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FLOODING PROCESS FOR RECOVERING OIL FROM SUBTERRANEAN OIL-BEARING STRATA

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This invention relates to the recovery of oil from subterranean oil sands and oil-bearing strata, and has for its main object to provide a practicable, inexpensive flooding process for recovering oil that is held by adsorption, absorption, or in some equivalent manner, on subterranean oil-bearing strata, such as, for example, the oil sands or oil-bearing strata of exhausted oil fields, or the oil sands or oil-bearing strata of oil fields that have been tested and abandoned because they did not contain a sufficient quantity of oil to make it feasible to attempt to recover the oil by conventional oil-producing procedure.

Briefly described, our process consists in introducing water with which a treating agent or addition agent is mixed to form an aqueous treating solution, into a number of oil wells located in an exhausted or abandoned oil field, and permitting said treating solution to travel through the subterranean oil sands or oil-bearing strata and rise to the surface of the ground through a predetermined opening. The treating solution or aqueous vehicle employed as the flooding medium, operates to liberate the film or coating of oil on the particles of the oleiferous structure, and then flush the oil off said particles and carry the oil upwardly to the surface of the ground.

Oil exists in oil sands or similar strata in two different states, i. e., as "free oil," that is located between the voids of the sands, and as "fixed oil," which is held by adsorption (and perhaps to some degree by absorption) on the particles of sand, and which is commonly referred to as the film of oil that adheres to the particles of sand or to the particles of the oleiferous structure. Such fixed oil may be said to be held by "sorption."

Free oil can be recovered by conventional methods of oil-producing, such as draining the oil in conjunction with liquid or gaseous pressure and creating an artificial fluid or gaseous pressure in the sand bed, so as to dislodge the oil from the sand bed and thereafter conduct the dislodged oil to the surface of the ground by any suitable means or method. Fixed oil, i. e., the coating or film of oil on the sand or organized strata, cannot be recovered by any of the conventional methods or means used to produce oil, because it is held as a film surrounding the grain of sand or strata, and cannot be dislodged economically by either fluid or gaseous pressure, as employed in conventional oil-producing procedure. In the various methods that have been proposed for flooding oil sands to recover "fixed oil" from exhausted oil fields and from oil-bearing strata which has never been previously involved in production by conventional methods, it is not always desirable to use old oil wells for either the purpose of introducing the aqueous vehicle into the subterranean oil sands or oil-bearing strata, or for expulsion of the oil or the fluid with its oil content in loose admixture or emulsion. In some instances the entire operation is carried out by means of wells drilled specifically for the purpose of flooding the formation in accordance with a predetermined plan. Sometimes the operation is conducted in part by means of some of the old existing wells, and in part by means of some new wells drilled in accordance with a predetermined arrangement. The above described procedure, which is commonly referred to as the "flooding process," has been employed successfully in numerous fields, including certain fields in Pennsylvania, certain fields in northern Oklahoma, certain fields in southeastern Kansas, and elsewhere.

Attention is directed to the bibliography of water-flooding which appears in "Petroleum Production," by Cloud, University of Oklahoma Press, 1937, page 435. See also U. S. Patent No. 1,826,371, dated October 6, 1931, to Spindler.

It is not necessary to indicate all the advantages to be obtained by the addition of a suitable chemical compound or treating agent to water so as to produce an aqueous treating solution that is intended to be used instead of ordinary water, which may in essence represent a dilute brine containing usually appreciable amounts of soluble calcium and magnesium salts. Such a treating solution, if properly prepared, constitutes an aqueous vehicle which has at least an apparent preferential wetting effect for the sand or strata, and thus loosens or removes the oil which might not be removed by water alone. Said aqueous vehicle also has the characteristics of tending to prevent the formation of emulsions as said aqueous vehicle and the liberated oil travel through the sand or strata, and through the various conducts, used in the procedure. It probably has the effect of decreasing the apparent viscosity of water; or to state the matter in other words, the aqueous vehicle or treating solution probably permeates sands and various oil-containing strata which might not be permeated at all by water alone, or at least under conditions of diminished pressure. There are numerous other advantages not necessary to mention, which result from the use of an aqueous vehicle or treating solution of the kind above mentioned.

In actual practice, it is found that very few chemical compounds are actually of value as addition agents to the water employed in recovering oil by flooding procedure. One reason is that although there are available thousands of wetting agents, and perhaps hundreds of demulsifying agents, very few have the desired property of being suitably resistant to the soluble calcium and magnesium salts, which are either invariably present in the water used for flooding the subterranean sands or strata, or liable to come in contact with said water and contaminate the same. Some wetting agents and demulsifying agents, although stable in the ordinary sense, are not stable for the purposes of flooding. Sometimes six to eighteen months may pass before the flood water re-appears at the surface, carrying the recovered oil. Accordingly, it is necessary that the addition agent must be stable for such a period of time; and furthermore, since the same flooding water is used over again, it is necessary that the addition agent must continue to be stable almost indefinitely. Furthermore, there are chemical compounds which meet the test of stability; but they do not sufficiently lower the surface tension of the aqueous vehicle within the limits of possible economic use. Then too, although some chemical compounds may lower the surface tension and may be feasible economically, they are not employed, for the reason that they do not show other desirable properties, as, for instance, apparent preferential wetting effect, etc. Some chemical compounds which appear stable under ordinary conditions, even when allowed to stand for a long period of time, for instance, eighteen months, decompose readily under conditions of use where they are subjected to pressures such as are required in the ordinary course of forcing the aqueous fluid through the sands or strata. Some addition agents are objectionable apparently for the reason that they build up deposits on the strata which greatly decreases the speed of flooding, and perhaps in some ways produce results which are inferior to those which are obtainable by the use of water alone. It has been suggested that this objectionable characteristic is related to excessive preferential wetting effect, but this is purely a matter of speculation, although the assumption may be correct.

We have found that a very desirable agent for addition to the water used in flooding procedure (the water usually consisting of dilute brine), is a glycol or polyglycol ether of the type obtainable by causing a water-insoluble, non-cyclic alcohol (including, however, aralkyl alcohols and aliphatic alicyclic alcohols where the hydroxyl radical is attached to the alkyl group, water-insoluble primary and secondary amines, and water-insoluble primary or secondary amides, to react with an alpha beta alkylene oxide, such as ethylene oxide, propylene oxide, butylene oxide, or the like. Such compounds, broadly speaking, are well known compositions of matter; but it may be desirable to indicate their method of manufacture in some detail.

Another class of materials represents acylated hydroxyamines characterized by the presence of at least one amino hydrogen atom, as for example, products of the kind obtainable by acylating ethanolamine or diethanolamine with a fatty acid or the like.

Needless to say, the same type of amine and the same type of amide, i. e., water-insoluble and having present at least one amino hydrogen, or at least, one amido hydrogen atom, appear in the form of polyamino compounds, and also in the form of polyamido compounds, and also in combined form, in which there is present at least one amino nitrogen atom, and at least one amido nitrogen atom. All these polyamino and polyamido types, or combinations thereof, may be reacted with alkylene oxides or the like to give suitable flooding agents.

The water-insoluble amines and the water-insoluble amides which are intended for treatment with an alkylene oxide or the like to give the addition agent or treating agent employed in our process, are obtained by reaction with higher molecular weight carboxy acids, or by reactions which involve the formation of compounds obtained by removing a radical group or residue from higher molecular weight carboxy acids. This also applies, not only to the amines and amides, but also to the alcohols. As is known, many of the higher molecular weight alcohols are obtained by the reduction of esters of carboxy acids. The methods of making such compounds, i. e., the raw materials intended for treatment with an alkylene oxide, are well known. It may be desirable, however, to enumerate the higher molecular weight carboxy acids which are desirable as reactants, and which are characterized by having more than six carbon atoms, and generally less than four carbon atoms; or to state the matter another way, the acyl radical must contain at least seven carbon atoms. With this in mind, the various members of the class may be indicated broadly as "higher molecular weight organic acids."

The expression "higher molecular weight carboxy acids" is an expression frequently employed to refer to certain organic acids, particularly monocarboxy acids, having more than six carbon atoms, and generally less than 40 carbon atoms. The commonest examples include the detergent-forming acids, i. e., those acids which combine with alkalies to produce soap or soap-like bodies. The detergent-forming acids in turn include naturally-occurring fatty acids, resin acids, such as abietic acid, naturally-occurring petroleum acids, such as naphthenic acids, and carboxy acids produced by the oxidation of petroleum. As will be subsequently indicated, there are other acids which have somewhat similar characteristics and are derived from somewhat different sources and are different in structure, but can be included in the broad generic term previously indicated.

Among sources of such acids may be mentioned straight chain and branched chain, saturated and unsaturated, carboxylic, aliphatic, alicyclic, fatty, aromatic, hydroaromatic, and aralkyl acids, including caprylic acid, heptylic acid, caproic acid, capric acid, erucic acid, saturated and unsaturated higher molecular weight aliphatic acids, such as the higher fatty acids containing at least eight carbon atoms, and including in addition to those mentioned, melissic acid, stearic acid, oleic acid, ricinoleic acid, diricinoleic acid, triricinoleic acid, polyricinoleic acid, ricinostearolic acid, ricinoleyl lactic acid, acetylricinoleic acid, chloracetylricinoleic acid, linoleic acid, linolenic acid, lauric acid, myristic acid, undecylenic acid, palmitic acid, mixtures of any two or more of the above mentioned acids or other acids, mixed higher fatty acids derived from animal or vegetable sources, for example, lard, cocoanut oil, rapeseed oil, sesame oil, palm kernel oil, palm oil, olive oil, corn oil, cottonseed oil, teaseed oil, sardine oil, tallow, soya bean oil, peanut oil,

castor oil, seal oils, whale oil, shark oil and other fish oils, partially or completely hydrogenated animal and vegetable oils, such as those mentioned; hydroxy and alpha-hydroxy higher carboxylic, aliphatic and fatty acids, such as hydroxy stearic acid, di-hydroxypalmitic acid, dihydroxystearic acid, dihydroxybehenic acid, alphahydroxy capric acid, alpha-hydroxystearic acid, alpha-hydroxy palmitic acid, alpha-hydroxy lauric acid, alphahydroxy myristic acid, alpha-hydroxy cocoanut oil mixed fatty acids, alpha-hydroxy margaric acid, alpha-hydroxy arachidic acid, and the like; fatty and similar acids derived from various waxes such as beeswax, spermaceti, montan wax, Japan wax, coccerin, and carnauba wax. Such acids include carmaubic acid, cerotic acid, lacceric acid, montanic acid, psyllastearic acid, etc. As suggested, one may also employ higher molecular weight carboxylic acids derived, by oxidation and other methods, from paraffin wax, petroleum and similar hydrocarbons; resinic and hydroaromatic acids, such as hexahydrobenzoic acid, hydrogenated naphthoic, hydrogenated carboxy diphenyl naphthenic acid, and abietic acid; aralkyl and aromatic acids, such as benzoic acid, Twitchell fatty acids, naphthoic acid, carboxy-diphenyl, pyridine carboxylic acid, hydroxybenzoic, and the like.

Other suitable acids include phenylstearic acid, benzoylnonylic acid, campholic acid, fencholic acid, cetyloxybutyric acid, cetyloxyacetic acid, chlorstearic acid, aminostearic acid, carboxydiphenyl acid, quinaldinecarboxy acid, etc.

In come inctances, obviously certain derivatives of dibasic acids would, in essence, act as if they were simple monocarboxylated acids, for instance, various phthalamic acids derived from phthalic anhydride, and amines, such as aniline, cyclohexylamine, octylamine, etc. Other similar amido acids can be derived by means of other comparable anhydrides. One may also employ materials such as ethyl ricinoleate monophthalate, etc., and also various acids which are derived from chloracetyl ricinoleic acid and its analogs, by replacing a chlorine atom with a suitable monovalent hydrocarbon or an oxy-hydrocarbon radical. The monocarboxy derivatives of pimelic, sebacic and other similar acids may be employed.

Another source of suitable acids are those commonly referred to as lac acids, such as for example, the acids derived from shellac. Such acids include various polyhydroxy acids, for example aleuritic acid, shelloic acid, and kerrolic acid.

As is well known, one may use substituted acids in which some other non-functional constituent enters the structure of the fatty acid. For instance, one may use aryl-, hydroxy-, alkoxy-, chloro-, keto-, and amino- derivatives. Generally speaking, however, it is always preferable to use the unsubstituted acid, particularly free from substituents which contain either oxygen or nitrogen atoms. Generally speaking, the introduction of hydrocarbon radicals, regardless of source, has little effect, except in altering the hydrophile-hydrophobe balance.

One may also employ the blown or oxidized acids, such as blown ricinoleic acid, blown oleic, etc., or estolides derived from blown oils, such as blown castor oil, blown soya bean oil, etc.

Needless to say, the acids themselves need not be employed; but one may readily employ any functional equivalent, such as the anhydride, the acyl chloride, or the like. In some instances, the esters, especially in presence of a trace or a significant amount of water, act as the acid itself, in that the acid is liberated. Unless specific reference is made to a particular isomer, one may employ any isomer or mixture of various isomers, if the acid or acids are so available.

Insofar as the various amides, amines, alcohols, etc., are well known products, or can be readily manufactured by well known means, further reference will be made only to the conversion of such products into suitable flooding agents by treatment with alkylene oxide, such as ethylene oxide or its functional equivalents.

The only exception to the above statement will be in regard to the acylated hydroxyamines, characterized by the presence of at least one amino hydrogen atom. Not only may these products be employed, but under certain conditions there are combinations with di-carboxy acids, such as phthalic acid, so as to produce carboxy compounds.

As to the acylated hydroxyamines, reference is made to the following patents: U. S. Patent No. 2,167,346; 2,167,347; 2,167,348; and 2,167,349, all dated July 25, 1939, and all to De Groote, Keiser and Blair. See also U. S. Patent No. 2,176,702, dated October 17, 1939, to De Groote, Keiser and Blair.

It is to be noted that, although the procedure described in the patents mentioned is concerned largely with fatty acids or detergent acids or acids derived from blown oils, the same procedure is adaptable in connection with higher molecular weight organic acids of the kind described. It is to be noted, however, that in the present instance, in connection with the process herein described, one is primarily interested in products that are water-insoluble prior to the treatment with the alkylene oxides. This means, for example, that one may use products which are either water-insoluble, or just show limited solubility in water, or rather, show a tendency to be self-emulsifying. One cannot use materials which, prior to treatment with ethylene oxide, are clearly water-soluble, so as to give a solution. Generally speaking, if any of the prior examples give water-soluble products, as for example, an esterified diethanolamine, then one can readily obtain an analogous water-insoluble product by any one of several modifications or combination of the same. For instance, one can employ an acid, as for example, a fatty acid which has a longer carbon atom chain. Thus, instead of employing caproic acid, one may employ stearic acid; or instead of introducing only one acid radical, one might introduce two, for instance, thus producing an ester from diethanolamine, for example, in which two acyl radicals are introduced. Similarly, instead of using a hydroxylated acid, such as ricinoleic acid, one may use a non-hydroxylated acid, such as oleic acid. Furthermore, water solubility is decreased by replacing diethanolamine or the like with an amine having a higher molecular weight without any additional hydroxyl radicals; for example, one might employ dipropanolamine or dibutanolamine, or the like. Likewise, one may employ an amine having fewer hydroxyl radicals, for example, amyl ethanolamine instead of diethanolamine. Similarly, in the formation of amides where monoethanolamine may give a water-soluble product, one might employ monobutanolamine, monohexanolamine, or the like. In any event, the introduction of a hydrocarbon radical, such as an octyl or octadecyl radical, into an amine prior to esterification, or the use of a higher molecular weight amine prior to amidification, also tends to produce water insolubility.

In a general way, the introduction of nitrogen atoms or oxygen atoms tends to increase solubility, while the introduction of hydrocarbon radicals tends to decrease solubility. With this in mind, there is no difficulty in obtaining suitable examples of all the preceding classes which are water-insoluble prior to treatment with an alkylene oxide, and which have at least one acyl radical present, and are characterized by the fact that such acyl radicals contain at least seven carbon atoms, and further characterized by the presence of a reactive hydrogen atom directly attached to an oxygen atom, said oxygen atom in turn being free from any combination with the cyclic carbon atom, thus eliminating from consideration acylated phenols and acylated hydroaromatic alcohols and the like.

As to other suitable types of materials within the broad category previously described and suitable for treatment with ethylene oxide to give a flooding agent of the kind herein contemplated, attention is directed to the phthalated derivatives described in U. S. Patents Nos. 2,154,422 and 2,154,423, both dated April 18, 1939, to De Groote, Keiser and Blair. See also U. S. Patents Nos. 2,166,431, 2,166,432, 2,166,433 and 2,166,434, all dated July 18, 1939, to De Groote. The various patents mentioned immediately preceding and the prior patents are concerned largely with monocarboxy detergent-forming acids. Obviously, the same procedure can be applied to any higher molecular weight organic acids previously described.

Example 1

200 parts of a mixture of higher alcohols, such as is obtained by the catalytic hydrogenation of animal or vegetable oils or fats by means of hydrogen at a temperature from about 250° to 300° C., in the presence of a finely-divided nickel catalyst, consisting mainly of alcohols of the formulae $C_8H_{17}OH$ to $C_{18}H_{37}OH$, whereby about 50 percent of dodecyl alcohol is present, are heated to about 180° C. in an autoclave with about 400 parts of ethylene oxide, which is introduced a little at a time.

Example 2

18 molecular proportions of ethylene oxide are added onto 1 molecular proportion of octadecylamine by heating in an autoclave to about 150° C.

Example 3

From 660 to 880 parts (from 15 to 20 molecular proportions) of ethylene oxide are led, while stirring at a temperature between 130° and 140° C., into 270 parts (1 molecular proportion) of octadecyl alcohol containing 2.7 parts of an aqueous caustic soda solution of 40° Bé.

Example 4

88 parts of ethylene oxide are introduced at 120° C. into 51 parts of the mixture of alcohols obtained by the saponification of sperm oil and containing 1 percent of caustic soda or of sodium ethylate.

Example 5

A mixture of 150 parts of N-stearyl-β, β', β''-trihydroxy-tertiary-butylamine with 90 parts of ethylene oxide (5.3 molecular equivalents) is heated in a closed vessel by raising the temperature to 120° C. uniformly during five hours, and then keeping at this temperature until the internal pressure falls to zero.

Example 6

100 parts by weight of the condensation product from oleic acid and triethylenetetramine are mixed in a vessel which can be closed with 50 parts by weight of ethylene oxide and left to stand for some hours. It is then heated to about 80° C. and the excess ethylene oxide removed.

Example 7

A molecular equivalent of 7–8 octadecane diol is mixed with 1% of caustic soda and then treated with 15 molecular equivalents of ethylene oxide.

Example 8

Octadecylamine is treated with seven molecular equivalents of ethylene oxide to give a water-soluble product.

Example 9

Dicyclohexylamine is treated with approximately 10–15 molecular equivalents of ethylene oxide to give a water-soluble product.

Example 10

One molecular equivalent of ethylene diamine is converted into the diamide by treatment with two moles of oleic acid. To the diamine so obtained there is added ten moles of ethylene oxide.

Example 11

One mole of dimethyl ethylene diamine is treated with one mole of oleic acid, and the amino amide so obtained is treated with approximately 10–20 molecular proportions of ethylene oxide to give a water-soluble product.

Example 12

Oleyl diethyl ethylene diamine is treated with approximately 10–12 equivalents of ethylene oxide to yield a water-soluble product.

Example 13

One molecular equivalent of dodecylamine is caused to react with two molecular proportions of epichlorhydrin which are added to the reaction mixture in small portions, 2 molecular equivalents of propylene oxide then being brought into reaction at zero C, in the presence of 0.5 percent of sodium ethylate.

Example 14

One molecular equivalent of cetyl amine is heated in an autoclave under pressure at about 150° C. with four molecular equivalents of propylene oxide, and then with from 12 to 16 molecular equivalents of ethylene oxide.

Example 15

From about 16 to 20 molecular equivalents of ethylene oxide are caused to react in a stirring vessel at 140° C. in the presence of 0.5% caustic soda solution of 40 Bé. strength with one molecular equivalent of the water-insoluble condensation product from one molecular equivalent of cetyl alcohol and four molecular equivalents of propylene oxide. The last mentioned condensation product is obtained by reacting one molecular equivalent of cetyl alcohol with four molecular equivalents of propylene oxide at a temperature of about 140° C.

A number of suitable alkylene oxides or their functional equivalents are suggested, but the following may be indicated; ethylene oxide; 1–2 propylene oxide; 1–2 or 2–3 butylene oxide, butadiene oxide; cyclohexene oxide; glycidol, epi-

chlorhydrin; betamethyl glycidol; beta methyl epichlorhydrin; isobutylene oxide, and the like.

As is well known, the reaction with ethylene oxide or the like is not limited to materials of the kind herein described; but alkylene oxides may react with hydrogen atoms linked to oxygen in phenols or cyclic alcohols. Similarly, ethylene oxide may react with various carboxy acids, hydroxylated amides, not containing any amino hydrogen atom, hydroxylated amines free from any amino hydrogen atom, and other related compounds. In event that such other reactive hydrogen atoms are present, then in that event, it is obvious that one may obtain a solubilizing effect, due in part, to the presence of such other reactive groups. For sake of simplicity, it is noted that compounds so obtained are contemplated for the same purpose of flooding subterranean sands or strata in our co-pending applications Serial Nos. 322,534 and 322,535, filed March 6, 1940.

No suitable means is available for clearly indicating the chemical structure of the various products of the kind described. It becomes obvious that a number of compounds may have more than one group which is reactive with ethylene oxide or the like; for instance, the various polyamino or polyamido compounds described. This is also true of a primary amide, and particularly one derived from a hydroxy acid such as ricinoleic acid. Furthermore, the composition is further complicated by the fact that instead of using ethylene oxide, for example, one may use glycidol or the like. Moreover, it is quite possible that the structure of the polymerized alkylene oxide chain or its equivalent, at least in some instances, is not as simple as indicated by the simplest chemical formula which suggests itself. This is based on the well known properties of polyethylene oxide and related compounds, and particularly polymerization products derived from ethylene oxide under various conditions. Reference is made to Chemistry of Synthetic Resins, by Ellis, 1935, chapter 50, and to U. S. Patent No. 1,921,378, dated August 8, 1933, to Wetzel, and U. S. Patent No. 1,976,628, dated October 9, 1934, to Wittwer. For this reason the previous structural formulas are submitted primarily to show the point of introduction and of the polymerized ether radical or its equivalent, rather than the actual structure itself, although such formulas may be applicable to a number of members of the broad genus. Thus, it would appear best to characterize the products referred to in the hereto appended claims, in terms of the method of manufacture of said products, rather than attempt to rely upon structural formulas, in view of what has been said.

In view of the vast number of suitable materials which can be obtained by action of ethylene oxide or the like, it may be well to indicate the preferred class of materials. Of the entire class of high molecular weight organic acids, we prefer to employ those raw materials in which the acyl radical containing more than six carbon atoms is supplied by the monocarboxy detergent-forming acid. More specifically, we prefer the fatty acids as the most suitable group of monocarboxy detergent-forming acids. Of the fatty acids, we particularly prefer the hydroxylated type, such as ricinoleic acid, hydroxystearic acid, diricinoleic acid, and the like. The most suitable specific member is ricinoleic acid. We prefer to use compounds in which there is no other non-functional group of atoms present, such as a chlorine atom, alkoxy radical, or the like.

Our preferred flooding agent, addition agent, or treating agent, is made by treating the ricinoleoamide derived from tris (hydroxymethyl) aminomethane, with approximately 8–12 moles of ethylene oxide, so as to yield a water-soluble material. However, just as satisfactory is the non-acylated material of the kind described in Example I. In many instances, the most suitable flooding agent is characterized by the fact that such agent contains no amino or amido nitrogen atom.

It is to be noted, as has been stated repeatedly, that the raw materials, prior to treatment with an alkylene oxide, must be water-insoluble, or at the most, the solubility should be no more than indicated by self-emulsifying properties to produce a suspension or the like. The product, after treatment with ethylene oxide, must be water-soluble, and must be resistant to soluble calcium and magnesium salts.

It is to be noted that, although the treatment with an alkylene oxide or its equivalent is necessary in all instances to produce water solubility, yet excessive treatment should be avoided, in that the compound may become extremely hydrophile. Generally speaking, it is safe to treat the water-insoluble product with ethylene oxide, so as to increase its molecular weight not less than 50%, and generally not more than 200%, although obviously, it is difficult to set a hard and fast rule. Such procedure is generally a satisfactory guide. If some other alkylene oxide is employed, for instance, propylene oxide, then of course, an increased amount of the alkylene oxide must be employed, based on the increased molecular weight of propylene oxide and the like; and also based on the fact that its solubilizing effect per mole is somewhat less than that of ethylene oxide. If too great an amount of ethylene oxide is used, the resultant product may lose its surface activity. Six to 18 moles of the alkylene oxide or its equivalent for each acyl radical represents the upper limit. Obviously, an acyl radical containing 18 carbon atoms would solubilize very readily; whereas, an acyl radical containing 32 to 40 carbon atoms would solubilize with greater difficulty.

Thus, a more rational guide is that for each carbon atom present in the original water-insoluble material, one must add at least one third or one-half molecular proportions of the alkylene oxide, if ethylene oxide is used, and possibly a greater amount, if an alkylene oxide of higher molecular weight is employed. An oxide such as benzyl ethylene oxide, may be employed where the original raw material is almost on the verge of being water-soluble per se. It also must be remembered that the solubility of the product obtained varies somewhat with the method of manufacture and the particular catalyst which is present. It has previously been stated that this is one of the reasons that the exact composition of the compounds cannot be indicated as satisfactorily as might be desired in all instances. If solubility is not obtained with any other alkylene oxide, then ethylene oxide should be employed, because it appears to be best suited for the reason that it reacts most readily, and because it promotes water solubility to a greater degree than other alkylene oxides or the equivalent. Glycidol, of course, or a similar type of compound is just as satisfactory as ethylene oxide. In any event, water solubility can always be obtained, and the range of surface activity is such that there is no difficulty in stopping short of the point where surface activity would disappear, due to the

presence of unusually excessive hydrophile properties. Oxygen atoms, if present in the parent material (in addition to the required hydroxyl radical or radicals), increase water solubility. If the product becomes water-soluble too easily (i. e., shows insufficient surface activity), repeat the procedure, but use an alkylene oxide of higher molecular weight.

It may be well to emphasize what has been said previously in regard to surface activity of the water-soluble compound. If a dilution of the water-soluble reaction product of one part in 3,000, or one part in 5,000 or 10,000, no longer shows any decrease in the surface tension of the resulting solution, as compared with the raw water from which it was prepared, then one has obtained a water-soluble product from the parent water-insoluble product; but surface activity has been destroyed, due to the introduction of an extremely hydrophilic property. Needless to say, such product should be removed and the changes made in the introduction of the alkylene oxide along the lines previously indicated, so as to obtain a product that is water-soluble and also surface-active. In order that it be understood that such extremely hydrophilic compounds are not contemplated for use in the present process, it will be noted that the hereto appended claims are limited to the surface-active type.

It is possible that any residual hydroxyl radical present may be combined with an acid, for instance, a monobasic or polybasic acid, or even a sulfonic acid; and such derivatives may be employed. In such instances it is to be noted that the sulfonic group is not a functional group in the sense that it particularly adds or detracts from the solubility of the compound, but may yield a product having some other desirable property. Similarly, a material like methyl sulfate may be employed to convert a residual hydroxyl to an ether. As has been previously indicated, although such conventional variants may be employed, it is our preference to avoid the use of such type of flooding agent.

Although, as has been previously pointed out, no general formula appears available to characterize all the compounds contemplated, yet some of the simpler types might be referred to as glycol or polyglycol ethers derived from water-insoluble compounds of the kind described, i. e., water-insoluble, non-cyclic alcohols or water-insoluble amino or amido compounds, characterized by the presence of at least one amino hydrogen atom. The glycol or glycol ether can be further characterized by containing a radical or residue derived from the water-insoluble products of the kind just described, and also containing the group $(—O—C_2H_4)_n—OX$, in which OX denotes a hydroxyl radical, an ether radical, or an ester radical, and n denotes a whole number, preferably above 3, generally not over 40, and usually not over 20. Our preference is that OX denotes a hydroxyl radical.

In practising or carrying out our process, the flooding of the subterranean sands or strata is effected in the conventional manner, except that in our process the flooding water has added to same, a treating agent or chemical compound of the kind previously described. The amount of said treating agent or compound added to the flooding water, is generally relatively small, varying from approximately 1 to 10,000 to approximately 1 to 100,000, and in some instances even less. In some particular cases, where the water employed has an extremely high salinity and where the oil to be recovered is particularly valuable, one might use a concentration as high as 1 to 5,000; but such concentration represents an unusual condition and one which would be ordinarily uneconomical. In fact, in the majority of cases a ratio of 1 to 40,000 to 1 to 80,000 represents a limit which gives both a valuable flooding vehicle and a cost that is economically feasible. As has been previously pointed out, the actual flooding procedure may involve the repeated use of the same flooding vehicle, and after the addition of the initial treating agent, it may be necessary to add small amounts of said treating agent from time to time to keep the effectiveness of the flooding vehicle at a predetermined standard of effectiveness.

It is understood that in the hereto appended claims reference to an alkylene oxide broadly or a specific member, as ethylene oxide, is intended to include obvious functional equivalents of the kind referred to, to wit, halohydrins, glycidol, epichlorhydrin, and the like. It is also understood that reference in the appended claims to an amino nitrogen atom, refers to either an amino nitrogen atom, or an amido nitrogen atom, or a substituted amido nitrogen atom, i. e., a radical derived from ammonia, characterized by the fact that one of the original hydrogen atoms has been replaced by either an acyl radical or a hydrocarbon radical directly attached.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A flooding process for recovering oil from subterranean sands and other oil-bearing strata, which consists in flooding the oleiferous structure with an aqueous treating solution, comprising a water-soluble, surface-active, alkaline earth-resistant polyglycol ether, which is derived by reacting an alkylene oxide with a water-insoluble member of the class consisting of non-cyclic alcohols; amines having at least one hydrogen atom attached to an amino nitrogen atom; acylated esters derived from hydroxylated amines characterized by the presence of at least one hydrogen atom attached to an amino nitrogen atom and at least one higher molecular weight carboxy acid acyl radical; and amides having at least one hydrogen atom attached to the amino nitrogen atom; and further characterized by the presence of at least one higher molecular weight carboxy acid acyl radical

2. A flooding process for recovering oil from subterranean sands and other oil-bearing strata, which consists in flooding the oleiferous structure with an aqueous treating solution, comprising a water-soluble, surface-active, alkaline earth-resistant polyglycol ether characterized by freedom from any polybasic carboxy acid radical, and which is derived by reacting an alkylene oxide with a water-insoluble member of the group consisting of non-cyclic alcohols; amines having at least one hydrogen atom attached to an amino nitrogen atom; acylated esters derived from hydroxylated amines characterized by the presence of at least one higher molecular weight carboxy acid hydrogen atom attached to an amino nitrogen atom in at least one acyl radical; and amides having at least one hydrogen atom attached to the amino nitrogen atom; and further characterized by the presence of at least one higher molecular weight carboxy acid acyl radical.

3. A flooding process for recovering oil from subterranean sands and other oil-bearing strata,

which consists in flooding the oleiferous structure with an aqueous treating solution, comprising a water-soluble, surface-active, alkaline earth-resistant polyglycol ether characterized by freedom from any polybasic carboxy acid radical, and which is derived by reacting an alkylene oxide with an amide having at least one hydrogen atom attached to an amino nitrogen atom; and further characterized by the presence of at least one higher molecular weight carboxy acid acyl radical.

4. A flooding process for recovering oil from subterranean sands and other oil-bearing strata, which consists in flooding the oleiferous structure with an aqueous treating solution, comprising a water-soluble, surface-active, alkaline earth resistant polyglycol ether characterized by freedom from any polybasic carboxy acid radical, and which is derived by reacting an alkylene oxide with an amide having at least one hydrogen atom attached to an amino nitrogen atom; and further characterized by the presence of at least one detergent-forming carboxy acid acyl radical.

5. A flooding process for recovering oil from subterranean sands and other oil-bearing strata, which consists in flooding the oleiferous structure with an aqueous treating solution, comprising a water-soluble, surface-active, alkaline earth-resistant polyglycol ether characterized by freedom from any polybasic carboxy acid radical, and which is derived by reacting an alkylene oxide with an amine having at least one hydrogen atom attached to an amino nitrogen atom; and further characterized by the presence of at least one fatty acid acyl radical.

6. A flooding process for recovering oil from subterranean sands and other oil-bearing strata, which consists in flooding the oleiferous structure with an aqueous treating solution, comprising a water-soluble, surface-active, alkaline earth-resistant polyglycol ether characterized by freedom from any polybasic carboxy acid radical, and which is derived by reacting an alkylene oxide with an amide having at least one hydrogen atom attached to an amino nitrogen atom; and further characterized by the presence of at least one hydroxylated fatty acid acyl radical.

7. A flooding process for recovering oil from subterranean sands and other oil-bearing strata, which consists in flooding the oleiferous structure with an aqueous treating solution, comprising a water-soluble, surface-active, alkaline earth-resistant polyglycol ether characterized by freedom from any polybasic carboxy acid radical, and which is derived by reacting an alkylene oxide with an amide having at least one hydrogen atom attached to an amino nitrogen atom; and further characterized by the presence of at least one ricinoleyl radical.

8. A flooding process for recovering oil from subterranean sands and other oil-bearing strata, which consists in flooding the oleiferous structure with an aqueous treating solution, comprising a water-soluble, surface-active, alkaline earth-resistant polyglycol ether characterized by freedom from any polybasic carboxy acid radical, and which is derived by reacting an alkylene oxide containing at least two carbon atoms and not more than four carbon atoms, with an amide having at least one hydrogen atom attached to an amino nitrogen atom; and further characterized by the presence of at least one ricinoleyl radical.

9. A flooding process for recovering oil from subterranean sands and other oil-bearing strata, which consists in flooding the oleiferous structure with an aqueous treating solution, comprising a water-soluble, surface-active, alkaline earth-resistant polyglycol ether characterized by freedom from any polybasic carboxy acid radical, and which is derived by reacting ethylene oxide with an amide having at least one hydrogen atom attached to an amino nitrogen atom; and further characterized by the presence of at least one ricinoleyl radical.

10. A flooding process for recovering oil from subterranean sands and other oil-bearing strata, which consists in flooding the oleiferous structure with an aqueous treating solution, comprising a water-soluble, surface-active, alkaline earth-resistant polyglycol ether characterized by freedom from any polybasic carboxy acid radical, and which is derived by reacting ethylene oxide with an amide having at least one hydrogen atom attached to an amino nitrogen atom, and characterized by the presence of at least one ricinoleyl radical; and further characterized by the presence of the amide radical derived from tris (hydroxymethyl) aminomethane.

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