drilling fluids which are electrically conductive. It further relates to means for [illegible] oil-base drilling fluids electrically conductive, and to means for conducting electrical well logging operations.

In drilling oil or gas wells by means of rotary drilling tools, a hollow drill pipe having a bit attached to its lower end is extended downwardly through the well bore and is rotated while the bit is pressed against the working face in the formation at the bottom of the hole. The action of the rotating bit grinds away the formation as the drilling progresses. During the drilling a fluid body known as a drilling fluid is continuously circulated down through the drill stem through the bit and against the working face of the hole, and then back up to the surface through the annular space between the drill stem and the walls of the bore hole. The drilling fluid serves a number of purposes, among which are cooling and lubricating the drill bit, suspending and removing cuttings from the bore hole, preventing the flow of liquids from the formations traversed by the bore into the same by exerting a hydrostatic pressure on such formations, and fulfilling other purposes.

In locations where the underground formations traversed and/or penetrated by the bore contain materials such as hydratable clays which swell and/or disintegrate in the presence of water it has become customary to employ drilling fluids which are relatively free of water e. g. fluids which contain less than about 10 per cent of water in order to preclude or minimize the introduction of water into the bore by means of the drilling fluid. Such drilling fluids are termed "oil-base" fluids since they almost invariably comprise mineral oil having dispersed or suspended therein minor proportions of various agents adapted to impart the requisite physical properties to the base oil. Among the most important of such agents are weighting agents, which are high density inert solids adapted to increase the apparent density of the base oil and thus increase the hydrostatic head provided by the drilling fluid within the bore; wall-building agents, which are materials such as clay or asphalt adapted to coat or plaster the walls of the bore with an impermeable layer which prevents escape of the drilling fluid into permeable formations, and dispersing agents, which serve to maintain solid components of the fluid uniformly dispersed therein.

Among the various methods for investigating and determining the nature of the subsurface formations traversed by a well bore, i. e., well logging, those involving the measurement of one or more of the electrical characteristics of such formations enjoy wide application. Most of such methods require that the bore hole be filled with a liquid capable of conducting relatively low voltage electric currents, and it is hence highly desirable that the drilling fluid employed in drilling the well be adapted for such use, i. e., the drilling fluid should have relatively good electrical conductivity. In general however oil-base drilling fluids are not sufficiently conductive to dept them for use during electric logging operations, and this deficiency has greatly restricted their general applicability despite their other highly desirable properties and characteristics. Typically oil-base drilling fluids have electrical resistivities of the order of 1×10^9 ohm-cms., which is far too high to permit their use in electric logging operations where it is usually desirable that the bore hole fluid have a resistivity not greater than about 50×10^3 ohm-cms. and preferably below about 5×10^3 ohm-cms.

Inasmuch as oil-base drilling fluids normally contain a small amount of water usually about 0.3–5 per cent by weight of the entire composition, it would appear that their electrical resistivity could be decreased simply by adding to the fluid a water-soluble electrolyte which would dissolve in the water to form an electrically conductive phase within the body of the fluid. I have found however that the addition of electrolytes such as sodium phosphates, sodium chloride calcium chloride, etc. to oil base drilling fluids has little effect on the electrical conductivity of the fluid, and, furthermore, often adversely affects other properties of the field. For example, the addition of about 2 per cent by weight of sodium phosphate to soap-stabilized drilling fluid of the type described in U. S. Patent 2,542,020 not only fails to reduce electrical resistivity appreciably but also increases the field loss value by more than fourfold. In this respect, the oil-base drilling fields to which the present invention relates differ markedly from the so-called emulsion-base fluids. The latter whether they be of the oil-in-water or water-in-oil type, contain a minimum of about 10 per cent by weight of water and when they contain about 20 or more per cent of water they are more or less readily be rendered electrically conductive without adversely affecting their field loss characteristics simply by dissolving ionizable salt in the aqueous phase. Oil-base drilling fields, on the other hand, derive their desirable characteristics from the fact that they contain a minimum amount, e. g. less than about 10 per cent, of water and in contrast to the emulsion-base fields, they cannot be rendered conductive simply by the addition of an ionizable salt or other electrolyte. It will accordingly be understood that the term "oil-base fluid" as herein employed refers to drilling fluid compositions in which the base fluid is mineral oil and in which the water content is less than about 10 per cent by weight.

I am aware that certain specific oil-base drilling fields, i. e. those which contain a mixture of alkali-metal and alkaline-earth metal soaps of heat-treated resin acids, can be rendered conductive by incorporating in the field carefully controlled amounts of sodium silicate. However in order to gain the benefit of the use of sodium silicate in this manner it is necessary that the amount of alkaline-earth metal soap employed and the water content of the field be likewise very carefully controlled. For best results it is necessary to employ a homogenizer to insure adequate dispersion of the sodium silicate in the base field. As will be apparent to those skilled in the art, such careful control of proportions and uncon-

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ventional mixing procedure is very difficult to achieve under field conditions where inadequate mixing facilities render almost impossible the preparation of completely uniform compositions and where the fluid is constantly subject to contamination.

It is accordingly an object of the present invention to provide improved oil base drilling fluids suitable for use in electric well-logging operations.

Another object is to provide oil-base drilling fluids having good electrical conductivity.

Another object is to provide means for improving the electrical conductivity of oil-base drilling fluids, which means are adapted to use under actual field conditions and do not adversely affect other desirable properties of the drilling fluid to any substantial extent.

A further object is to provide a composition of matter adapted to imparting the property of electrical conductivity to oil-base drilling fluids which are normally substantially nonconductive.

A still further object is to provide an improved method for conducting electric well logging operations.

Other objects will be apparent from the following detailed description of the invention and various advantages not specifically referred to herein will occur to those skilled in the art upon employment of the invention in practice.

I have now found that the above and related objects may be realized by incorporating an electrolyte and surface active agent into the oil-base drilling fluid. More particularly I have found that the electrical resistivity of oil-base drilling fluids may be reduced to values within the range required for electric logging operations by adding to the field relatively small amounts each of a water-soluble ionizable metallic compound as an electrolyte, and certain types of surface active agents in many instances the normal water content of the oil-base fluid will be sufficient to dissolve the added electrolyte, but in other cases a small amount of water is added for this purpose. In order to retain the desirable general characteristics of oil-base drilling fluids, however the water content should be maintained below about 10, preferably between about 4 and about 8 per cent by weight of the entire composition.

The water-soluble ionizable metallic compounds which are employed in accordance with the invention to impart electrical conductivity to oil base drilling fluid are for the most part water-soluble salts of the alkali- and alkaline-earth metals and alkali-metal hydroxides. In accordance with customary nomenclature the ammonium radical is herein included within the term "alkali-metal." Water-soluble salts of the heavy metals are not inoperable insofar as suitably imparting electrical conductivity to the field is concerned, but because of the tendency of such salts to hydrolyze in aqueous solution to form insoluble hydroxides, their effect on electrical conductivity is not usually permanent. Specific examples of the foregoing class of water-soluble ionizable metal compounds employed in practice of the invention include the hydroxides of sodium, potassium and lithium, sodium chloride barium chloride, potassium iodide, ammonium chloride, calcium bromide, magnesium chloride, calcium nitrate barium nitrate, magnesium nitrate, sodium silicate, potassium sulfate, magnesium sulfate, sodium carbonate, lithium carbonate, potassium bicarbonate, sodium sulfate, potassium silicate, sodium phosphate ammonium phosphate, sodium polyphosphate potassium bisulfate sodium sulfite, sodium acetate, potassium arsenate, sodium borate, potassium dichromate sodium cyanide calcium nitrite, ammonium hydrogen phosphate sodium chromate, sodium thiosulfate sodium molybdate potassium phosphite, sodium manganate, etc. Mixtures of such compounds may likewise be employed. In general best results are obtained by employing compounds which dissociate in water to form alkaline solutions, i. e. hydroxides and salts of strong bases and weak

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acids. The alkali-metal hydroxides, silicates, and phosphates are particularly preferred.

The surface active agents which are employed in conjunction with the aforementioned electrolytes in accordance with the invention are of the non-ionic type, i. e., they are compounds in which the polar and non-polar portions of the molecule are so balanced that they are substantially incapable of ionization. This type of compound forms a well-recognized class of surface active agents (see Schwartz, "Introduction to Emulsions, Chemical Publishing Company 1946) and the most widely available members thereof are members of the class consisting of (1) partial esters of polyhydric alcohol with long-chain carboxylic acids and (2) esters of hydroxyalkyl ethers of polyhydric alcohol with long-chain carboxylic acids. The term "long-chain carboxylic acid" refers to aliphatic carboxylic acids containing at least 12, preferably 12 to 18 carbon atoms. The term "polyhydric alcohol" refers to aliphatic compounds containing at least two hydroxyl groups. A third important class of non-ionic surface active agents comprises polyethylene ether alcohols such as are obtained by condensing ethylene oxide with alcohol or phenols.

The non-ionic partial esters of polyhydric alcohols with long-chain carboxylic acids are for the most part oil-soluble hydrophobic materials which promote the formation of stable water-in-oil emulsions. Typical members of this class of surface active agents include glycerol mono-oleate, sorbitan mono-oleate, pentaerythritol mono-ester of soybean fatty acids, sorbitan mono-laurate, glycerol mono-stearate, sorbitan tri-oleate butylene glycol mono-laurate, mannitan dilaurate etc. Many of the surface active agents of this group are available commercially under such trade names as Arlacel Emsol Fentamul, Protexarin, Span, Tegin, etc.

The esters of hydroxyalkyl ethers of polyhydric alcohols and long-chain carboxylic acids are for the most part hydrophilic substances which tend to promote oil-in-water emulsions, particularly when the other-alcohol group is of relatively high molecular weight. Examples of this class of surface active agents are diethylene glycol lauric acid, tri-ethylene glycol mono-stearate dodecaethylene glycol mono-oleate, nonaethylene glycol dilaurolenate, diethylene glycol mono-oleate, fatty acid condensate of ethylene oxide, tetradethylene glycol mono-stearate, polyoxyethylene condensates of sorbitan mono-oleate, polyoxyethylene condensate of sorbitan mono-palmitate, etc. Many of such agents are available commercially under such trade names as Emcol DL, Emulphor AG Glycerol Renex, Triton, Tween etc.

Many further examples of non ionic surface active agents, together with their respective trade names and manufacturers, are found in Industrial and Engineering Chemistry vol. 35 pp. 107–117 and 126–130 (1943). A preferred group of such agents comprises the hydroxypolyoxyethylene ethers of long-chain fatty acid partial esters of sorbitan which are avail ble commercially under the generic trade nam "Tweens. Such agents are prepared from sorbitan by the following series of operations

1. Esterification of one or more, but not all of the hydroxyl groups of the sorbitol molecule with a long-chain fatty acid, e. g. oleic acid, stearic acid, palmitic acid is ric acid and other fatty acids containing at least 12 carbon atoms, to form sorbitan partial ester

2. Etherification of the remaining hydroxyl group or groups of said partial ester with ethylene oxide to form a hydroxypolyoxyethylen ether thereof. The quantity of ethylene oxide employed should be such that the ether product contains from 10 to 30 oxyethylene groups.

Means for carrying out these reactions are well known in the art, and further details concerning the preparation of the products in question are set forth in that pa-

tion of U S. Patent No. 2,380,166 which relates to the preparation of the so-called "Type B emulsifiers. These products are for the most pa t oily yellow liquids which are soluble in water acetone, alcohol and other common organic solvents. They vary in viscosity from about 250 to about 600 cps. at 25 C., depending upon the nature of the long-chain fatty acid residue, the number of such residues in the molecule, and the length of the hydroxypolyoxyethylene chains. As examples of the surface active agents of this group there may be mentioned hydroxypolyoxyethylene sorbitan monolaurate (Tween 20) hydroxypolyoxyethylene sorbitan monopalmitate (Tween 40) hydroxypolyoxyethylene sorbitan monooleate (Tween 80) hydroxypolyoxyethylene sorbitan trioleate (Tween 85) etc. Further information concerning these materials and the sorbitan partial esters (Spans) is set forth in Atlas Surface Active Agents" Atlas Powder Co. Wilmington, Delaware, 1950.

The proportions in which the water-soluble metal salt or hydroxide and the surface active agent are incorporated in the drilling fluid are to a certain extent interdependent, i. e., with increasing amounts of the metal compound the amount of surface active agent may be decreased, and les verse. Also, certain particular metal compounds require the presence of more of a particular surface active agent than others, and certain types of surface active agents ar more effectiv in a given amount than others. In general, however the water-soluble metal salt or alkali-metal hydroxide is provided in an amount representing between about 0.01 and about 5 per cent, preferably between about 0.1 and about 2 per cent, by weight of the entire composition, and the surface active agent is employed in an amount representing between about 0.1 and about 8 per cent, preferably between about 0.4 and about 4 per cent, by weight of the entire composition.

As previously stated, it is necessary that the drilling fluid contain sufficient water to dissolve the water-soluble metal salt or hydroxide so that the latter becomes dispersed in the fluid in the form of a relatively dilute solution. In many instances the drilling fluid will normally contain sufficient water for this purpose to which case no water need be added along with the metal salt or hydroxide. In some instances, however it will be necessary to add a small amount of water. In general, it is desirable that the drilling fluid contain at least about 3 per cent, preferably at least about 5 per cent, by weight of water. The upper limit on the water content of the fluid is established at about 10 per cent by weight since those fluids which contain substantial amounts of water lose the desirable characteristics of oil-base drilling fluids in general, and are more properly classifiable as emulsion-base fluids.

The use of a water-soluble metal salt or alkali-metal hydroxide in combination with a surface active agent of the above-defined class in accordance with the invention is applicable to oil-base drilling fluids in general, regardless of their exact formulation. In general, all oil-base drilling fluids essentially comprise a mineral oil dispersion of solids and a dispersing agent which serves to maintain the solids more or less stably dispersed in the oil. When a hydratable clay is included as a wall-building agent the fluid usually also contains a small quantity of water Almost invariably the base oil is a mineral oil, and may be crude oil, a distillate, or a residual fraction. Very often blends of distillate and residual fractions are employed, e. g. a blend of light distillate such as kerosene or Diesel fuel and a light residual fraction such as furnace oil or a light fuel oil. The dispersed solids may serve solely as a weighting agent, in which case they usually take the form of finely-divided inert metallic compounds such as lead dust, baryte, iron oxide, calcined clay whiting and the like, or they may serve as wall-building agents to coat or plaster the walls of the bore with an impermeable layer which prevents escape of the drilling fluid into permeable formations traversed by the bore. Such wall-building agent usually comprises a hydratable clay such as bentonite, in which case a small amount of water is included in the fluid for the purpose of effecting hydration of the clay Asphalt is also employed as a wall-building agent. In many instances the dispersed solids may comprise both a weighting agent and a wall-building agent. A wide variety of materials may be employed as dispersing or suspending agents to maintain the solids uniformly dispersed in the base oil For the most part however the dispersing agent will comprise a metal soap of a fatty resin or naphthenic acid. In some instances such soaps are formed in situ by incorporating into the fluid soap-forming acid, such as tall oil, rosin, oleic acid, sulfonic acid, linoleic acid, linseed acids, and the like and a basic inorganic compound such as sodium hydroxide, lime, or sodium silicate. In other cases the soap may be formed in situ by incorporating an alkali-metal soap and an alkaline earth metal base into the fluid, whereby metathesis reaction occurs to form the corresponding alkaline-earth metal soap. Soap mixtures, including mixtures of water-dispersible and oil-dispersible soaps may also be employed. In addition to the soap-type dispersing agents, such materials as lampblack and diatomaceous earth have been employed for the same purpose.

While the principle of the invention is applicable to all types of oil-base drilling fluids, it is particularly applicable to the soap-emulsified fluids of the type described in U S Patent 2,342,020. Such fluids are prepared by dispersing small amounts each of a hydratable clay an alkaline-earth metal base and an alkali-metal soap of a heat-treated rosin in suitable base oil. A partial metathesis reaction occurs between the rosin soap and the alkaline-earth metal base whereby there is obtained a mixture of the corresponding alkaline-earth metal rosin soap and unreacted alkali-metal rosin soap The alkali-metal rosin soap employed in preparing this type of drilling fluid is obtained by reacting an alkali-metal alkali, a. g. sodium or potassium hydroxide, with heat-treated wood or gum rosin in such a manner that the reaction is only partially complete and the saponified product contains from about 1 to about 15 per cent of free unsaponified resin acids

The heat-treatment of resin, whereby the resin acids thereof are isomerized and/or otherwise modified, is well known in the naval stores art, and may be effected in various ways to obtai modified resin products which vary somewhat in their physical and chemical properties depending upon the nature and extent of the heat-treatment. Thus, any of the various color grades of refined wood or gum rosin may be heated under non-oxidizing conditions at temperatures between about 250 C. and about 350 C. for a length of time sufficient to raise the specific rotation of the rosin from its original negative value to a value between about +5 and about +19 The resulting resin product closely resembles the original rosin in appearance, ease of saponification, etc. but is considerably altered chemically as evidenced by its increased specific rotation, increased dehydroabietic acid content lower iodine n mber etc. By carrying out the heat-treatment at somewhat higher temperatures and/or over longer periods of time, the specific rotation may be raised further e g. to +25 or even higher and the degree of chemic unsaturation further decreased Also, under such conditions decarboxylation takes place with the formation of unsaponifiable bodies which are usually referred to a rosin oils. The heat treatment of resin to secure the desired modification of the resin acids as indicated by increase in specific rotation to a value above about +5 may also be effected in the presence of catalysts at relatively low temperatures as described in U S. Patent 2,154,629 The catalysts employed are of the hydrogenation type, e. g., metallic platinum or palladium, although the treatment is carried out in the

absence of added hydrogen. The reaction which takes place is termed "disproportionation since it involves the simultaneous hydrogenation and dehydrogenation of abietic-type acids with the consequent formation of dihydroabietic and dehydro-abietic acids and their analogues, and the resulting product is referred to as "disproportionated rosin. Similarly the product obtained by heat-treating rosin under conditions sufficiently drastic that carboxyl groups are removed from the rosin acids i moved "decarboxylated rosin, and th product obtained by heat-treating rosin under less drastic conditions so that the change effected is substantially only one of molecular rearrangement f referred to as isomerized rosin. All of these modified rosi products are characterized by having been prepared by heat-treating rosin nder conditions of time and temperature, ad in the presence o absence of a hydrogenation catalyst but in the absence of added hydrog sufficient to ius the specific rotation of the rosin to value above about +5

Any of th bove described modified rosin products may be ued to obtain the saponification products employed in preparing the preferred drilling fl id compositions of th present invention. Procedure for carrying ou t the saponification reaction is well known i the art and in general consists merely of adding th modified rosin in the solid or molten t t to hot aqueous solutions of the desired lkali-metal alkali and thereafter heating the mi ture until the reaction is complete ame use product contains the desired amount of wate The amount of alkali employed is somewhat less than that required for the comp ete saponification of the resin acids i order that th ponification product may contai the requisite amount of free unsaponified resin acids. The concentration of the aqueous alkali is usually so adjusted that the pread ct obtained takes the form of viscous liquid or thick paste containing 60–85 per cent solids. The physical form of the product lso depends somewhat upon the type of modified rosin employed. Th saponification product obtained from decarboxylated wood rosin contai ing a substantial amount of resi alls, for example, i a relatively fluid liquid even though it may contain only 5–10 pe cent of water

While y of the alkali-metal alkali saponification products of rosin which has been heat-treated to raise its specific rotation to a nine here about +5 may be employed i preparing the oil base drilling fluids, I have found that superior results particularly with respect to the fluid loss value f the drilling fluid ra ntained by employing either of two specific products of this type. The firs. of such preferred saponification products is an alkali-metal alkali saponification product of rosin which has been heat-treated t temperatures between about 250 C and bout 350 C. in the bsence of catalyst to such extent th t it contains only bout 30–60 per cent of free rosin acids, 30–40 per cent of unsaponifiabl oils, a d small amounts of phenolic materials, water and products of unknown constitution. A particularly preferred product of this type is the potassium hydroxide saponification product of such heat-treated rosin containing about 45–55 per cent potassium rosin acid soaps, bout 30–35 per cent unsaponifiabl materials also t 5–10 per cent free rosin acids, and about 5–10 per cent water The second of the preferred class of saponification products is the product obtained by heating rosin at temperature of about 225 –300 C. for bout 15–60 minutes in contact with a hydrogenation catalyst but in the absence of added hydrogen, distilling the resulting product and collecting fraction distilling at about 210 –275 C. under about 5–10 mm pressure, and thereafter saponifying such fraction with aqueous sodium hydroxide in the known manner Such product is available commercially under the trade name "Dymtacta 731

Mixtures of these two types of saponified heat-treated rosin products may also be employed.

The proportions in which the components of this type

of drilling fluid are employed may be varied between certain limit depending on the identity of such components and the specific properties desired in the composition. Ordinarily however the saponified heat-treated rosin product is employed in an amount representing between about 1 and about 10 preferably between about 4 and bout 6, per cent by weight of the entire composition. The alkaline-earth metal base, which is preferably calcium hydroxide or calcium oxide i employed in a amou t corresponding approximately to that chemically equivalent to the saponified rosi product. When the latter is com of the preferred products hereinbefore described and the lkaline-earth metal base is calcium oxide or hydroxide, the saponification product is provided in the above-contained amount and the base is employed in amount representing between bout 0 1 and about 5 preferably between about 0.4 and about 2 per cent by weight of the entire composition. The hydratable clay is employed in an amount representing between about 0.1 and about 3 preferably between about 0.4 and about 1 2. per cent by weight of the entire composition and the water is provided in an amount representing between about 0.2 and about 10, preferably between about 1 and about 5 pe cent by weight of the entire composition. These proportions of water include any water which may be contained in the saponified rosin product and/or other components and accordingly the amount of water actually added during preparation of the composition "21 b. adjusted according to the water content of the other components so that the final composition will contain water in the above-mentioned proportions

In determining the electrical resistivity of the drilling fluids provided by the invention, an electrode assembly comprising two 1-inch square nickel plates spaced about one inch apart is immersed in a sample of the fluid being tested, and the voltage which must be applied across the electrodes to obtain a predetermined current flow through th fluid (usually 400 milliamperes) is ascertained. By calibrating the electrode assembly against a liquid of known resistivity the resistivity of the fluid sample being tested may be determined from such voltage reading. It has been found, however that many drilling fluids undergo a dielectric breakdown during such testing procedure. Thus, when the fluid is first subjected to the test the voltage cross the electrodes may be increased to a relatively high value, e. g 130 volts before substantial current flow As soon as the current starts to flow however the voltage may be substantially reduced without the flow of current falling below the aforesaid predetermined value. Accordingly I making the resistivity determination, the electrode assembly is immersed i the fluid and the voltage applied to the electrode plates is gradually raised until the predetermined flow of current is obtained A so-called "initial resistivity" value is determined from th applied voltage. The voltage is then gradually reduced, and the minimum voltage required to maintain the predetermined current flow is ascertained, and so-called "ultimate resistivity" value is determined from such minimum voltage reading. The dielectric breakdow of the fluid is more or less permanent and the ultimate resistivity value represents the resistivity which the fluid will have during electric logging operations.

The following examples will illustrate a number of ways in which the principle of the invention has been applied, but are not to be construed as limiting the same.

EXAMPLE I

The following concentrate composition was prepared

	Parts by weight
Diesel fuel	2800
Saponified decarboxylated rosin	1400
Saponified disproportionated rosin	1400
Bentonite	840
Water	560

The diesel fuel was a light domestic diesel oil having an API gravity of about 31 a viscosity at about 40 SUS at 100° F and a boiling range of about 400–720 F The saponified decarboxylated rosin contained 45–55 per cent of potassium resin acid soaps, 30–35 per cent of unsaponifiable rosin oils, 5–10 per cent of free resin acids and 5–10 per cent of water The saponified disproportionated rosin was the hereinabove described "Dresinate 731

This concentrate composition was then partially diluted with a further quantity of the diesel fuel in a ratio of 3 gallons of diesel fuel per 2 gallons of concentrate, and the partially diluted concentrate was then further diluted with fuel oil in a ratio of 17 gallons of fuel oil per 5 gallons of the partially diluted concentrate. Approximately 740 parts by weight of calcium oxide were then stirred into the completely diluted concentrate. The fuel oil was a light domestic fuel oil having an API gravity of about 34.9 viscosity of about 36 SSF at 127 F and a flash point of 170° F

The finished drilling fluid had the following approximate composition

	Percent by weight
Domestic diesel fuel	13 7
Light domestic fuel oil	77 7
Saponified decarboxylated rosin	1.9
[illegible]	1.5
Calcium oxide	0.8
Water	0.8
Bentonite	1 1
	100.0

The following Table I presents data illustrating the effect of adding various electrolytes in combination with water and one of the surface active agents of the present class to the above drilling fluid. In each experiment, the indicated proportions of the electrolyte, water and surface active agent were stirred into a 1500 ml. sample of the drilling fluid, and the electrical resistivity of the resulting composition was determined as hereinbefore described. The surface active agent employed was an alkylated aryl polyether alcohol sold under the trade name "Triton X-100" by Rohm and Haas Company

Table I

Expt. No.	Electrolyte		Water, percent	Surface Active Agent		Resistivity, Ohm-cm. X10³	
	Identity	Percent		Identity	Percent	Initial	Ultimate
1	None	0.0	5.0	None	0.0	1,000	1,000
2	do	0.0	5.0	Triton X-100	0.5	1,000	1,000
3	Trisodium phosphate	0.5	5.0	None	0.0	1,000	1,000
4	do	0.5	5.0	Triton X-100	0.5	25	0.5
5	do	0.5	10.0	do	0.5	25	0.5
6	Sodium chloride	0.5	5.0	do	0.5	1.25	0.5
7	do	0.5	7.5	do	0.5	25	0.5
8	Sodium bicarbonate	0.5	7.5	do	0.5	25	0.5
9	Sodium carbonate	0.5	7.5	do	0.5	25	0.5
10	Sodium hydroxide	0.5	7.5	do	0.5	25	0.5
11	Sodium silicate (N-Grade)	0.5	7.5	do	0.5	25	0.5

Based on weight of entire composition

EXAMPLE II

The data presented in the following Table II, illustrate the use of a number of different emulsifying agents of the present class in accordance with the principle of the invention. In each experiment, approximately 100 parts of water 10 parts of trisodium phosphate and 40 parts of the indicated emulsifying agent were added to 1500 parts of the oil-base drilling fluid prepared in Example I. The resulting fluid had the following approximate composition

	Percent by weight
Oil-base drilling fluid	90.2
Trisodium phosphate	0.6
Water	6.8
Emulsifying agent	2.4
	100.0

Table II

Expt. No.	Surface Active Agent	Resistivity, Ohm-cm. X10³	
		Initial	Ultimate
12	Alkylated aryl polyether alcohol (Triton X-100)	25	0.5
13	Polyoxyethylene sorbitan monolaurate (Tween 20)	125	50
14	Sorbitan monolaurate	25	12.5
15	Polyoxyethylene sorbitan monolaurate	125	50
16	Polyethylene glycol monostearate	125	125
17	Polyethylene glycol monolaurate	125	125
18	Sorbitan monolaurate	125	0

[illegible] Triton X-100. [illegible] Tween 20. [illegible] Span 20.

EXAMPLE III

Approximately 90 parts of tall oil, 45 parts of sodium silicate (N grade) 150 parts of air-blown asphalt and 45 parts of 50% aqueous sodium hydroxide were stirred into about 700 parts of light diesel fuel, and the resulting composition was diluted with about 540 parts of light domestic fuel oil. The resulting oil-base drilling fluid was stirred for one hour after which it was divided in 1500 part portions. To each portion there was then added 100 parts of water and 40 parts of hydroxypolyoxyethylene sorbitan mono-oleate (Tween 40) Approximately 10 parts of the salt indicated in the following Table III were then added to each of the portions of the drilling fluid and the resistivities of the resulting compositions were determined.

Table III

Expt. No.	Salt	Resistivity, Ohm-cm. X10³	
		Initial	Ultimate
19	None	1 000	1 000
20	Sodium bicarbonate	25	5
21	Borax	25	5
22	Trisodium phosphate	25	5
23	Trisodium polyphosphate	25	5
24	Sodium silicate	25	5

1 A sodium orthophosphate-silicate mixture.

EXAMPLE IV

Approximately 400 parts of a commercial drilling fluid concentrate comprising asphalt and lime were stirred into 980 parts of light diesel fuel. The resulting drilling fluid was divided into 1500 part portions, and to each portion was added 100 parts of water 40 parts of alkylated aryl polyether alcohol (Triton X-100) and 10 parts of the salt indicated in the following Table IV The resistivity of each sample is indicated in the table

Table IV

Expt. No.	Salt	Resistivity, Ohm-cm. X10³	
		Initial	Ultimate
26	None	1 000	1,000
27	Sodium bicarbonate	125	5.0
28	Trisodium phosphate	125	5.0
29	Trisodium polyphosphate	0	7.5

The foregoing examples illustrate the use of various electrolytes and surface active agents of the present class for imparting electrical conductivity to several different types of freshly-prepared oil-base drilling fluids. In many instances, however it is desirable to treat drilling fluids which have previously been used in the field. Such "field fluids" are almost invariably contaminated with calcium and/or sodium compounds, and while the principle of the present invention is broadly applicable to such drilling fluids, I have found that superior results are attained when the electrolyte comprises a mixture of an alkali-metal hydroxide and water-soluble salt of strong base and weak acid e. g. sodium silicate, sodium carbonate, sodium phosphate, etc. Such mixed electrolyte and the surface active agent may be added separately to the drilling fluid, but a more convenient procedure comprises in preparing pre-mixed compositions which may be packaged and sold as such as "conductivity additives" to be admixed with the drilling fluid whenever desired. Such composition suitably comprises 100 parts by weight of water between about 10 and about 40 parts by weight of a mixture of an alkali-metal hydroxide and a water-soluble salt of strong base and weak acid, and between about 20 and about 80 parts by weight of one of the surface active agents of the present class. If desired, water-miscible organic solvent such as isopropyl alcohol may be included to promote solubility of the surface active agent in the water The electrolyte mixture will comprise from about 10 to about 90 per cent by weight of the alkali-metal hydroxide and from about 90 to about 10 per cent by weight of the water-soluble salt. In employing such a "conductivity additive" composition to impart electrical conductivity to an oil-base drilling fluid the composition is simply stirred into the field in amount equal to between about 5 and about 20 per cent by weight of the entire composition. The use of such "conductivity additive composition is of course not limited to contaminated field fluids but is also applicable to drilling fluids which have not previously been used

The following example illustrates the use of mixed electrolyte in conjunction with a typical field fluid as above described

EXAMPLE V

A simulated field fluid was prepared by adding 12 parts of calcium chloride, 30 parts of sodium chloride and 250 parts of water to 15,000 parts of the drilling fluid prepared in Example I. The resulting composition was divided into 1500 part portions and to each portion there was added 100 parts of water 40 parts of hydroxypolyoxyethylene sorbitan mono-laurate (Tween 20) and varying amounts of electrolyte as indicated in the following Table V

Table V

Expt. No.	Electrolyte	Resistivity, Ohm-cm. X10³	
		Initial	Ultimate
30	None	>200	75
31	Trisodium phosphate—14 parts	125	45
32	Sodium hydroxide—10 parts Sodium silicate—14 parts	10	2.1
33	Trisodium phosphate—14 parts Sodium hydroxide—10 parts	2.5	<1.0
34	Sodium silicate—14 parts Sodium hydroxide—10 parts	2.5	<1.0
35	Sodium silicate—14 parts		

The following examples are illustrative of typical "conductivity additive" compositions which may be employed as described above

EXAMPLE VI

	Parts
Glycerol mono-oleate	27
Sodium hydroxide	3
Sodium silicate	10
Trisodium phosphate	10
Water	20
Isopropyl alcohol	10

This composition is added to the drilling fluid in an amount representing about 10 per cent by weight of the entire composition.

EXAMPLE VII

	Parts
Diethylene glycol mono-laurate	30
Sodium hydroxide	10
Sodium bicarbonate	10
Water	50

EXAMPLE VIII

	Parts
Ethylene oxide-fatty acid condensate (Emulphor AC)	40
Potassium hydroxide	5
Sodium silicate	20
Water	35

As will be apparent to those skilled in the art many variations in the composition of the drilling fluid and/or the conductivity additives may be made without departing from the scope of the invention. The essence of the invention lies in adding to normally non-conductive oil base drilling mud between about 0.01 and about 5 per cent by weight of a water-soluble metal salt or hydroxide between about 0.1 and about 0.5 per cent of a non-ionic surface active agent and sufficient water to adjust the total water content of the composition to between about 3 and about 10 per cent, all of said proportions being based on the weight of the entire composition

The conductive drilling fluids provided by the invention may be employed in any of the various well logging methods which require that one or more electrodes be positioned within a well bore filled with a conductive fluid Certain of such methods comprise measurement of the electrical resistivity of the earth formations traversed by the bore Others comprise measuring the so-called "self-potential" of such formations Regardless of the exact nature of the logging method however the hereinbefore described drilling fluids are well adapted to use as the conductive fluid with which the bore filled and within which a electrode is submerged

Other modes of applying the principle of my invention may be employed instead of those explained change being made as regards the methods or materials employed provided the compositions stated by any of the following claims, or the equivalent of such stated compositions, be obtained.

I therefore, particularly point out and distinctly claim as my invention

1 An oil-base drilling fluid comprising a mineral oil carrying suspended solids and sufficient of a dispersing agent to maintain said solids dispersed in said oil, between about 3 and about 10 per cent by weight of water between about 0.01 and about 5 per cent by weight of an electrolyte selected from the class consisting of water-soluble metal salts and alkali-metal hydroxides, and between about 0.1 and about 5 per cent by weight of a non-ionic surface active agent.

2. An oil-base drilling fluid according to claim 1 wherein the dispersing agent is a metal soap.

3 An oil-base drilling fluid according to claim 1 wherein the dispersing agent comprises a mixture of water-dispersible and oil-dispersible resin soaps.

4. An oil-base drilling fluid according to claim 1 wherein the surface active agent is selected from the class consisting of (1) partial esters of polyhydric alcohols with long-chain carboxylic acids, (2) esters of hydroxy alkyl ethers of polyhydric alcohols with long-chain carboxylic acids, and (3) polyalkylene ether alcohols.

5. An oil-base drilling fluid comprising a mineral oil having suspended therein a solid wall-building agent and a finely divided inert weighting agent and sufficient of a dispersing agent to maintain said solids dispersed in said oil, between about 3 and about 10 per cent by weight of water between about 0.01 and about 5 per cent by weight of an electrolyte selected from the class consisting of water-soluble metal salts and alkali-metal hydroxides, and between about 0.1 and about 6 per cent by weight of a non-ionic surface active agent selected from the class consisting of (1) partial esters of polyhydric alcohols with long-chain carboxylic acids, (2) esters of hydroxy alkyl ethers of polyhydric alcohols with long-chain carboxylic acids and (3) polyalkylene ether alcohols.

6. An oil-base drilling fluid according to claim 5 wherein said wall-building agent is a hydratable clay.

7. An oil-base drilling fluid according to claim 5 wherein the dispersing agent is a metal soap.

8. An oil-base drilling fluid according to claim 5 wherein the surface active agent is a hydroxypolyoxyethylene ether of a long-chain fatty acid partial ester of sorbitan.

9. An oil-base drilling fluid according to claim 5 wherein the electrolyte is selected from the class consisting of alkali-metal hydroxides, alkali-metal silicates, and alkali-metal phosphates.

10. An electrically conductive oil-base drilling fluid comprising (1) normally non-conductive drilling fluid prepared by dispersing in a mineral oil between about 1 and about 10 per cent by weight of an alkali-metal alkali saponification product of rosin which has been heat-treated at a temperature between about 250° and about 350° C. for a period of time sufficient to raise its specific rotation to a value above about +5 said saponified rosin product containing between about 1 and about 15 per cent by weight of free rosin acids between about 0.1 and about 5 per cent by weight of a hydratable clay between about 0.2 and about 10 per cent by weight of water and an amount of an alkaline-earth metal base corresponding approximately to that chemically equivalent to said saponified rosin product (2) between about 0.01 and about 5 per cent, based on the weight of the entire composition, of an electrolyte selected from the class consisting of water-soluble metal salts and alkali-metal hydroxides; (3) between about 0.1 and about 3 per cent, based on the weight of the entire composition, of a non-ionic surface active agent selected from the class consisting of (a) partial esters of polyhydric alcohols with long-chain carboxylic acids, (b) esters of hydroxy alkyl ethers of polyhydric alcohols with long-chain carboxylic acids, and ( ) polyalkylene ether alcohols and (4) sufficient water to adjust the water content of the entire composition to between about 3 and about 10 per cent by weight.

11. An electrically conductive oil-base drilling fluid according to claim 10 wherein the electrolyte is provided in an amount representing between about 0.1 and about 2 per cent by weight of the entire composition, the emulsifying agent is provided in an amount representing between about 0.4 and about 4 per cent by weight of the entire composition, and sufficient water is provided to adjust the water content of the entire composition to between about 5 and about 10 per cent by weight.

12. An electrically conductive oil-base drilling fluid according to claim 10 wherein the surface active agent is a hydroxypolyoxyethylene ether of a long-chain fatty acid partial ester of sorbitan.

13. An electrically conductive oil-base drilling fluid according to claim 10 wherein the alkaline-earth metal base component of the normally non-conductive fluid is selected from the class consisting of calcium hydroxide and calcium oxide.

14. An electrically conductive oil-base drilling fluid according to claim 10 wherein the alkali-metal alkali saponification product is the potassium hydroxide saponification product of rosin which has been heated at a temperature between about 200 and about 300° C. for a period of time sufficient to raise its specific rotation to a value above about +5 and comprises between about 45 and 55 per cent of potassium resin soaps, between about 30 and about 35 per cent of unsaponifiable materials, between about 5 and about 10 per cent of free resin acids, and between about 5 and about 10 per cent of water.

15. An electrically conductive oil-base drilling fluid according to claim 10 wherein the alkali-metal alkali saponification product is that obtained by heating rosin at a temperature between about 225 and about 300 C. for from best 15 to best 60 minutes in the presence of a hydrogenation catalyst but in the absence of added hydrogen, distilling the resulting product and collecting a fraction distilling between about 210° and about 275 C. under 5–10 mm. pressure, and thereafter saponifying such fraction with aqueous sodium hydroxide.

16. In a well logging method wherein at least one electrode is positioned within a well bore filled with an electrically conductive fluid, the improvement which consists in employing as said fluid the conductive oil-base drilling fluid defined by claim 1.

17. In a well logging method wherein at least one electrode is positioned within a well bore filled with an electrically conductive fluid, the improvement which consists in employing as such fluid the conductive oil-base drilling fluid defined by claim 5.

18. In a well logging method wherein at least one electrode is positioned within a well bore filled with an electrically conductive fluid, the improvement which consists in employing as such fluid the conductive oil base drilling fluid defined by claim 10.

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Evidence for Synergism in Nonionic Surfactant Mixtures Enhancement of Solubilization in Water in Oil Microemulsions

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It is well known that certain mixtures of surfactants can provide better performance than pure surfactants for a wide variety of applications [1,2] and thus it is expected that enhanced solubilization of water in water in oil (w/o) microemulsions will also be achieved with certain surfactant mixtures The formation of w/o microemulsions involves dissolving an aqueous phase into an oil phase creating a transparent and thermodynamically stable suspension of droplets with diameters in the range of 10–100 nm It is desirable to accomplish this with a minimum amount of surfactant [3] and in order to achieve this goal mixtures of surfactants can be used We intend to address different surfactant mixtures that exhibit *synergism* in the solubilization of water in w/o microemulsions showing the existence of at least two different mechanisms of synergism

Synergism in surfactants may be defined as any situation where mixtures of surfactants have superior properties when compared to the properties of any of the single components alone Although certain mixtures of dissimilar surfactants can be expected to show synergism enhancement in properties may also occur with mixtures of similar structures Shinoda et al [4,5] have demonstrated that *macro*emulsions made with nonionic surfactants that have been purified to a single poly(ethylene oxide) chain length are generally less able to solubilize the dispersed phase into the continuous phase when compared to *macro*emulsions made with surfactant having the same average length but an ethylene oxide size distribution Ordinarily one would not expect strong synergistic effects in mixtures of nonionic surfactants as synergism in anionic/nonionic surfactant mixtures has been attributed to Coulombic ion–dipole or hydrogen bonding interactions among the polar groups Nonionics which have minimum intermolecular interactions should have by comparison the lowest synergism of all mixtures [6] In light of this previous work we are able to demonstrate strong synergism in nonionic surfactant mixtures

When formulating water in oil microemulsions one must account for several factors including the partitioning of the surfactant (or its components) between the oil water and interfacial domains (Figure 1) For maximum solubilization it is desirable to have most of the surfactant at the interface between the oil and water rather than

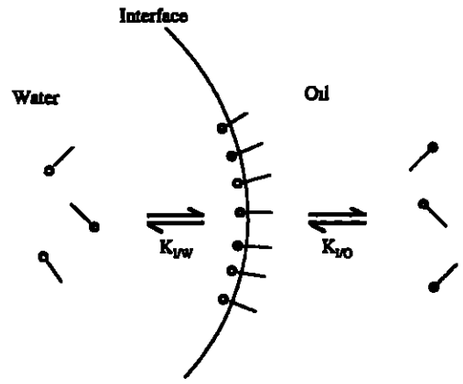

Figure 1 In microemulsions all surfactant molecules are distributed between the oil water and interface

Table 1 Surfactants Used in This Study[a]

surfactant (Igepal)	abbrev	EO number	HLB	water soluble	oil soluble
CO 210	$C_9PhE_{1.5}$	1.5	4.6	no	yes
CO-430	C_9PhE_4	4	8.8	no	yes
CO 520	C_9PhE_5	5	10.0	no	yes
CO 530	C_9PhE_6	6	10.8	no	yes
CO 610	$C_9PhE_{7.5}$	7.5	12.2	yes	yes
CO-720	C_9PhE_{12}	12	14.2	yes	yes

[a] The Igepal CO family of surfactants are nonylphenyl ethoxylates (p-t $C_9H_{19}C_6H_4(OC_2H_4)_nOH$)

dissolved in the oil or water phases Increasing the interfacial area should also increase solubilization Synergism in microemulsion solubilization has been previously reported for a nonionic–anionic system designed for pharmaceutical applications using mixtures of AOT (sodium bis(2-ethylhexyl)sulfosuccinate) and Arlacel 20 (sorbitan laurate) in different proportions [7,8] The present paper reports similar improvements using nonionic–nonionic surfactant mixtures for solubilization of water in water in-oil microemulsions and provides evidence for two different synergism mechanisms

Experimental Procedure

Microemulsion solubilization experiments were performed by titrating water into a mixture of surfactant and oil The transition from a clear to a cloudy solution indicates that the maximum water solubilization has been exceeded The rate of solubilization decreases as the maximum solubilization is approached Due to these kinetic considerations the final cloudy transition was established only after several hours of stirring of a sample All experiments were performed at 25 C The initial surfactant to oil ratio was 0.20 by weight with nonylphenyl ethoxylate surfactants (Igepal CO series Rhone-Poulenc Cranbury NJ) and cyclohexane (Fisher Scientific Fair Lawn NJ) as the oil phase Similar microemulsions have been well-characterized and used for nanoparticle synthesis [9]

The surfactants used in the solubilization experiments are commercial grade nonylphenyl ethoxylates (C_9PhE_n) with properties summarized in Table 1 This family of surfactants has the same hydrophobic domain (nonylphenol) and variation only in the length of the hydrophilic domain which consists of poly(ethylene oxide) No attempt was made to further purify these materials These surfactants are synthesized by polymerization of ethylene oxide to nonylphenol resulting in a wide distribution of the number of ethylene oxide residues on any given molecule around an average EO number for the mixture

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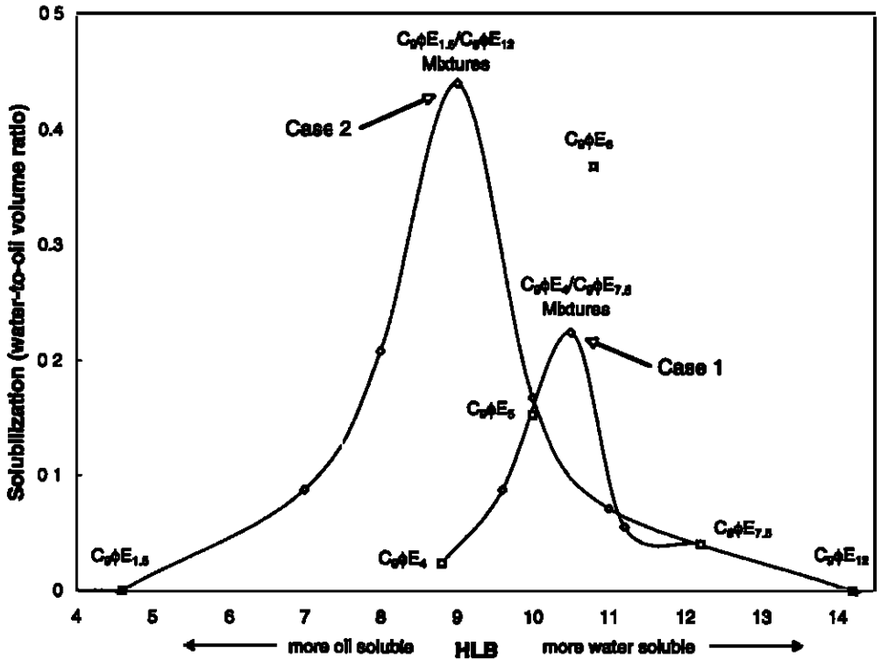

Figure 2 Maximum water solubilization (as a w/o microemulsion) vs HLB for mixtures of nonylphenyl ethoxylate surfactants in cyclohexane

The distribution of these chain lengths is often assumed to be a Poisson distribution and may also include a few percent unreacted nonylphenol or material with EO = 1 or EO = 2 in excess of that predicted by the Poisson calculation. All surfactants were soluble in cyclohexane and only the two with the largest EO number were soluble in water. It is expected that the surfactants with lower EO number are more oil soluble especially in *n*-alkane oils.

Solubilization results are presented as a maximum water-to-oil volume ratio (x) solubilized. To convert to weight fractions of water (W), oil (O), and surfactant (S), the following formulas may be used, based on sample sizes of 1.2 g of surfactant and 4.8 g of oil (6.16 mL for cyclohexane):

$$W = 6.16x/(6 + 6.16x)$$

$$O = 4.8/(6 + 6.16x)$$

$$S = 1.2/(6 + 6.16x)$$

The maximum solubilization of 0.44 water/oil volume ratio for the optimum $C_9PhE_{1.5}/C_9PhE_{12}$ case represents a total of 31 wt % water, 55 wt % oil, and 14 wt % surfactant, or a 0.56 water/oil weight ratio.

Discussion

Figure 2 shows water solubilization in water in oil microemulsions for single nonylphenyl ethoxylates as well as binary mixtures vs HLB. The HLB can be calculated for these surfactants from the average EO content of the molecule. HLB is defined as the hydrophile–lipophile balance of a surfactant and for ethoxylated surfactants can be calculated as 20 times the weight fraction of poly(ethylene oxide) in the molecule.[10,11] HLB was initially intended to aid in the selection of surfactant mixtures for *macro*emulsion formulation.

Of the single surfactants studied, nonylphenyl ethoxylate (C_9PhE_6) with an HLB of 10.8 achieved the largest solubilization of water in cyclohexane (Figure 2). This system compares favorably with previous water in oil microemulsion formulation results using *n*-alkanes and sorbitan ester ethoxylates[12] where it was established that optimum w/o microemulsions were created for surfactant mixtures that fell in the HLB 8.5–11 range. This range is much different from that of macroemulsions where w/o emulsions are expected to form for surfactant mixtures in the HLB 3–6 range while o/w emulsions generally form in the HLB 10–18 range.[10,11]

Two different surfactant mixtures were investigated. Case 1 (Figure 2) involved two surfactants C_9PhE_4 and $C_9PhE_{7.5}$ that were close in molecular size to C_9PhE_6 which was the best performing single surfactant. Case 2 (Figure 2) involved $C_9PhE_{1.5}$ and C_9PhE_{12} which were much less similar in molecular size than the previous case. Both of these mixtures showed superior solubilization results over either pure component at some mixture ratio with case 2 clearly showing superior results over both case 1 and the best single surfactant case. The underlying reasons for these differences become more clear when we examine the composition of the mixtures.

Surfactant Size Distributions. As the surfactants we consider here are not pure single component species but rather a wide distribution of homologous compounds, let us compare the actual distributions of the different surfactants and mixtures. In Figure 3 we plot the mole fraction of each EO component in each surfactant vs the HLB number of that particular fraction. These size distributions arise from the method of synthesis of the surfactant, as ethylene oxide is polymerized to nonylphenol by anionic polymerization the resulting EO distribution is ideally a Poisson distribution. Thus for a surfactant with an EO number of N the relative mole fraction x of any EO number component can be calculated by

$$P(x) = N^x e^{-N}/x! \qquad (1)$$

For all of these components of EO = x the HLB of the

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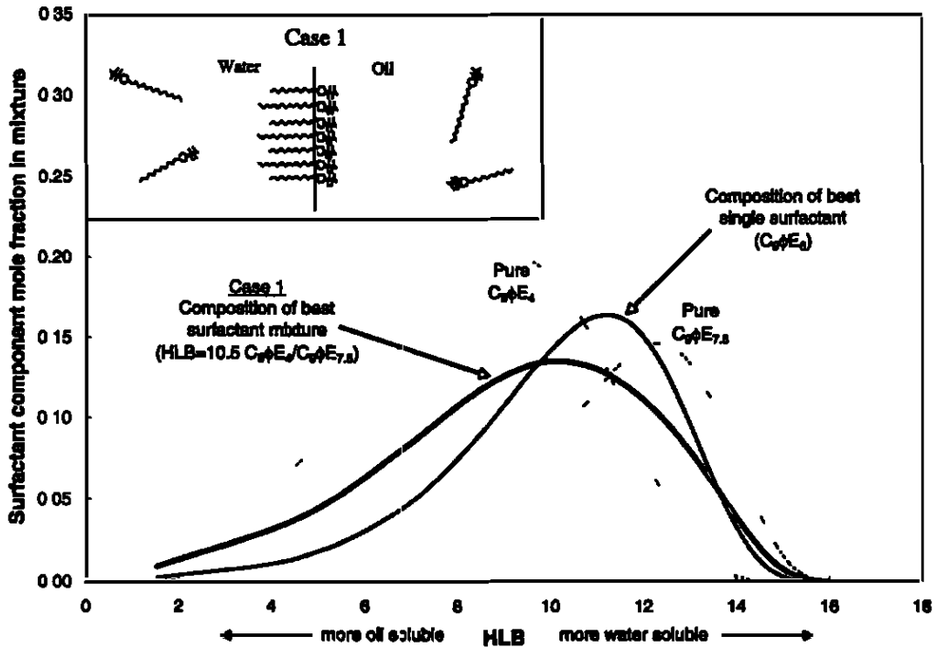

Figure 3 Distribution of components in single nonylphenyl ethoxylate surfactants as well as mixtures for case 1

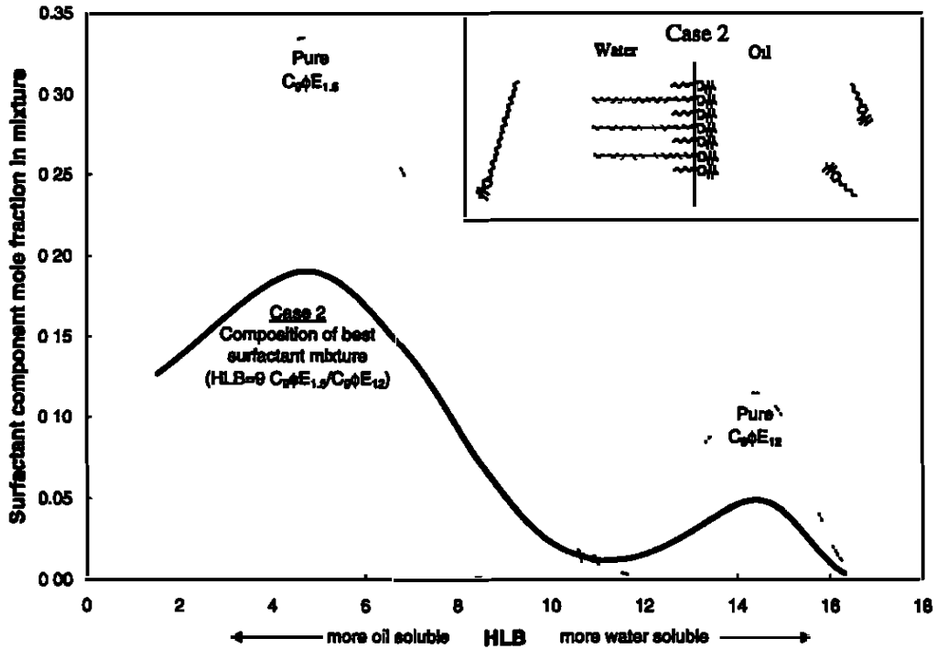

Figure 4 Distribution of components in single nonylphenyl ethoxylate surfactants as well as mixtures for case 2 showing evidence for synergism

component can be calculated for nonylphenyl ethoxylates using

$$\mathrm{HLB}(\mathrm{EO} = x) = 20\ (17 + 44x)/(220 + 44x) \quad (2)$$

where we include the terminal hydroxyl group (MW = 17) in addition to the ethylene oxide residues (MW = 44) into the hydrophilic domain

Case 1 For the first case Figure 3 shows the distribution of components for the best single surfactant C_9PhE_6 along with the two components of the mixture C_9PhE_4 and $C_9PhE_{7.5}$ The curves represent the actual HLB values of the components within each of the surfactants or surfactant mixtures with the distribution of components calculated from eq 1 and the HLB values for each EO component from eq 2 From Figure 3 it can be seen that C_9PhE_6 has the bulk of its material in the HLB 9−13 region which can be expected for good water in-oil microemulsion solubilization For the mixtures the peak solubilization case (a 50 50 mixture of C_9PhE_4 and $C_9PhE_{7.5}$ with an $HLB_{mix} = 10\ 5$) is plotted This EO distribution of the mixture has a shape similar to the distribution curve for the best single surfactant (C_9PhE_6) although somewhat wider Again it appears that the best solubilization for the mixture occurs where the mixture

has most of its components in the HLB 9−13 region This supports the concept that good solubilization occurs when most of the surfactant falls in a certain HLB region being neither very water soluble nor very oil soluble This should cause conditions where it is most favorable for the surfactant to partition at the interface In such a case solubilization for the mixtures is better than that of either component The best mixture does not solubilize more than the best single surfactant C_9PhE_6 with a similar EO number distribution (Figure 2) Thus the solubilization ability in this case appears to be related only to simple additive contributions of the surfactant material in the HLB 9−13 region with no apparent additional benefit from synergism between the two surfactants

Case 2 Figure 4 shows a second much different scenario The two components in this mixture C_8PhE_{15} and C_9PhE_{12} are very oil soluble and very water soluble respectively Both surfactants have little of their material in the HLB 9−13 region The plot of the distribution for the optimum mixture (43 wt % C_9PhE_{12} $HLB_{mix} = 9$) does not have a single maximum Given the composition of individual components the optimum mixture actually has a minimum of material in the HLB 9−13 region In this case the high level of solubilization has nothing to do with the amount of this material which is completely opposite to the previous case in Figure 3 Given the conclusions of the first case one would expect less surfactant to partition to the interface as the two surfactant components are highly soluble in the oil (C_9PhE_{15}) or the water (C_9PhE_{12}) phases This must not be the case though as mixtures of these two surfactants clearly show the highest water solubilization even greater than the best single surfactant (C_9PhE_8) Some true synergistic effect must cause these components to preferentially partition to the interface for only if the majority of surfactant partitions to the interface can such a high level of solubilization be achieved

Conclusions

Two different approaches for surfactant selection can be considered in order to achieve a high level of water solubilization in water in-oil microemulsion formulations The first approach is to maximize the amount of surfactant in the HLB 9−13 region where it is intermediate between high oil solubility and high water solubility Achieving more surfactant partitioning to the interface as opposed to partitioning into the bulk phases will allow for stabilization of a larger interfacial area and thus a high level of solubilization Even greater solubilization can result if some synergism between surfactant components can be achieved As a second approach mixtures of a highly oil soluble surfactant and a highly water soluble surfactant achieved the maximum water solubilization evidently overcoming the expected partitioning of the two surfactant components into the oil and water phases and enhancing their partitioning to the interface

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Apoderado

Solicitante **Halliburton Energy Services, Inc**

ASUNTO	Radicacion	**04-10426**
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	9353
	Folios	014

Como resultado del examen de fondo, realizado con fundamento en el articulo 45 de la Decisión 486 de la Comision de la Comunidad Andina, se le comunica

1 Documentos estudiados

1 1	Descripcion	Folios 7 a 22
1 2	Reivindicaciones	Folios 23 a 25
1 3	Prioridad	Folio 29, Solicitud de Estados Unidos No 09/939,990 del 27 de agosto de 2001

2 Objeto de la invencion

- El titulo de la solicitud es **"LODO CONDUCTOR BASADO ELECTRICAMENTE EN ACEITE"** (Folio 1)

- La presente invencion se refiere a lodos o fluidos basados en aceite para uso en la perforación de pozos en formaciones subterraneas Mas en particular, la invencion se refiere a lodos basados en aceite, aptos o compatibles para uso con imagenes de resistividad del pozo o de la formacion

  En la **reivindicación independiente 1** se plantea un metodo para obtener imágenes de resistividad de una formacion durante la perforación de un pozo en dicha formación con un fluido de perforacion conductivo basado en aceite, dicho fluido comprende un aceite de base de éster polar, un surfactante derivado de éster sorbitan y un surfactante derivado de éster sorbitan etoxilado, en donde dichos surfactantes son en cantidades suficientes para crear micelas que tienen una mayor concentracion en la capa de la palizada

  En la **reivindicación independiente 10** se plantea un metodo para perforar un pozo mientras se obtienen imagenes de resistividad de la formacion en la que se perfora el pozo, dicho método comprende utilizar un fluido de perforacion eléctricamente conductivo basado en aceite dicho fluido comprende surfactantes de ácido graso complementarios y un aceite base polar

En la **reivindicacion independiente 13** se define un fluido de perforacion que comprende un aceite base polar y surfactantes complementarios, de modo que dichos surfactantes formen micelas que tienen una concentracion más densa en la capa de la palizada de dicho fluido que cualquier surfactante pudiera tener por si solo

- Existe la necesidad de nuevos fluidos de perforación basados en aceite de emulsion invertida con propiedades conductivas adecuadas para uso con registros de resistividad

- El objeto de la invencion definido se catalogó como **C09K 7/06**, segun la Clasificación Internacional de Patentes (IPC)

3 De la solicitud de Patente

3 1 Titulo

- El titulo de la invención segun se encuentra en el folio 1 es "LODO CONDUCTOR BASADO ELECTRICAMENTE EN ACEITE No obstante, esta traducción resulta deficiente y confusa Se recomienda que el título sea modificado del siguiente modo **"LODO ELECTRICAMENTE CONDUCTOR BASADO EN ACEITE"**

3 2 Descripcion (articulo 28 D 486)

- El capitulo descriptivo contiene cantidades expresadas en el sistema inglés de unidades Se recomienda realizar la conversión al Sistema Internacional de Unidades

- En conclusión, la descripción no cumpliria con el requisito de acuerdo con el art 28 de la Decisión 486

3 3 Reivindicaciones (articulo 30 D 486)

- La reivindicacion independiente 1 se plantea como 'Un método para obtener imágenes de resistividad de una formación durante la perforacion de un pozo en dicha formacion con un fluido de perforacion conductivo basado en aceite' Sin embargo, se hace una caractenzación de la naturaleza quimica del fluido base aceite No es coherente definir un metodo de monitoreo de formaciones subterráneas como lo es el de imagenes de resistividad, tan solo mencionando la naturaleza del fluido de perforación pues dicho método es una tecnología que implica otras operaciones

  Segun la materia de la invención descnta con la solicitud, el objeto central de esta corresponde al fluido de perforación, su naturaleza y composición, por ello, se recomienda que el preambulo de la reivindicacion independiente 1 sea coherente con la materia de la invención, es decir, se plantee en términos del fluido de perforación

- En la reivindicación independiente 1 se menciona que 'dichos surfactantes son en **cantidades suficientes para crear micelas que tienen una mayor concentración en la capa de la palizada**' No obstante, la expresión 'cantidades suficientes' no es clara pues genera dudas sobre las magnitudes precisas relacionadas con las cantidades de cada surfactante Además cuando menciona que es para crear micelas que tienen una mayor concentración en la capa de la palizada' esta informacion corresponde a un resultado a alcanzar y no a una caracteristica propia de la formulación del fluido de perforación Dado lo anterior, se recomienda considerar que si es importante la cantidad de surfactantes, se incluyan numéricamente en la reivindicacion 1 de modo que se elimine la

expresión 'cantidades suficientes' De otra parte, se recomienda que la información que se incluya en la reivindicacion independiente 1 corresponda a la solucion tecnica y no a los efectos o resultados que esta pueda tener, entonces se recomienda eliminar la información que corresponde a resultados a alcanzar

- La reivindicacion dependiente 3 se relaciona con la reivindicación 1 pero incluye caracteristicas de la preparacion del fluido de perforación, lo cual es incoherente pues en la reivindicación 1 no se ha mencionado el método de preparacion del fluido Dado lo anterior, si el señor solicitante considera que su propuesta también abarca el método de preparación del fluido de perforacion, se recomienda que plantee una reivindicación independiente para este y defina las caracteristicas novedosas que constituyen el aporte con la propuesta de la solicitud Si asi lo hace, tambien debe modificar el titulo de la invencion

- En las reivindicaciones dependientes 4 y 16 no se hizo una traduccion adecuada En dichas reivindicaciones se menciona que la 'emulsion comprende entre 85 y 95 **volumen porcentaje** de éster y entre 5 y 15 **volumen porcentaje** de salmuera Se recomienda que la expresión resaltada en negrilla sea **porcentaje en volumen** o **%V/V**

- Las reivindicaciones dependientes 6 y 7 incluyen fórmulas del éster sorbitan y del éster sorbitan etoxilado pero no son legibles Se recomienda mejorar la legibilidad de las estructuras para facilitar la compresion y para efectos de digitalizacion

- En la reivindicación 11 se hace mención de que los surfactantes son complementarios pero no está clara dicha propiedad porque se especifica que al menos uno de dichos surfactantes de ácido graso complementarios es **más soluble en agua** que los demas, y al menos uno de los demas surfactantes de ácido graso complementarios es **más soluble en agua** que los demás', mientras que en la descripción se explica que *"Los surfactantes son complementarios, es decir uno es más soluble en **agua** que el otro y uno es más soluble en **aceite** que el otro"* (Negrita Personal) (Folio 10, resumen de la invencion) Se recomienda rectificar la información que se especifica en la reivindicación 11

- En la reivindicación independiente 13 se plantea un fluido de perforación pero se caracteriza por los resultados a alcanzar diciendo 'que dichos surfactantes formen micelas que tienen una concentración más densa en la capa de la palizada de dicho fluido que cualquier surfactante pudiera tener por si solo Esto no constituye una definición de la materia de la invencion sino de un resultado, por ello se recomienda que en el capítulo reivindicatorio se plantee una sola reivindicacion independiente para el fluido de perforacion y que su parte caracterizante incluya la naturaleza quimica y proporciones de los componentes del fluido, eliminando la informacion correspondiente a los resultados a alcanzar

- En la reivindicacion dependiente 16 se incluye la expresión "aproximadamente" que no confiere precisión a la invención Se recomienda eliminar dicha expresion

- En conclusion, el capitulo reivindicatorio no cumpliria con el requisito de claridad como se requiere segun el art 30 de la Decisión 486

4 Determinacion del Estado de la Técnica

Considerando que la fecha de presentacion de la primera solicitud de patente de la cual se reivindica prioridad es **27 de agosto de 2001**, se buscaron documentos del estado de la técnica relacionados con fecha de publicacion anterior a esta y se encontraron los siguientes

N°	D cumento	Titulo	Publicación
D1	US2739120	"ELECTRICALLY CONDUCTIVE DRILLING FLUIDS"	20 de marzo de **1956**
D2	"EVIDENCE OF SYNERGISM IN NONIONIC SURFACTANT MIXTURES ENHANCEMENT OF SOLUBILIZATION IN WATER-IN-OIL MICROEMULSIONS"		*Langmuir* **1997**, 13, 5762 – 5765

Se anexan copias en el documento adjunto

5 Analisis de patentabilidad (segun requisito) (articulo 14 D486)

5 1 Nivel inventivo (artículo 18 D486)

- Comentarios sobre el estado de la tecnica

La investigacion del estado de la técnica relacionado con lodos de perforación permitio identificar la evolucion en este campo, observándose una tendencia inicial (1920) al empleo de lodos base aceite y a la incorporacion de petróleo (1930) para aumentar velocidades de perforación En décadas posteriores (1960 a 1980) se avanzo en el empleo de emulsiones base aceite o emulsiones inversas con los consiguientes desarrollos en materia de aditivos, sin embargo, los problemas ambientales fueron identificados, motivando al desarrollo de fluidos sintéticos biodegradables En 1990 y 1991 los ésteres y las polialfaolefinas respectivamente, fueron los primeros fluidos sinteticos conocidos y desde ese momento, los avances se han dado con base en fluidos no tóxicos

El documento **US2739120** (D1) forma parte del estado de la técnica y enseña fluidos de perforacion electricamente conductivos empleados en la investigacion y determinacion de la naturaleza de las formaciones subterráneas (Columna 1, lineas 62 – 66), que consisten en emulsiones agua en aceite y que incluyen agentes surfactantes particulares no iónicos como por ejemplo, monooleato sorbitan, monopalmitato sorbitol, trioleato sorbitan, (se hace mencion de SPAN®) condensados de polioxietileno de monooleato de sorbitan, condensados de polioxietileno de monopalmitato de sorbitan (se hace mencion de TWEEN®)

En D1 tambien se particulariza la incorporacion de agentes de superficie como monolaurato hidroxipolioxietilen sorbitan, monopalmitato hidroxipolioxietilen sorbitan, trioleato hidroxipolioxietilen sorbitan, sin embargo, aun se situa dicha información en la generacion de los lodos base aceite (aceite mineral por ejemplo)

El documento ***"EVIDENCE OF SYNERGISM IN NONIONIC SURFACTANT MIXTURES ENHANCEMENT OF SOLUBILIZATION IN WATER-IN-OIL MICROEMULSIONS"*** (D2) forma parte del estado de la técnica y en una etapa más avanzada de desarrollo (década de los 90's) enseña que en las microemulsiones agua en aceite (w/o) se puede aumentar la solubilización mediante la incorporación de mezclas de surfactantes no iónicos dado que se demuestra un **efecto sinergico** importante

D2 contiene informacion sobre lo conocido que es el desarrollo de ciertas mezclas de surfactantes porque proveen un desempeño mejor que al adicionar surfactantes puros De hecho, se logra sinergia en la solubilización de agua en emulsiones w/o

En D2 se explica que para maximizar la solubilizacion es deseable tener más surfactantes en la interfase entre el aceite y el agua que disueltos en la fase agua y en la fase aceite, pues el incremento del area interfacial permite incrementar la solubilizacion

En D2 se demuestra que mezclas de un surfactante altamente soluble en aceite y un surfactante altamente soluble en agua alcanzan máxima solubilizacion

- Comentanos sobre la propuesta y la informacion del estado de la técnica

El señor solicitante realiza una propuesta (año 2001) de un fluido de perforación base aceite y eléctricamente conductor que se define en las reivindicaciones del caso en estudio Al analizar el planteamiento de la propuesta, se entiende que el principio tecnico sobre el cual se fundamenta consiste en fluidos de perforacion basados en aceite con propiedades conductivas, que incluyen **composiciones sinérgicas** de surfactantes derivados de éster sorbitan y de éster sorbitan etoxilado

Es claro que para el señor solicitante es muy importante incorporar la composicion sinergica de los surfactantes derivados de éster sorbitan y éster sorbitan etoxilado como bien lo sustenta en la descripción No obstante, al analizar el estado de la técnica es posible afirmar que un técnico de nivel medio versado en la materia, como puede ser un ingeniero quimico con experiencia en emulsiones y que también realiza mejoramientos en su campo de trabajo, tiene acceso a información como la reportada en D1 y D2

Basándose en D1 el tecnico puede motivarse a desarrollar lodos electricamente conductivos que consistan en una emulsión agua en aceite (w/o) en la que se empleen surfactantes con la misma naturaleza quimica que tienen los propuestos en la solicitud De hecho, hasta en D1 se hace referencia a las mismas denominaciones comerciales de la composición citada en la descripción de la solicitud en estudio (SPAN® y TWEEN®)

Con D1 un técnico optaria por incluir un solo surfactante pues en ningun momento se hace mencion de los efectos sinergicos No obstante, con D2 se demuestra que un tecnico conoce la posibilidad de mejorar la estabilidad de las emulsiones mediante incorporar varios surfactantes Así las cosas, con la información contenida en D1 y D2, el técnico se veria motivado a desarrollar ensayos de rutina para determinar combinaciones de surfactantes sugeridos en D1 donde uno de los surfactantes sea soluble en agua y el otro sea soluble en aceite para obtener un desempeño sinérgico en el sistema w/o

Lo anterior permite afirmar que proponer lodos base aceite eléctricamente conductivos con la composicion sinérgica propuesta en las reivindicaciones, no parece ser una solucion tecnica que genere un efecto sorprendente que evidencie un salto tecnologico respecto al arte previo Por el contrario parece un mejoramiento que puede realizar un técnico de nivel medio y que cae dentro de la linea normal de avance de la tecnologia

Asi, la propuesta definida en las reivindicaciones de la solicitud no parece cumplir con el requisito de nivel inventivo como se requiere segun el articulo 18 de la Decisión 486

6 Conclusi n

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados asi

N°	Documento N°	Reivindicaciones Afectadas	Requisito que Afecta
D1	US2739120	1 - 20	Nivel Inventivo
D2	*"EVIDENCE OF SYNERGISM IN NONIONIC SURFACTANT MIXTURES ENHANCEMENT OF SOLUBILIZATION IN WATER-IN-OIL MICROEMULSIONS"*		

En cumplimiento del articulo 45 de la Decisión 486 de la Comision de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de **sesenta** días contados a partir de la fecha de notificacion de la presente comunicación En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5 2, literal e), del capitulo quinto del titulo primero de la circular unica No 10 de 2001

ALIX CARMENZA CESPEDES DE VERGEL
Jefe de División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 03 AGO 2007

CONCEPTO TECNICO No 1149	EXAMINADOR TECNICO Codigo No 202042