

UNITED STATES PATENT OFFICE

2,233,382

FLOODING PROCESS FOR RECOVERING
OIL FROM SUBTERRANEAN OIL-BEARING
STRATA

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No Drawing. Application March 6, 1940,
Serial No. 322,535

12 Claims. (Cl. 166—21)

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 eco-

nomically 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 characteristic 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 conduits used in the procedure. It probably has the effect of decreasing the apparent vis-

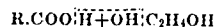
cosity of water; or to state the matter in another way, the aqueous vehicle or treating solution probably permeates sand and various oil-containing strata which might not be permeated at all by water alone, or at least under conditions of diminished pressure. There are numerous other advantages not necessary 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.

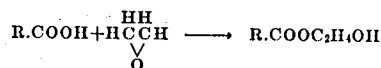
We have found that a very desirable agent for addition to the water used in flooding procedure (the said water usually consisting of a dilute brine), is a glycol or polyglycol ether of the type obtainable by causing a water-insoluble, non-cyclic, hydroxy compound characterized by the presence of an acyl radical having at least seven carbon atoms, 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.

Before considering such various examples in detail, it may be well to note another fact which

is the basis for including carboxy compounds as the substantial functional equivalents of the hydroxy compounds of the kind described. If a carboxy acid be indicated by the formula $R.COOH$, then if the compound reacts with ethylene glycol, for example, the reaction may be indicated thus:



The result of the reaction is a fractional ester or ester alcohol, and thus is just as suitable for treatment with ethylene oxide as the various hydroxylated esters or the like, which will be described subsequently. However, if the acid $R.COOH$ is treated with ethylene oxide, the same final reaction product is formed without the elimination of water, thus:



Broadly speaking, the reagents or compounds intended to be added to water to produce the aqueous treating solution employed in the present process, are obtained by the reaction between an alkylene oxide or its functional equivalent and a non-cyclic compound characterized by the presence of a reactive hydrogen atom directly attached to an oxygen atom and containing an acyl radical characterized by the presence of at least seven carbon atoms. Such materials are additionally characterized by being water-insoluble prior to treatment with the selected alkylene oxide.

Types of materials which are suitable for reaction with alkylene oxides include various carboxy acids, hydroxy esters characterized by the presence of a hydroxyl group in the alcohol residue, as in the case of mono-olein, di-olein, etc., or esters characterized by the presence of a hydroxyl group as part of the acyl radical, as in the case of tricinolein, or characterized by the presence of hydroxyl radicals in both positions, as in the case of monoricinolein, diricinolein, etc. Some of the materials previously referred to are readily recognized as being ordinarily referred to as super-glycerinated fats. Somewhat comparable to superglycerinated fats are certain hydroxy acylated derivatives of tertiary amines. Examples of this class are the ricinoleic acid ester, or dioctyl ethanolamine, or the mononoleic acid ester of octadecyl diethanolamine.

Another suitable class of materials is an amido type compound, characterized by freedom from an amino hydrogen atom and characterized by the presence of a hydroxyl group in either the acyl radical, as in the amide derived from ricinoleic acid and diamylamine, or a hydroxyl in the amine residue, as in the case of the amide derived from oleic acid and octylethanolamine, or an amide characterized by a hydroxyl in both positions, as the amide derived from ricinoleic acid and octadecylethanolamine. The other "amide" is employed without limitation to the type in which there is only one substituent for an amino hydrogen atom. Thus, "amido" type of compound is intended to include secondary or tertiary amides and also substituted amides, i. e., amides derived from amines; and the nitrogen atom present is referred to as an amino nitrogen atom. This is purely a matter of convenience, although this nomenclature is frequently employed.

It is obvious that these compounds, which are intended for treatment with an alkylene oxide or the like to give the agent which is contemplated

for use in the aqueous flooding vehicle, are obtained by reaction with higher molecular weight carboxy acids which are characterized by having more than six carbon atoms, and generally less than 40 carbon atoms; or to state the matter another way, that the acyl radical must contain at least seven carbon atoms. With this in mind, it may appear well to indicate immediately the various members of the class which may broadly be indicated as "higher molecular weight carboxy 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 alkalis 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, ricinostearic acid, ricinoleyl lactic acid, acetylricinoleic acid, chloracetyl-ricinoleic 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, coconut oil, rapeseed oil, sesame oil, palm kernel oil, palm oil, olive oil, corn oil, cottonseed oil, sardine oil, teaseed 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 these mentioned; hydroxy and alpha-hydroxy higher carboxylic, aliphatic and fatty acids, such as hydroxy stearic acid, dihydroxy-palmitic acid, dihydroxystearic acid, dihydroxybehenic acid, alpha-hydroxy capric acid, alpha-hydroxystearic acid, alpha-hydroxy palmitic acid, alpha-hydroxy lauric acid, alpha-hydroxy myristic acid, alpha-hydroxy coconut 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 carnaubic 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, carboxydiphenyl, pyridine carboxylic acid, hydroxybenzoic acid, 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 some instances, 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 kerolic 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 course, 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.

The preparation of suitable compounds adapted for treatment with an alkylene oxide or the like to yield a suitable agent from the various acids of the kind mentioned, is relatively simple. Reference has already been made to superglycerinated fats. Needless to say, the manufacture of these compounds is well known; and in general, they may be characterized by the following formula: $(R.COO)_m.T(OH)_n$ in which $R.COO$ represents a higher molecular weight monocarboxy acid of the kind previously described, R being characterized by containing at least six carbon atoms; T represents a polyhydric alcohol residue and m represents a small whole number. As to the types of polyhydric alcohols which may be employed and as to the general method of manufacture, reference is made to U. S. Patent No. 2,052,284, dated August 25, 1930, to De Groote. Although, the aforementioned

tioned patent is concerned primarily with detergent-forming monocarboxy acids, the same procedure is applicable to all the acids previously described. In addition to the specific polyhydric alcohols indicated in said aforementioned De Groote patent, one may also employ the sugar type, such as erythritol, pentaerythritol, pentitols, hexitols, heptitols, etc. Of particular interest are such materials as sorbitol and mannitol and their anhydrides, such as sorbitan, mannitan, and mannide. It is to be noted that hydroxylated esters of these last mentioned compounds are available in the open market.

Similarly, as to the preparation of hydroxylated amides, reference is made to U. S. Patent No. 2,078,653, dated April 27, 1937, to De Groote and Keiser. Although this patent is concerned primarily with the production of hydroxylated amides, such as ricinoleamide, similar amides can be derived from any suitable higher molecular weight carboxy acid of the kind described, provided that it contains an alcoholiform hydroxyl. Reference is also made to U. S. Patent No. 2,106,241, dated January 25, 1938, to De Groote and Keiser. The procedure therein employed for manufacture of hydroxylated amides, although concerned primarily with detergent-forming acids, is applicable to all the various higher molecular weight organic acids previously described.

As to the production of esterified tertiary hydroxyamines, reference is made to the following patents: U. S. Patents Nos. 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 triethanolamine, 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 triethanolamine, 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 triethanolamine or the like with an amine having a higher molecular weight without any additional hydroxyl radicals; for example, one might

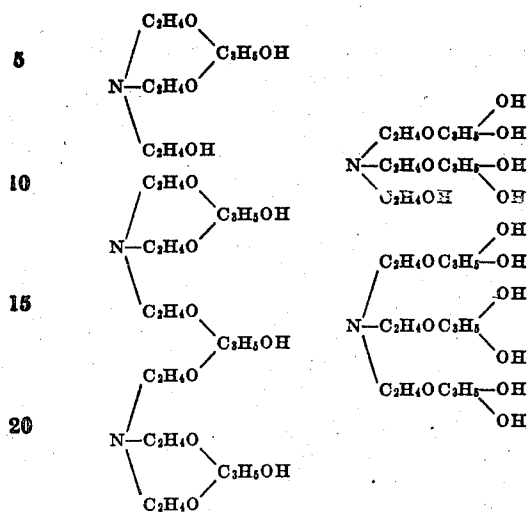
employ tripropanolamine or tributanolamine or the like. Likewise, one may employ an amine having fewer hydroxyl radicals, for example, amyl diethanolamine instead of triethanolamine. Similarly, in the formation of amides, where monoethanolamine or diethanolamine may give a water-soluble product, one might employ monobutanolamine, monohexanolamine, or dibutanolamine, dihexanolamine, 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 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.

As to similar products derived from acylated methylene diamines, reference is made to the following four co-pending applications: Serial No. 273,220, of De Groote, Keiser and Wirtel, filed May 12, 1939; Serial No. 273,223, of De Groote and Keiser, filed May 12, 1939; Serial No. 300,842, of De Groote, Keiser and Wirtel, filed October 23, 1939; and Serial No. 300,845, of De Groote and Keiser, filed October 23, 1939. Such co-pending applications are concerned largely with monocarboxy detergent-forming acids, but obviously the same procedure can be applied to any of the higher molecular weight organic acids previously described. Attention is directed to the fact that the acylated hydroxy ethylene diamines can be treated just the same as acylated triethanolamine. For instance, two moles of diethanolamine can be treated with one mole of formaldehyde to give tetraethanol methylene diamine. Such product can be acylated so as to yield a water-insoluble product by means of a fatty acid or the like; and the product can be subjected to reaction with an alkylene oxide, or can be treated with a polybasic acid or polybasic acid compound containing a fatty acid radical, as described in the last four aforementioned co-pending applications.

Other suitable hydroxylated amines which may be acylated are described in co-pending application for patent Serial No. 273,278, of De Groote and Keiser, filed May 12, 1939. For instance, said co-pending application describes amines obtained by converting triethanolamine or the like into an alcoholate and then reacting with a

chlorhydrin, such as glycerol chlorhydrin. Such amines include the following types:



Needless to say, such amines can be acylated in the same manner previously described by any of the higher molecular weight organic acids, so as to yield water-insoluble compounds which are suitable for treatment with an alkylene oxide.

Similarly, the amides containing only one amino hydrogen atom, for instance, the amide derived from lauric acid and amylamine, may be treated with formaldehyde or the like, so as to unite two moles to give a water-insoluble diamide. Such diamide may be treated with ethylene oxide or the like to yield a suitable flooding agent.

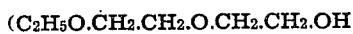
It is understood, of course, that there is no objection to a non-functional atom or radical of the kind previously referred to in regard to the constitution of suitable higher molecular weight organic acids. Furthermore, there is no objection to the introduction of an acyl radical derived from an acid having less than 7 carbon atoms, providing there is always present at least one acyl radical of the kind specified. Furthermore, in some instances it is more desirable to polymerize the ethylene oxide and then unite the same with a selected higher molecular weight organic acid, particularly a fatty acid.

Example 1

1.06 kilograms of diethylene glycol are heated to 150° C. in an autoclave and then 8.8 kilograms of ethylene oxide are added a little at a time. The pressure is about 10 atmospheres. After the whole of the ethylene oxide has been introduced, the autoclave is heated until the pressure has practically disappeared. A quantitative yield of a colorless water-soluble condensation product is obtained. A mixture of three parts of the condensation product and one part of oleic or ricinoleic acid is heated to about 130° C., until esterification is complete.

Example 2

10 molecular proportions of ethylene oxide are added to one molecular proportion of the monoethyl ether of diethylene glycol



obtainable by acting with ethylene oxide on the mono-ethyl ether of ethylene glycol in the manner described in Example 1. 100 parts of the resulting ether are heated with 30 parts of palmitic acid for about twelve hours at 150° C.

Example 3

3 parts of a condensation product from one molecular proportion of diethylene glycol and ten molecular proportions of ethylene oxide are esterified with 1 part of oleic acid in the manner described in Example 1.

Example 4

20 molecular proportions of ethylene oxide are added to the monoethyl ether of diethylene glycol in the manner described in Example 2. 100 parts of the reaction product are heated with 22 parts or slightly less of castor oil, so as to produce a water-soluble product. If water solubility is not obtained, approximately 3-5 additional parts of ethylene oxide are added, so as to obtain water solubility.

Example 5

A condensation product derived from one molecular proportion of diethylene glycol and 10 molecular proportions of ethylene oxide, as described in Example 1 above, are treated with an equal weight of cocoanut oil fatty acids and heated until condensation is completed. The product should be readily water-soluble; but if not, slightly additional amounts of ethylene oxide may be required.

Example 6

The reaction product obtainable by the reaction of 18 molecular proportions of ethylene oxide on one molecular proportion of octadecyl alcohol, is heated with oleic acid whereby the hydroxyl group at the end of the chain is esterified. A suitable water-soluble product is obtained.

Example 7

One part of monoricinolein is heated at 100-150° C. in a closed vessel with approximately 3 parts of ethylene oxide. The resultant product is a water-soluble yellow oil which is suitable for use as a flooding agent.

Example 8

100 parts of diethanololeoamide are treated with approximately 30-70 parts of ethylene oxide at a temperature of 130-170° C. in presence of a small amount of alkali.

Example 9

Diamyl ricinoleoamide is treated in the same manner as described in the previous example.

Example 10

A secondary amide is prepared from two moles of stearic acid and one mole of tris-hydroxymethylaminomethane (trimethylol methylamine). The product thus obtained is treated in the same manner as Example 9 preceding.

Example 11

One part of ricinoleic acid is treated with ethylene oxide at a temperature of approximately 130-170° until a water-soluble product is obtained and the reaction is complete.

Example 12

One part of castor oil is treated with approximately 40 molecular equivalents of ethylene oxide in the manner previously described, so as to produce a water-soluble product.

Example 13

Oleic acid is treated with ethylene oxide in the molar proportions of six parts ethylene oxide to

one part of oleic acid under conditions previously described. The product so obtained is water-soluble.

Example 14

The product is made from castor oil in the manner previously described; but instead of using 40 molecular proportions of ethylene oxide for each portion of castor oil, a smaller number of equivalents are employed and propylene oxide is substituted for ethylene oxide.

Example 15

Non-acylated water-insoluble hydroxylated tertiary amines, as for example, dicyclohexylethanolamine, dioctylpropanolamine, octadecylamylethanolamine and the like, may be treated in a manner comparable to the procedures outlined in previous examples to give suitable flooding agents. Similarly, analogous water-insoluble diamines or the like, free from any amino hydrogen atom, may also be employed.

A number of suitable alkylene oxides or their functional equivalents have been previously suggested, but the following may be indicated: ethylene oxide; 1—2 propylene oxide; 1—2 or 2—3 butylene oxide; butadiene oxide; cyclohexane oxide; glycidol, epichlorhydrin; 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 the materials of the kind herein described, but alkylene oxide may react with hydrogen atoms linked to oxygen in an ordinary high molecular weight alcohol and with various cyclic alcohols and phenols; or such oxides may react with a hydrogen atom linked to an amido or an amino nitrogen atom. If 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, i. e., the flooding of subterranean oil sands or strata, in our co-pending applications Serial Nos. 322,534 and 322,536, and 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 the compounds may have more than one group which is reactive with ethylene oxide or the like, for instance, triricinolein, various acylated hydroxylated amines, and polyamines, etc. Furthermore, the composition is further complicated by the fact that instead of 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 Webel, 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 in the hereto appended claims in terms of the method of manufacture, 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 6 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 present, such as a chlorine atom, alkoxy radical, or the like. Furthermore, our preferred flooding agents, addition agents, or treating agents, are derived from suitable fatty acid compounds, particularly ricinoleic acid compounds, which do not contain a nitrogen atom, i. e., an amino nitrogen atom, amide nitrogen atom, or the like. Our preferred reagent is made from ricinoleic acid by means of ethylene oxide, either alone or in conjunction with a glycol in the manner described.

One of the most desirable types of flooding agents is prepared by reacting ricinoleic acid with diethylene glycol and then introducing approximately 4 to 8 moles of ethylene oxide for each mole of fatty acid ester. However, insofar that such procedure is apt to lead to the introduction at both reactive points, i. e., at both the alcoholic hydroxyl, which is part of the original glycol, and also at the alcoholic hydroxyl, which is part of the acyl radical, one is apt to obtain a more suitable product by reacting one mole of diethylene glycol to approximately 4—8 moles of ethylene oxide in the manner previously indicated and then esterifying with ricinoleic acid. By this procedure all the ethenoxy groups are introduced in the carboxylic position. This preferred method of conducting the reaction is apt to give the most suitable types of flooding agent in the majority of instances.

It is to be noted that some of the previous examples illustrate classes of compounds which are derived by first polymerizing an alkylene oxide, such as ethylene oxide, with a polyhydric alcohol, such as glycerol, ethylene glycol, diethylene glycol, or the like, and then reacting such polymer with a suitable higher molecular weight carboxy acid, and particularly, fatty acid, such as oleic acid, or ricinoleic acid. Possibly, such types of materials could be classified conveniently as either glycol ethers, or polyglycol ethers, derived from carboxy acids of the kind described, or glycol or polyglycol ethers derived from hydroxylated esters. For the sake of convenience we will consider them as belonging to the latter sub-class, i. e., contemplated within the scope of hydroxylated esters.

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 of the acyl radical represents the upper limit, although obviously, an acyl radical containing 18 carbon atoms would solubilize very readily; whereas, an acyl radical containing 32 or 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 great 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 decreases in the surface tension of the resulting solution, as compared with the raw

water from which it was prepared, than 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 oxides 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 perhaps some of the simpler types might be referred to as glycol or polyglycol ethers derived from water-insoluble acylated hydroxy compounds, characterized by the fact that there is present at least one hydroxyl radical as part of an acyl radical, or as part of a carboxyl radical, or as part of a hydroxy hydrocarbon radical, which in turn is a substituent for an amino nitrogen atom, or a hydroxyl radical which is part of a polyhydric alcohol radical or residue; said water-insoluble acylated compound being additionally characterized by the presence of at least one acyl radical containing more than six carbon atoms; and the glycol or polyglycol ether being 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 about 3, generally not over 40, and usually not over 20. Our preference is that OX denote a hydroxyl radical.

In practicing 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 1-10,000 to approximately 1-100,000, 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 1-5000; but such concentration represents an unusual condition and one which would be ordinarily uneconomical. In fact, in the majority of cases, a ratio of 1-40,000 to 1-80,000 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 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 higher molecular weight carboxy acids; hydroxylated amides containing at least one higher molecular weight carboxy acid acyl radical; and characterized by the presence of at least one hydroxyl radical and freedom from an amino hydrogen atom; acylated derivatives of basic hydroxylated amines characterized by the presence of at least one higher molecular weight carboxy acid acyl radical; and the presence of at least one hydroxyl radical and the absence of an amino hydrogen atom; non-acylated hydroxylated tertiary amines; and hydroxylated esters of higher molecular weight carboxy acids.

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 class consisting of higher molecular weight carboxy acids; hydroxylated amides containing at least one higher molecular weight carboxy acid acyl radical; and characterized by the presence of at least one hydroxyl radical and freedom from an amino hydrogen atom; acylated derivatives of basic hydroxylated amines characterized by the presence of at least one acyl radical derived from higher molecular weight carboxy acids and the presence of at least one hydroxyl radical and the absence of an amino hydrogen atom; non-acylated hydroxylated tertiary amine; and hydroxylated esters of higher molecular weight carboxy acids.

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 a water-insoluble hydroxylated ester of a higher molecular weight carboxy acid.

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 a water-insoluble hydroxylated ester of a detergent-forming carboxy acid.

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 a water-insoluble hydroxylated ester of a fatty acid.

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 a water-insoluble hydroxylated ester of a hydroxylated fatty acid.

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 a water-insoluble hydroxylated ester of ricinoleic acid.

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 having at least two carbon atoms and not more than four carbon atoms, with a water-insoluble hydroxylated ester of ricinoleic acid.

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 a water-insoluble hydroxylated ester of ricinoleic acid.

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 a water-insoluble hydroxylated ester

of ricinoleic acid in which a glycol supplies the alcohol radical.

11. 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 a water-insoluble hydroxylated ester of ricinoleic acid in which diethylene glycol supplies the alcohol radical.

12. 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 diethylene glycol and then reacting such polymer with ricinoleic acid.

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