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PHASE SEPARATION PROCESS

Roy N. Lucas, Houston, Tex., assignor to Petrolite Corporation, Wilmington, Del., a corporation of Delaware

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This invention relates to a process of breaking petroleum emulsions. This invention is more particularly adapted to breaking petroleum emulsions formed in removing oil from rocks and sands such as for example tar sand emulsions, or other heavy crude emulsions.

Oil is often found in conjunction with various kinds of rocks and sand. Tar sands, sands which are impregnated with heavy petroleum, are found in most areas of the world where petroleum is present such as in France, Poland, Rumania, Russia, the Middle and Far East, the U.S.A., etc. In the United States the largest and richest accumulations are in California and Utah although substantial deposits are found in Kentucky, Oklahoma and Texas. However, the largest and most important deposits are the Athabasca tar sands found primarily in Northern Alberta, Canada.

The Athabasca oil sands in northeastern Alberta contain one of the world's largest reserves of recoverable oil. The amount of oil in the formation is estimated to be between 300 and 500 billion barrels. Using a conservative estimate for the recovery ratio, there are at least 100 billion barrels of marketable oil reserves.

The oil sand layer averages 150 feet in thickness and is made up of layers of unconsolidated oil-bearing sand interspersed with clay, shale and lignite as well as some rock and boulders. The sand is primarily quartz with varying percentages of silt and clay. The oil saturation in the sand varies from 3 to 18 percent; sand with oil saturation in excess of 10 percent is classed as a "good" grade.

The oil sand overburden, which varies from zero to 2,000 feet in thickness, dictates the method of oil recovery. With a ratio of oil sand to overburden of 1:1 or greater, some form of open-pit mining is the most economical recovery method. With a larger ratio of overburden to sand, in situ recovery methods are required. It is estimated that 4 billion barrels are recoverable by open-pit mining methods. To place this number in perspective, it should be recalled that the proven reserves in the United States do not exceed 35 billion barrels.

In general, the oil found in the formation is a heavy, viscous, low quality hydrocarbon containing 4% sulfur and 0.4% nitrogen. The specific gravity varies from 1.002 to 1.027, i.e., the API gravity is between 9 and 6. The viscosity is greater than 3,000 poise at 60° F.

In general, oil is recovered from the oil sands by (1) mining or (2) in situ recovery methods.

One method of separating the oil from the sand is by hot water washing which has been developed by the Research Council of Alberta. In this process the first step is to heat and mix the oil sand into a pulp containing 12–15% water. The pulp is then abruptly flooded with excess water in a manner which involves minimum entrainment of air. The oil collects on the surface of the water as a buoyant froth from which it can be removed by skimming. This froth contains about 5% by weight of mineral matter and about 30–35% water. A temperature of 185° F. is about optimum for pulping and flooding operations.

When oil sand is mixed and heated to a pulp of 12–15% water content, the oil lies among the sand grains as oil flecks, all of which are small, and some of which are very small. On flooding the pulp with water, the coarser

of the oil flecks form bubbles and float to the surface. The very fine flecks do not form bubbles and remain suspended in the water. The gas phase of the froth appears to be water vapor supplemented by air to increase the pressure to that of the atmosphere.

Entrainment of air at the point of flooding the pulp causes a fluffy froth that is loaded with sand particles. At the Bitumount plant there was obtained a recovery of 90% of the oil as froth which contained 30–35% water and 4–8% mineral matter, on a dry basis.

Another process employed for example by Abasand Oils, Ltd. is the cold water washing process. The principles involved in the cold water treatment are simple.

In order to increase the fluidity of the oil content of the oil sand so that it will flow readily at room temperatures and to reduce its density below that of water so it will float, a distillate such as kerosene is mixed with the oil sand. Soda ash and a wetting agent are added to the pulp to assist the disengagement of oil and sand. The oil so treated is agitated in water. The diluted oil floats, as a water-in-oil emulsion, and mineral matter sinks. The oil is collected and then settled to reduce its content of mineral matter and water.

At present all of the promising projects for recovery of oil from tar sands except that developed by Shell involve stripping. Shell Oil Company of Canada has developed an in situ process of removing oil from the tar sands wherein steam and caustic are pumped into drilled wells which may be summarized as follows:

Shell's program involves the development of a continuous steady work load process, whereby drilled wells are brought on production and abandoned in a continuous pattern. A group of 84 wells will be drilled, completed and put on production every 58 days for the life of the project, probably a minimum of 25 years.

This program will first attain and then maintain a production rate of 130,000 b./d. of bitumen, yielding a net saleable product of 100,000 b./d. The minimum number of wells operating at any one time will be 1,580.

Wells will have to be drilled to an average depth of 1,000 ft. They will be completed with a 7-inch surface casing, 4½ inch production casing, slotted liners within the production interval, and 2⅜ inch tubing.

Tubing will be hung in a packer in the injection wells to provide a dead air space between casing and tubing for heat conservation. Tubing will be hung open-ended in the production wells, so the annulus may be used for lifting the well by passing inert gas around the bottom of the tubing. Gas lift was selected as most suitable for the production well.

Pipe distribution systems will be needed for multiple phases of steam and inert lift gas, and gathering systems for the produced emulsion and the lift gas. Block stations will be established in the center of each producing section, and each station will service 168 production and 168 injection wells through a lateral piping system. Production wells will be drilled on the unprecedented density of four-acre spacing. A central steam generation plant will provide injection steam.

Thus, one of the non-stripping methods for recovering oil from these sands involves the in situ production of oil by a process which in essence comprises injecting steam and caustic under pressure to emulsify the oil deep in the tar sands and then bringing this emulsion to the surface by an inert gas lift. Thereupon the emulsion is then broken, and the oil recovered therefrom.

I have now found a novel method of breaking tar sand emulsions which is characterized by being a combination chemical-electric treatment employing the chemical agents of this invention. In the preferred embodiment the chemical agent should be intimately mixed with the oil prior

to electric treatment. The results of this invention are unexpected since neither chemical treatment alone, nor electric treatment alone, nor electric treatment then chemical treatment is capable of effecting the same result, i.e. yield a commercially satisfactory product by a commercially satisfactory process. Where chemical and electrical treatment are performed simultaneously, the combination treatment is most effective if the chemical reagent is intimately mixed in the oil at the time of electrical treatment. Thus, in practice the oil is conditioned with chemicals prior to electric treatment.

The demulsifiers of this invention are characterized by being polyesters, of alkyleneether glycols and dicarboxylic acids. Examples of such polyesters are described in U.S. Patents 2,562,878, 2,950,299, 2,943,061, 2,911,434, 3,057,890, 3,057,891, 3,057,892, 3,110,682 and elsewhere which are by reference incorporated into the present application.

The alkyleneether glycols of this invention are in essence "oxyalkylated water" and can be represented by the formula

$$O[(AO)_nH]_2$$

where A is the radical derived from the alkylene oxide, for example, ethylene oxide, propylene oxide, butylene oxide, etc. and n represents the number of moles of alkylene oxide added about 5–500 or more, for example about 10–200 such as about 15–100, but preferably about 25 to 50. In the above formula the total moles of alkylene oxide added equal $2n$. Preferably the alkyleneether glycol should have a molecular weight of at least about 1,000, such as about 1,000 to 10,000, advantageously about 1500 to 5000, but preferably 2,000 to 3,000. However, the optimum molecular weight will vary with the specific alkylene oxides employed and the order by which they are added i.e. as heteropolymers (mixed oxides), as block polymers of more than one oxide, but each added sequentially, such as first 10 moles of EtO, then 25 more of PrO, then 10 moles BuO, etc. In addition, one or more of the blocks can be a heteric block. In general, the alkyleneether glycols are usually cogeneric statistical mixtures.

In certain cases, it is advantageous to react alkylene oxides with water in a random fashion so as to form a random copolymer on the oxyalkylene chain, i.e. the $-(OA)_n-OH$ could be AABABABBAAABB or the alkylene oxides can be reacted in an alternate fashion to form block copolymers on the chain, for example $A_nB_mC_x$, where A is the unit derived from one alkylene oxide, for example, ethylene oxide, and B is the unit derived from a second alkylene oxide, for example ethylene oxide, and B is the unit derived from a second alkylene oxide, for example propylene oxide, and C is the unit derived from a third alkylene oxide, for example, butylene oxide, etc. Thus, these compounds include bis- and terpolymers or higher copolymers polymerized randomly or in a block-wise fashion or in many variations of sequential additions.

Thus, the term, "oxyalkylated water" or alkyleneether glycol refers to compounds derived from water as base material or its equivalent. Thus, if diethylene glycol is the base material to be oxyalkylated, it is equivalent to one mole of water and two moles of ethylene oxide, tripropylene glycol would be one mole of water and three moles of propylene oxide, etc. In certain instances a higher poylalkylene oxide is employed as the base material, for example polypropylene glycol 1025. The number indicates the molecular weight of the glycol which is the reaction product of the number of moles of propylene oxide reacted with one mole of water necessary to yield a polypropylene glycol of the molecular weight indicated.

Specific examples of oxyalkylated water include the Pluronics such as disclosed in U.S. Patent 2,674,619, the Ucons (carbide and carbon), 2,425,845, the compositions disclosed in applications S.N. 677,907, 677,908, 677,982 (all filed on Aug. 13, 1957, and now abandoned), the composition disclosed in patent application No. 28,216, filed May 11, 1960, and now abandoned, etc.

These are, by reference, incorporated into the present application.

The terms "alkyleneether glycol," "polyalkyleneether glycol," and "oxyalkylated water" have the same meaning and may be used interchangeably.

It should be noted that the sum of the moles of alkylene oxide added in preparing the polyalkyleneether glycol do not necessarily yield the true molecular weight of the glycols. It is, therefore, preferably to determine the molecuar weight of the glycol by hydroxy values or other means such as osmotic pressure. In addition, the hydroxy values give a truer value for determining the stoichiometry of reactants in preparing the polyester. Thus, the molar value of alkylene oxide and molecular weights stated herein are those determined by hydroxy values and not necessarily by the actual moles of alkylene oxide added. The method for determining hydroxy values is the Ogg, Porter & Willit modification of the Verley Bolsing Method for determining hydroxy values described in Industrial Engineering Chemistry, Analytical Addition, vol. 17, pp. 394–7 (1945).

The following table presents examples of polyalkylene-ether-glycols which can be employed in this invention.

TABLE I

In the table the Roman numerals indicate the order of oxide addition: first addition (I), second (II), third addition (III). Where mixed oxides are employed the ratios are molar ratios.

Ex.	Base Material	Moles EtO	Moles PrO	Moles BuO	Other Oxides
1	Triethylene glycol	24.6 (III)	27.8 (II)	10.5 (I)	
2	do	30.2 (III)	37.6 (II)	10.5 (I)	
3	do	36.2 (III)	47.9 (II)	10.5 (I)	
4	do	39.1 (III)	53.1 (II)	10.5 (I)	
5	do	37.6 (III)	64.7 (II)	10.5 (I)	
6	do	40.6 (III)	70.0 (II)	10.5 (I)	
7	do	17.4 (III)	77.7 (II)	10.5 (I)	
8	do	47.8 (III)	77.7 (II)	10.5 (I)	
9	do	54.7 (III)	77.7 (II)	10.5 (I)	
10	do	61.4 (III)	77.7 (II)	10.5 (I)	
11	do	68.3 (III)	77.7 (II)	10.5 (I)	
12	do	74.1 (III)	77.7 (II)	10.5 (I)	
13	do	75.2 (III)	77.7 (II)	10.5 (I)	
14	Dipropylene glycol	52.1 (II)	37.9 (I)		PrO:42.1 (III).
15	do				PrO:EtO (2.26:1.1) 101.4.
16	do				PrO:EtO (0.758:1.0) 150.27.
17	do	24.8 (II)			PrO:EtO (4.43:1.0) 43.3 (I).
18	do	26.69 (II)			PrO:EtO (4.43:1.0) 46.69 (I).
19	do	17.6 (II)			PrO:EtO (4.43:1.0) 123.38 (I).
20	do	3.71 (II)			PrO:EtO (3.04:1.0) 56.61 (I).
21	do	42.39 (II)			PrO:EtO (3.04:1.0) 99.93 (I).
22	do		11.13 (II)		PrO:EtO (0.758:1.0) 47.97 (I).
23	do		7.32 (II)		PrO:EtO (0.758:1.0) 85.22 (I).
24	H_2O	2.39 (II)	16.37 (I)		
25	H_2O	21.6 (II)	16.37 (I)		

Ex.	Base Material	Moles EtO	Moles PrO	Moles BuO	Other Oxides
26	H_2O	86.36 (II)	16.37 (I)		
27	Polypropylene glycol 1025	16.0			
28	H_2O	6.81 (II)	20.6 (I)		
29	H_2O	18.0 (II)	20.6 (I)		
30	H_2O	40.9 (II)	20.6 (I)		
31	Dipropylene glycol	22.5 (II)	26.2 (I)		
32	H_2O	9.94 (II)	30.17 (I)		
33	H_2O	17.04 (II)	30.17 (I)		
34	H_2O	26.51 (II)	30.17 (I)		
35	H_2O	39.77 (II)	30.17 (I)		
36	H_2O	69.60 (II)	30.17 (I)		
37	H_2O	159.09 (II)	30.17 (I)		
38	Dipropylene glycol	46.3 (II)	31.3 (I)		
39	do	103.0 (II)	31.3 (I)		
40	Polypropylene glycol 2025	33.2 (II)	1 (I)		
41	H_2O	46.59 (II)	35.34 (I)		
42	H_2O	108.71 (II)	35.34 (I)		
43	Dipropylene glycol	22.1 (II)	36.8 (I)		
44	do	34.09 (II)	36.8 (I)		
45	do	51.13 (II)	36.8 (I)		
46	do	250.57 (II)	36.8 (I)		
47	do	52.5 (II)	37.4 (I)		
48	do	121.4 (II)	37.4 (I)		
49	do	209.0 (II)	37.4 (I)		
50	Polypropylene glycol 4000	25.4			
51	do	29.1			
52	do	42.7			
53	do	84.5			
54	Dipropylene glycol	23.5 (II)	69.0 (I)		
55	do	40.0 (II)	69.0 (I)		
56	do	62.4 (II)	69.0 (I)		
57	Polypropylene glycol 2025	96.8 (II)	50.7 (I)		
58	do	117.5 (II)	50.7 (I)		
59	Dipropylene glycol	88.4 (II)	97.5 (I)		
60	do	96.5 (II)	109.8 (I)		
61	do	94.0 (II)	111.7 (I)		
62	do	105.8 (II)	117.9 (I)		

Suitable polyesters of the above are prepared from dicarboxylic acids such as alkane dicarboxylic acids, such as adipic acid, etc., alkene dicarboxylic acids, maleic or fumaric acid, etc., aryl dicarboxylic acid such as the phthalic acids, etc., alkyleneether dicarboxylic acids such as diglycollic acid, etc.

It is well known that when a polybasic acid, and more specifically, a polycarboxy acid, $X(COOH)_2$ is reacted with a glycol, $X(OH)_2$ a mixture of polyesters of varying molecular weights result. This reaction is generally written:

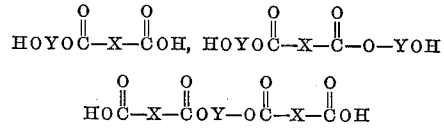
$$n\text{HOOC.X.COOH}+n\text{HO.Y.OH}\rightarrow \text{H[—OOC.X.COO.Y—]}_n\text{OH}+(2n-1)\text{H}_2\text{O}$$

In actual practice, the polymeric ester product consists not of a single material, compound or ester, but of a mixture of co-generic polyesters containing small amounts of unreacted monomers. The number-average molcular weight of the product depends upon the conditions and extent of reaction, increasing with the degree of esterification and loss of water of reaction. It has been shown that the actual content of the various cogeners in the polyester product may be estimated from the number-average molecular weight (see e.g., P. J. Flory, Chemical Review, 39, 137 (1946)).

In the preparation of polyesters, including those employed in the present invention, it is not necessary to employ equal molal proportions of polybasic acid and glycol. However, when unequal proportions of the reactants are employed, the degree of polymerization or average molecular weight of the polyester product will generally be less, for given reaction conditions, than where equal molal proportions are employed. This effect results from the formation of end groups derived from the reactant in excess, and is greater the further the proportion of reactants is from equality. In this connection it should be pointed out that, regardless of the proportions of reactants used, the polymeric product will contain cogeners of varying end group composition. As a simple example, let us consider a dibasic acid reactant, represented by $Y(OH)_2$. Then the various polyesters in the product may be represented by the following formulae, which show the three different types of end groups appearing in the cogeners:

$$\text{HO[—Y'X'—]}_p\text{COOH}$$
$$\text{HO[—Y'X'—]}_p\text{Y.OH}$$
$$\text{HOOC.X[—Y'X'—]}_p\text{COOH}$$

Here p is a whole number which may be as low as 1 or 2, generally less than 40, and between about 4 and 20 in the preferred products of this invention. X' and Y' in these formulae are residues of $X.(COOH)_2$ and $Y(OH)_2$ joined by ester linkages. Where the polybasic acid contains three or more carboxyl groups, the formulae representing the various polyester products are, of course, more complex, but one still obtains three types of products, from the standpoint of end-group composition, similar to those shown for the simplified case. For purposes of this invention, polyesters also include certain monoesters which may also be formed, such as where $p=1$ such as



and the like.

Suitable polycarboxy acids for use in preparing the present demulsifiers, include the commonly available organic dicarboxy and polycarboxy acids which are resistant to decarboxylation and pyrolysis under the usual esterification conditions. Of particular value and interest for the preparation of the present products, are the dicarboxylic acids, such as the aliphatic dicarboxylic acids: oxalic, malonic, succinic, glutonic, adipic, pimelic, azelaic, sebacic, maleic, fumaric, diglycollic, ethylene bisdiglycollic, citroconic, itaconic, dimeric fatty acids and the like. These and similar dibasic acids are easily reacted with the glycols specified below to yield linear polyesters. Carbonic acid is another suitable acid reactant, but is best employed as its diester, such as diethyl carbonate, with which polyesters are formed by ester interchange and evolution of the low boiling alcohol. Likewise, any of the polybasic acids can be used in the form of esters of low boiling monohydric alcohols. Also, the acid anhydrides, where they exist, may be used in place of the polybasic organic acid.

Other readily usable dibasic acids include phthalic acid, terphthalic acid, isophthalic acid, and adducts of maleic

acid with various unsaturated hydrocarbons, such as diisobutylene, butadiene, retene, a-pinene and similar compounds.

Organic acids having a functionality greater than two may also be employed to obtain polyesters suitable for use in the present process. Where such acids are used, it is necessary to control, rather carefully, the reaction conditions and/or proportions of acid and glycol to avoid the formation of insoluble gel-like or rubbery polyester products. Examples of suitable acids of higher functionality, include aconitic acid, hemimellitic acid, trimellitic acid, acids obtained from brown coal, maleic acid adducts of linoleic acid, and the like.

The electric treaters employed in this invention are of the conventional type. Illustrative examples thereof are described in the following U.S. patents: 2,855,359, 2,355,678, 2,404,405 and 987,115, which are by reference incorporated into the present application.

The electric treater may be of the turbulent or the quiescent type although the latter may be more satisfactory. A voltage gradient sufficient to effect satisfactory demulsification is employed, for example a voltage gradient of about 0.3 to 15 kv./in. or greater may be employed, but a voltage gradient of about 2.0 to 8.0 kv./in. is generally preferred. Either AC or DC may be employed. By way of illustration, the process is carried out in the following manner.

Example 1

High pressure steam and caustic are forced into the formation through an input well in a sort of water flooding operation. The resulting effluent from the output well is a tar of about 9° API (which represents 30% of the product) containing less than 1% solids but about 20–30% water. The other 70% of the effluent consists of water containing about 2% oil and clay. A hydrocarbon such as (40–50° API) naphtha is added to dilute the tar and this product is passed through API separators. The supernatant oil diluted to eight parts tar to one part naphtha contains about 20% water.

To the supernatant oil is added the polyester of this invention which conditions the oil. The conditioned oil is then led into an electrical treater operated at a temperature of 250° F. and a voltage gradient of 6 kv./in. wherein the phase separation is accomplished.

This product is then flashed for recovery of the naphtha diluent. The resultant oil has a water content of less than 1% BS and W. The resulting oil goes to visbreaking and the visbreaker products enter the pipelines whereas the visbreaker bottoms are burned as fuel to supply the steam requirements. The oil-breaking sediment for the API separators is recovered by air flotation and added to the visbreaker charge without going through the dehydrator. The preferred chemical agent in this process is a diglycolic polyester of

$$O[(PrO)_{17.5}(EtO)_{7}H]_2$$

Although this glycol was prepared by adding 58 moles of PrO and 14 moles of EtO to water in that order, hydroxyl values and osmotic pressure molecular weights determinations indicate the above formula.

In addition to the use of the present invention in conjunction with the in situ production of tar sands, the invention can also be used in conjunction with resolving emulsions in other tar sand processes. For example, in the Great Canadian process which is a hot water process, tar sand which contains 7–18% oil and from 10–20% water is treated with enough diluent to equal 2 parts diluent (generally naphtha) to one part of oil in the sand and then some of the product oil (also called recycle stock) is added to make the mixture fluid enough to handle. This mixture is thoroughly blended and the slurry run to the contactor where it is mixed with 25–30 volumes of water at about 185° F. In the contactor the coarse sand settles out and takes very little oil with it (about 0.2%).

The oil and some of the water then flows to the oil-water separator. A sludge of solids, water and 15% oil settles to the bottom and is driven off. The oil, emulsion layer and some water overflow a weir and then flow to the emulsion separator. This is primarily a tank with a baffle dividing it into two compartments. The oil and emulsion overflow the baffle and the emulsion settles to the bottom where it is drawn off. It consists of about 50% oil and 50% water with fines in it. The oil is then settled in a heater-settler.

The present invention can be used to break emulsions formed in these tar sand processes.

The emulsions of the above example are facilely broken by the preferred polyesters of this invention which are polyesters formed from block polyalkyleneether glycols, for example block polyalkyleneether glycols of propylene oxide and ethylene oxide. In the most preferred embodiment these glycols have terminal ethylene oxide units. Thus, representative examples would be glycols of the formula

$$O[(PrO)_n(EtO)_m{}^H]_2$$

having a molecular weight of 2,000–3,000 and a PrO to EtO weight ratio of approximately 2:1 to 4:1 but preferably about 3:1.

The preferred dicarboxylic acid employed in preparing the polyesters of this invention is diglycolic acid.

A specific example of a very effective polyester employed in the above example is a polyester of diglycolic acid and a polyalkyleneether glycol of the general formula

$$O[(PrO)_n(EtO)_m{}^H]_2$$

having a molecular weight of 2600 where the weight of PrO is about 2,000 and the weight of EtO is about 600. This polyester is prepared by reacting under esterifying conditions approximately one mole of diglycolic acid with approximately one mole of the glycol. It is advantageously employed in concentrations of 75–200 p.p.m. at a voltage of about 5–7 kv./in.

These chemical agents produce a product of commercially acceptable BS&W at a commercial acceptable voltage and amperage.

The concentration of demulsifier will vary widely depending on the particular emulsifier and the particular system employed. Thus, any concentration capable of demulsification according to this invention can be employed, for example concentrations of from about 10–10,000 p.p.m. or greater, based on weight of oil treated, such as from 50–5,000, advantageously 75–500, but preferably about 100–300 p.p.m. Naturally, one desires to employ the minimum amount of demulsifier capable of achieving a commercial result; so that although larger concentrations may be employed there is generally no advantage in doing so. It is often advantageous to employ solutions of the demulsifier.

In addition to the use of the present invention in the recovery of oil from Athabasca tar sand, the invention can be employed in the recovery of oil from oil-bearing sands and shale in other parts of the world such as in the U.S. where emulsions are a problem, for example in the oil sand of California and Utah.

As is quite evident, new polyesters will be constantly developed which could be useful in this invention. It is, therefore, not only impossible to attempt a comprehensive catalogue of such compositions, but to attempt to describe the invention in its broader aspects in terms of specific chemical names of polyesters used would be too voluminous and unnecessary since one skilled in the art could by following the description of the invention herein select a useful polyester. This invention lies in the use of suitable polyesters in conjunction with an electric field of suitable voltage and the individual compositions are important only in the sense that their properties can affect this function. To precisely define each specific use-

ful polyester in light of the present disclosure would merely call for chemical knowledge within the skill of the art in a manner analogous to a mechanical engineer who prescribes in the construction of a machine the proper materials and the proper dimensions thereof. From the description in this specification and with the knowledge of a chemist, one will know or deduce with confidence the applicability or specific polyesters suitable for this invention by applying them in the process set forth herein. In analogy to the case of a machine, wherein the use of certain materials of a construction or dimensions of parts would lead to no practical useful result, various materials will be rejected as inapplicable where others would be operative. One can obviously assume that no one will wish to use a useless polyester nor will be misled because it is possible to misapply the teachings of the present disclosure to do so. Thus, any polyester-electrical system that can perform the function stated herein can be employed.

This process, in addition to being employed in the recovery of oil from tar sands, can also be employed in the recovery of very heavy oils, such as heavy crudes, by similar processes. For example, certain heavy crudes which are so difficult to recover by conventional procedures (so that they have been deemed noncommercial reserves) may be recovered by methods similar to the steam injection method employed by Shell Oil Company described above. Thus, when heavy crudes, for example those found in East Texas, in California and elsewhere, are treated by secondary recovery methods utilizing steam injection, the oil produced can be demulsified by the chemical of this invention in conjunction with an electric field. Thus, the present process and claims include the demulsification of these steam injection treated heavy crudes recovered by secondary recovery methods.

Having thus described my invention what I claim as new and desire to obtain by Letters Patent is:

1. A chemical-electric process of demulsifying petroleum characterized by subjecting petroleum emulsions, containing a polyester of polyalkyleneether glycol and a polycarboxylic acid, to an electric field.

2. A chemical-electric process of demulsifying heavy crude emulsions characterized by subjecting the emulsions, containing a polyester of a polyalkyleneether glycol and a polycarboxylic acid, to an electric field.

3. A chemical-electric process of demulsifying tar sand oil emulsions characterized by subjecting the emulsions, containing a polyester of a polyalkyleneether glycol derived from ethylene oxide and propylene oxide and a dicarboxylic acid, to an electric field.

4. A chemical-electric process of demulsifying tar sand oil emulsions which is characterized by subjecting the emulsions, containing a polyester of a polyalkyleneether glycol derived from ethylene and propylene oxides and diglycolic acid, to an electric field.

5. The process of claim **4** where the polyalkyleneether glycol which has a molecular weight of 500–5000 and a weight ratio of ethylene oxide to propylene oxide to about 1:4 to 1:2 is an oxyethylated polypropyleneether glycol.

6. The process of claim **5** where the molecular weight of the polyalkyleneether glycol is 2000–3000.

7. The process of claim **6** where the polyalkyleneether glycol has a molecular weight of 2500–2700 and an ethylene oxide to propylene oxide weight ratio of approximately 1:3.

8. A chemical-electric process of demulsifying tar sand emulsions which is characterized by subjecting the emulsions, containing a polyester of a polyalkyleneether glycol of the approximate formula

$$O[(PrO)_{17.5}(EtO)_7H]_2$$

and diglycolic acid, to an electric field.

9. A chemical-electric process of demulsifying heavy crude emulsions which is characterized by subjecting the emulsions, containing a polyester of a polyalkyleneether glycol of the approximate formula

$$O[(PrO)_{17.5}(EtO)_7H]_2$$

and diglycolic acid, to an electric field.

References Cited

UNITED STATES PATENTS

2,050,925	8/1936	Groote	204—190
2,447,530	8/1948	Perkins	204—190
2,755,296	7/1956	Kirkpatrick	252—358
3,200,059	8/1965	Mills	204—186

JOHN H. MACK, *Primary Examiner.*

T. TUFARIELLO, *Assistant Examiner.*