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PROCESS FOR PREVENTING AND/OR REMOVING ACCUMULATIONS OF SOLID MATTER FROM OIL WELLS, FLOW LINES, AND PIPE LINES

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This invention relates to a process for preventing and/or removing accumulations of solid matter from oil wells and pipe lines, and thereby improving their productivity and capacity.

In many oil wells, deposits of paraffin, wax, asphaltic and bituminous organic solids and similar materials accumulate in objectionable quantities on the face of the producing formation, on the screen or liner, or in the pump, the casing or the tubing of the well. Such deposits operate to decrease materially the productivity of the wells in which they occur. Similarly, deposits of the same character are found in some oil flow lines and oil pipe lines, where they effectively reduce the capacity of the pipes, sometimes to the point where little or no fluid can be passed through such conduits in the normal manner of operation.

The accumulations with which this invention is concerned are to be distinguished at the outset from accumulations of mud solids in the form of mud sheaths, the removal of which is the subject-matter of my co-pending application Serial No. 719,925, filed January 2, 1947. The present deposits quite naturally and frequently contain minor proportions of inorganic materials like sand or shale fragments from the productive formation, or minor proportions of residual drilling mud solids of the character of clay or weighting materials. They are, however, essentially organic in character; whereas, drilling mud solids are essentially inorganic in nature.

Further to distinguish the two types of deposits and the character of the respective problems they present, it should be noted that mud solids are ordinarily deposited in a well, or in or on a geological formation penetrated by a well, as a result of the drilling operation or some subsequent servicing operation, like "killing" the well with mud. Such man-produced mud deposits or mud sheaths constitute non-recurring deposits. Once such a deposit or sheath has been removed, e. g., by the process of my companion application, just referred to, it can never again appear or occur in that well.

On the contrary, the organic deposits, with the removal of which the present invention is concerned, are essentially progressive deposits produced naturally during the operation of the well and its accessories. Whereas the mud sheaths occur only at the geological formations penetrated during drilling of the well, the present organic deposits may occur at the formation, at various levels in the well itself, or at various points in the transportation lines reaching from

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the well to the refinery, including tanks. Their deposition is progressive; or, if they are removed periodically, they may be said to be recurring. Such removal is usually only intentionally achieved; but in some instances, such organic deposits slough off their supporting metallic structure. In such instances, they give the appearance of being recurring, because continuing deposition soon produces a new accumulation of appreciable and detectable proportions.

Although such organic deposits may at times contain minor proportions of inorganic materials like sand, such inorganic components are not material to the deposition of the organic accumulations, their essential characteristics, or their removal by the process constituting my invention. In a sense, the minor inorganic constituents are the result of entrapment by the waxy, sticky, or gummy organic material constituting the bulk of the ultimate deposit.

The purpose of removing such deposits is obvious. In some areas, wells decline in productivity at a more or less rapid rate, because of deposition of such deposits on the face of the producing formation. In some cases, the decline is sufficiently rapid that the wells must be serviced in some manner or other at a frequency ranging from several days to several weeks. In some instances, the deposition is so slow that servicing at long intervals is sufficient to maintain the well at a satisfactory level of productivity. The same is true of the various conduits through which the oil travels from the well to the refinery; and periodic servicing of such elements is also required. The capacity of a conduit of circular cross-section is reduced greatly by such deposits, usually well beyond the reduction expected from the ratio of effective cross-sectional areas of the conduit and the fouled conduit. Where organic deposits of the present type occur on formation walls, well productivity may fall substantially to zero, especially in low-pressure fields. Pipe capacities are frequently reduced to a small fraction of their capacities when clean. Ultimately, of course, such pipes may be found completely clogged by such deposits. In the case of pipe lines, the operator may find himself burdened with the cost of a 6" or 8" line, yet benefiting from a capacity equal to that of a 3" or 4" line.

The process which constitutes the present invention consists in subjecting such clogging organic deposits of wax, paraffin, asphaltic or bituminous substances and the like, to the action of a chemical reagent of the character described

below, to the end that such deposits are removed from the surfaces to which they were originally adherent. By means of the process, the productivity of wells is restored as is the capacity of flow lines, pipe lines, traps, tanks, pumps, and other equipment, through which such oil travels from formation to refinery.

It will be obvious that, if the first minute deposit of such organic materials is subjected to my reagent, and if such application of reagent is practised continuously or periodically with sufficient frequency, the operation has the appearance of a preventive process rather than a corrective process. In addition, it should be noted that my reagent has a more real claim to acting as a preventive, in that surfaces effectively cleaned by its application tend to resist renewed deposition of such materials, and to remain clean and operative for longer periods than if the reagent had not been applied. Therefore, I have entitled my process as being both a preventive and a corrective one. It may obviously be applied in either sense, and achieve the same ultimate goal, the improvement of efficiency of operation of wells and equipment. In the appended claims, I have used the word "removing." It should be clearly understood that I thereby include the prevention of organic deposits of the present kind.

The reagent which I employ in practising my process is the heart of the present invention. Its composition and characteristics will be described in detail.

The reagent which I employ in practising my process consists of a basic acylated aminoalcohol in which an acyloxy radical derived from a detergent-forming acid having from 8 to 32 carbon atoms is joined to a basic nitrogen atom by a carbon atom chain, or a carbon atom chain which is interrupted at least once by an oxygen atom, said acylated aminoalcohol being used in combination with one or more water-insoluble organic liquids capable of acting as an oil solvent.

The basic acylated aminoalcohols employed as ingredients of my reagents may have molecular weights ranging from 273 to about 4,000, in monomeric form. The minimum figure is derived by considering the amino-alcohol reactant to be triethanolamine and the acylating agent to be a C_8 unsaturated monocarboxy acid. To produce a compound of maximum molecular weight, the acylating agent could furnish three $C_{31}H_{63}CO$ radicals; the element, OR', could be 10 times $OC_{10}H_{20}$; and R'' could be a polyaminoalcohol radical, rather than the simple alkanol radical, $HOC_{10}H_{20}$. Such largest elements add up to produce a product of molecular weight, 4,000, or slightly higher.

I prefer to employ my reagent in the form of a relatively stable aqueous dispersion. By "relatively stable aqueous dispersion," I mean one that is not resolved into its components spontaneously, on standing for protracted periods of time, e. g., for more than one hour. However, it may be employed in undiluted form or dispersed in oil. In general, I have found the aqueous dispersions to be somewhat more effective. Sometimes, such aqueous dispersions will be effective, whereas the undiluted reagent or its non-aqueous dispersion or solution will be substantially ineffective.

The basic acylated aminoalcohol employed as an ingredient of the reagent employed in the present process, consists of an acylated aminoalcohol in which an acyloxy radical derived from a detergent-forming acid having from 8 to 32

carbon atoms is joined to a basic nitrogen atom by a carbon atom chain, or a carbon atom chain which is interrupted at least once by an oxygen atom. The aminoalcohols may have more than one amino radical, or, for that matter, more than one basic amino radical. The compounds herein contemplated as ingredients of my reagent are well-known compounds and are produced by conventional procedures. Stated another way, the compounds herein contemplated are esters of aminoalcohols which may contain ether linkages as well as more than one amino nitrogen atom.

The phrase "basic amino nitrogen atom" is used in its conventional sense. ("Unsaturated groups, or negative groups, if substituted for one or more of the hydrogens of ammonia, reduce the basicity of the nitrogen atom to a remarkable degree. In general, the presence of one negative group linked on the nitrogen in sufficient to destroy the ordinary basic properties." Textbook of Organic Chemistry, Richter, second edition, page 253.)

Reference to an amine and the subsequent amino compounds is intended to include the salts and the anhydro base. In instances where water is present, the term includes the hydrated base as well. Both the anhydro base and the hydrated base are obviously present when an aqueous system is being subjected to the reagent, or when the reagent is used as a water solution or dispersion. ("In an aqueous solution of the amine, the anhydro base, $R-NH_2$, the hydrated base, $R-NH_3-OH$, and the two ions are all present." Richter, s. v., page 252.)

As has been previously stated, the reagents contemplated as ingredients in the compositions employed in the present process, are old and well known products. For convenience and for purpose of brevity, reference is made to the following three U. S. patents to De Groote and Keiser, to wit: Nos. 2,324,488, 2,324,489, and 2,324,490, all dated July 20, 1943. Said patents are concerned with processes for breaking water-in-oil emulsions. The demulsifying agent employed is in each instance the resultant derived by reaction between a certain fractional ester and an acylated aminoalcohol. The aminoalcohols described collectively in the aforementioned three patents are used as reactants for combining with a fractional acidic ester. Thus, said aminoalcohols must have present an alcoholiform hydroxyl as part of an acyl radical, or as part of a substituent for an amino hydrogen atom. In the instant case, such aminoalcohols are not employed as reactants, except as to salt formation reactions, and the hydroxyl group is not functional. Thus, one may employ, not only the aminoalcohols described in the three aforementioned United States patents, but also the obvious analogues in which there is no hydroxyl radical present. Subsequent reference will be made to this particular type and examples will be included.

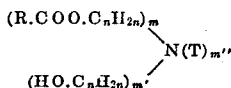
Aforementioned U. S. Patent No. 2,324,488, describes hydroxylated acylated amino-ether compounds containing:

(a) A radical derived from a basic hydroxy-amino-ether and said radical being of the kind containing at least one amino nitrogen free from attached aryl and amido-linked acyl radicals; said hydroxyamino-ether radical being further characterized by the presence of at least one radical derived from a basic hydroxyamine and being attached by at least one ether linkage to at least one radical selected from the class con-

sisting of glycerol radicals, polyglycerol radicals, glycol radicals, polyglycol radicals, basic hydroxylamine radicals, amido hydroxylamine radicals, and aryl alkanolamine radicals, said basic hydroxylamine-ether radical being characterized by containing not more than 60 carbon atoms; and

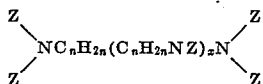
(b) An acyl radical derived from a detergent-forming monocarboxy acid having at least 8 carbon atoms and not more than 32 carbon atoms, said acylated amino-ether being additionally characterized by the fact that said aforementioned acyl radical is a substituent for a hydrogen atom of an alcoholic hydroxyl radical.

Aforementioned U. S. Patent No. 2,324,489 describes hydroxylated acylated monodamino compounds free from ether linkages, said hydroxylated acylated amino compounds being of the following type:



in which R.COO represents the oxy-acyl radical derived from a monobasic detergent-forming acid; T represents a member of the class consisting of hydrogen atoms, non-hydroxyl hydrocarbon radicals, and acylated radicals, obtained by replacing a hydrogen atom of the hydroxyl group of an alkylol radical by the acyl radical of a monobasic carboxy acid having less than 8 carbon atoms; n represents a small whole number which is less than 10; m represents the numeral 1, 2, or 3; m' represents the numeral 0, 1, or 2; and m'' represents the numeral 0, 1, or 2; with the proviso that $m+m'+m''=3$.

Aforementioned U. S. Patent No. 2,324,490 describes basic hydroxylated acylated polyamino compounds free from ether linkages, said compounds being of the following formula:



in which n represents a small whole number varying from 2 to 10; x is a small whole number varying from 0 to 10; Z is a member of the class consisting of H, RCO, R'CO, and D, in which RCO represents an acyl radical derived from a detergent-forming monocarboxy acid; R'CO is an acyl radical derived from a lower-molecular-weight carboxy acid having 6 carbon atoms or less; and D is a member of the class consisting of alkyl, hydroxylalkyl, aminoalkyl, and acyloxyalkylene, in which instance the acyl group is a member of the class consisting of RCO and R'CO; and the acylated polyamine is further characterized by the fact that there must be present a member of the class consisting of

(a) Acyloxyalkylene radical in which the acyl group is RCO; and

(b) Joint occurrence of an amino radical in which the acyl group is RCO and a hydroxyalkyl radical.

A description of certain high molal monocarboxy acids, and more particularly, those commonly referred to as detergent-forming monocarboxy acids, appears in U. S. Patent No. 2,324,490. For convenience, the following description is substantially a verbatim form of the same subject-matter as it appears in said patent:

"It is well known that certain monocarboxy organic acids containing eight carbon atoms or more, and not more than 32 carbon atoms, are characterized by the fact that they combine with

alkyl, hydroxylalkyl, aminoalkyl, and acyloxy. These detergent-forming acids include fatty acids, resin acids, petroleum acids, etc. For the sake of convenience, these acids will be indicated by the formula R.COOH. Certain derivatives of detergent-forming acids react with alkali to produce soap or soap-like materials, and are the obvious equivalent of the unchanged or unmodified detergent-forming acids. For instance, instead of fatty acids, one might employ the chlorinated fatty acids. Instead of the resin acids, one might employ the hydrogenated resin acids. Instead of naphthenic acids, one might employ brominated naphthenic acids, etc.

"The fatty acids are of the type commonly referred to as higher fatty acids; and of course, this is also true in regard to derivatives of the kind indicated, insofar that such derivatives are obtained from higher fatty acids. The petroleum acids include not only naturally-occurring naphthenic acids, but also acids obtained by the oxidation of wax, paraffin, etc. Such acids may have as many as 32 carbon atoms. For instance, see U. S. Patent No. 2,242,837, dated May 20, 1941 to Shields."

I have found that the acylated aminoalcohol ingredient of the composition of matter herein described and employed in the present process, is preferably derived from unsaturated fatty acids having 18 carbon atoms. Such unsaturated fatty acids include oleic acid, ricinoleic acid, linoleic acid, linolenic acid, etc. One may employ mixed fatty acids, as, for example, the fatty acids obtained from hydrolysis of cottonseed oil, soyabean oil, etc. The preferred acylated aminoalcohol ingredient of my reagent is obtained from unsaturated fatty acids, and, more especially, unsaturated fatty acids containing a hydroxyl radical, or unsaturated fatty acids which have been subjected to oxidation. In addition to synthetic carboxy acids obtained by the oxidation of paraffins or the like, there is the somewhat analogous class obtained by treating carbon dioxide or carbon monoxide, in the presence of hydrogen or an olefin, with steam, or by causing a halogenated hydrocarbon to act with potassium cyanide and saponifying the product obtained. Such products or mixtures thereof, having at least 8 and not more than 32 carbon atoms and having at least one carboxyl group, or the equivalent thereof, are suitable as detergent-forming monocarboxy acids; and another analogous class equally suitable is the mixture of carboxylic acids obtained by the alkali treatment of alcohols of higher molecular weight formed in the catalytic hydrogenation of carbon monoxide.

As is well known, one need not use the high molal carboxy acid, such as a fatty acid, for introduction of the acyl group or acyloxy group. Any suitable functional equivalent such as the acyl halide, the anhydride, ester, amide, etc., may be employed.

The reagent employed in the present process includes an aminoalcohol ester, as described; and particular attention is directed to the fact that, although such esterified aminoalcohol need not contain a hydroxyl radical, my preferred form is the hydroxylated type. Other aminoalcohol esters of the kind herein contemplated are described in U. S. Patent No. 2,259,704, dated October 21, 1941, to Monson and Anderson.

In light of what has been said, it hardly appears necessary to include a list of reactants and reagents derivable therefrom. However, for convenience, the following amines are included.

Suitable primary and secondary amines, which may be employed to produce materials of the kind above described, include the following: Diethanolamine, monoethanolamine, ethylethanolamine, methylethanolamine, propanolamine, dipropanolamine, propylpropanolamine, etc. Other examples include cyclohexylolamine, dicyclohexylolamine, cyclohexylethanolamine, cyclohexyl propanolamine, benzylethanolamine, benzylpropanolamine, pentanolamine, hexanolamine, octylethanolamine, octadecylethanolamine, cyclohexanoethanolamine, etc.

Similarly, suitable tertiary amines which may be employed include the following: Triethanolamine, diethanolalkylamines, such as diethanol-ethylamine, diethanolpropylamine, etc. Other examples include diethanolmethylaniline, tripropanolamine, dipropanolmethylaniline, cyclohexanoldiethanolamine, dicyclohexanoethanolamine, cyclohexyldiethanolamine, dicyclohexylethanolamine, dicyclohexanoethylaniline, benzyl-diethanolamine, benzyl-dipropanolamine, tripentanolamine, trihexanolamine, hexyldiethanolamine, octadecyldiethanolamine, etc.

Additional amines include ethanoldiethylamine, propanoldiethylamine, ethanoldipropylamine, propanoldipropylamine, dibenzylethanolamine, etc. Ether-type aminoalcohols may be obtained from the above-mentioned aminoalcohols, for example, by treating them with one or more moles of an oxyalkylating agent, such as ethylene oxide, propylene oxide, butylene oxide, glycid, etc. It is to be noted that comparable products are obtained by treating primary or secondary amines other than arylamines with an olefin oxide. Aminoalcohols containing a primary or secondary amino group, i. e., having at least one or two amino hydrogen atoms present, may be employed under especially controlled conditions to give an ester, rather than an amide. One procedure is to permit amidification to take place and then cause a rearrangement to the ester form. See U. S. Patent No. 2,151,788, dated March 28, 1939, to Mauersberger.

AMINOALCOHOL ESTER

Example 1

One pound mole of ricinoleic acid is reacted with one pound mole of triethanolamine at approximately 180° to 240° C. for approximately 10 to 25 hours, until there is substantially complete esterification.

AMINOALCOHOL ESTER

Example 2

Ricinoleic acid in the preceding example is replaced by methyl naphthenate.

AMINOALCOHOL ESTER

Example 3

Methyl abietate is substituted for ricinoleic acid in Example 1, preceding.

AMINOALCOHOL ESTER

Example 4

Ethyl oleate is substituted for ricinoleic acid in Example 1, preceding.

AMINOALCOHOL ESTER

Example 5

One pound mole of triethanolamine is reacted with one pound mole of ethylene oxide and the

etherized amine so obtained is substituted for triethanolamine in Examples 1 to 4, preceding.

AMINOALCOHOL ESTER

Example 6

One pound mole of triethanolamine is reacted with two pound moles of ethylene oxide and the etherized amine so obtained is substituted for triethanolamine in Examples 1 to 4, preceding.

AMINOALCOHOL ESTER

Example 7

One pound mole of triethanolamine is reacted with three pound moles of ethylene oxide, and the etherized amine so obtained is substituted for triethanolamine in Examples 1 to 4, preceding.

AMINOALCOHOL ESTER

Example 8

One pound mole of triethanolamine is reacted with 4 to 6 pound moles of ethylene oxide and the etherized amine so obtained is substituted for triethanolamine in Examples 1 to 4, preceding.

AMINOALCOHOL ESTER

Example 9

One pound mole of ethanoldiamylamine obtained by reacting one pound mole of diamylamine with one pound mole of ethylene oxide is employed in place of triethanolamine in Examples 1 to 4, preceding.

AMINOALCOHOL ESTER

Example 10

The same procedure is employed as in the preceding example, except that an etherized amine is obtained by treating diamylamine with 2, 3 or 4 moles of ethylene oxide and such etherized amine is employed instead of ethanoldiamylamine.

AMINOALCOHOL ESTER

Example 11

One pound mole of castor oil is reacted with 3 pound moles of triethanolamine, as described in the aforementioned U. S. Patent No. 2,324,489, to De Groote and Keiser, under the heading "Intermediate hydroxylated amine, Example 1."

AMINOALCOHOL ESTER

Example 12

The same procedure is followed as in the preceding example, except that either one pound mole or two pound moles of glycerol are added to the reaction mass consisting of one pound mole of castor oil and three pound moles of triethanolamine.

AMINOALCOHOL ESTER

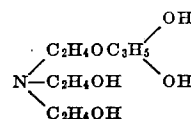
Example 13

The resultants obtained in Examples 1 to 4, preceding, are treated with equal molal ratios of an olefin oxide.

AMINOALCOHOL ESTER

Example 14

One follows the directions of U. S. Patent No. 2,293,494, to De Groote and Keiser, dated August 18, 1942, to produce an amine of the following composition:



Such amine is substituted for triethanolamine in the preceding examples.

AMINOALCOHOL ESTER

Example 15

One pound mole of hydroxyethyl ethylenediamine is reacted with 4 moles of ethylene oxide to give the corresponding tetrahydroxylated derivative. Such compound is employed in place of triethanolamine in the preceding examples.

AMINOALCOHOL ESTER

Example 16

The same procedure is followed as in the preceding example, except that 5 to 8 moles of ethylene oxide are employed instead of 4 moles.

AMINOALCOHOL ESTER

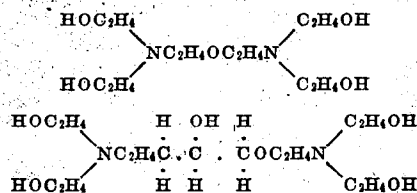
Example 17

The same procedure is employed as in the preceding example, except that diethylenetriamine is substituted for ethylenediamine.

AMINOALCOHOL ESTER

Example 18

An amine of the following composition:



is substituted for ethylenediamine in the preceding examples.

AMINOALCOHOL ESTER

Example 19

In the preceding examples, where more than one high molal acyl radical can be employed, two ricinoleyl radicals or the equivalent are introduced into the polyaminoalcohol.

AMINOALCOHOL ESTER

Example 20

Unsymmetrical diphenyl diethylenetriamine is treated with ethylene oxide and substituted for oxyethylated ethylenediamine in the preceding examples.

AMINOALCOHOL ESTER

Example 21

Symmetrical diacetyl triethylenetetramine is treated with 4 moles of ethylene oxide and substituted for oxyethylated ethylenediamine in the preceding examples.

AMINOALCOHOL ESTER

Example 22

Additional examples are prepared in the manner previously described, except that one employs aminoalcohols obtained by the oxyalkylation of morpholine; 1,3-diamino-2-propanol; 2-amino-1-butanol; 2-amino-2-methyl-1-propanol; 2-amino-2-methyl-1,3-propanediol; 2-amino-2-ethyl-1,3-propanediol; tris-(hydroxymethyl)aminomethane; or piperidine. One may use enough of the olefin oxide, for instance, ethylene oxide, to convert all amino hydrogen atoms into hydroxyethyl radicals, or one may employ a

greater amount so as to introduce ether linkages in addition.

AMINOALCOHOL ESTER

Example 23

The same procedure is followed as in Example 22, preceding, except that one employs the amines described in Examples 9, 10, 11 and 13 of U. S. Patent No. 2,306,329, to De Groote and Keiser, dated December 22, 1942.

AMINOALCOHOL ESTER

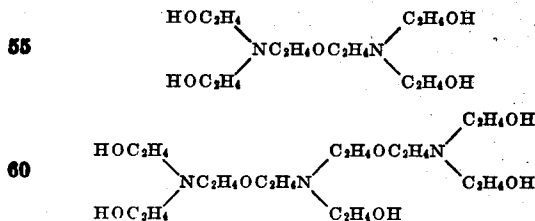
Example 24

Soyabean oil, blown soyabean oil, blown castor oil or blown teaseed oil is substituted for castor oil in the preceding examples.

In the above examples it is obvious that free hydroxyl radicals may be present as part of a hydroxyalkyl radical, or as part of the acyl radical of a fatty acid such as ricinoleic acid.

Some of the acylated aminoalcohols contemplated as ingredients in my reagent are freely dispersible in water in the free state. Presumably, such aqueous systems comprise the reagent in the form of a base, i. e., a substituted ammonium compound. In other instances, the free forms of the reagents are substantially water-insoluble, but the salt forms (e. g., the acetates) are very water-dispersible. I prefer to employ the acylated aminoalcohol in water-dispersible form. In some instances, therefore, it is desirable to neutralize the acylated aminoalcohol to produce a salt which will be water-dispersible. I have found, for example, that the acetate, hydroxyacetate, lactate, gluconate, propionate, caprate, phthalate, fumarate, maleate, benzoate, succinate, oxalate, tartrate, chloride, nitrate, or sulfate, prepared by addition of the suitable acid to the acylated aminoalcohol, usually constitutes a reagent which is somewhat more soluble or dispersible in water than the original acylated aminoalcohol. It is to be understood that references to an acylated aminoalcohol, in these specifications and claims, include the reagent in the form of salts, as well as in the free form and the hydrated form.

As an example of a preferred type of acylated aminoalcohol reagent which is effective as an ingredient in the composition used in my process, the following is submitted: I prepare a mixture of diamino and triamino materials which correspond essentially to either one of the two following type forms:



After determining the average molecular weight of such mixture, I combine the same with the ricinoleyl radical by heating it with castor oil in the proportion of 1 pound mole of castor oil for 3 pound moles of the mixed amines, "pound mole" in the latter case being calculated on the average molecular weight, as determined. Such mixture is heated to approximately 160-260° C. for approximately 6 to 25 hours, until reaction is complete, as indicated by the disappearance of all of the triricinolein present in the castor oil. Castor oil is used instead of some other source of the ricinoleyl radical, e. g., ricinoleic acid, in

the example, because of its ready commercial availability and lower price.

Depending upon the choice of acylated amino body and its molecular weight, the solubility may be expected to range from ready water-solubility in the free state substantially to water-insolubility. As stated above, the salts, and specifically the acetates, generally show improved water-solubility over the simple acylated amino bodies; and I have obtained the best results by using salt forms of the acylated amino bodies which possess appreciable water-solubility.

The other component of my reagent is a water-insoluble organic liquid which is capable of acting as an oil solvent. Many materials lend themselves to this use. One of the commonest is the aromatic fraction of petroleum distillates which is quite generally found to disperse the acylated aminoalcohols, mentioned above. Another is the fraction removed from distillates by application of the Edeleanu liquid sulfur dioxide extraction process, and which comprises aromatic and unsaturated compounds. In some cases, stove oil or similar petroleum distillate is usable. Oil solvents like carbon tetrachloride or carbon disulfide are usable, although their comparatively high cost militates against their use. Amylene dichloride is sometimes a desirable material for the present purpose, as are tetrachloroethane, tetralin, trichloroethylene, benzol and its homologues, cyclohexane, etc. This component of my reagent must be water-insoluble and must be an oil solvent. Otherwise, its selection is not limited, although it should be compatible with the other ingredient of my reagent. Naturally, its cost and availability will influence the selection. I prefer to use aromatic petroleum solvent, as a widely available reagent of low cost and good properties for the present use.

I do not desire to be limited to any specific water-insoluble organic liquid, other than that it shall be capable of acting as an oil solvent. The choice of liquid employed is influenced in part by the bottom-hole temperatures expected to be encountered. The character of the oil being produced may also affect the choice. The choice will frequently depend on relative cost of solvents.

I have found that a mixture of organic liquids having the specific property of dissolving petroleum oil is very effective. One such mixture which I have employed contains benzol, toluol, carbon tetrachloride, tetralin and kerosene.

To prepare my reagent, one simply mixes the two components together in suitable proportions. The optimum proportion of each will vary, depending upon its properties; but in general, the resulting mixture should be homogeneous.

I also require that the finished reagent produce a relatively stable aqueous dispersion in water, as noted above. In cases where the two ingredients form thoroughly homogeneous mixtures, which, however, are not water-dispersible, transformation of the acylated aminoalcohol component into its salt form will sometimes accomplish this purpose. In such cases, I have preferably employed acetic acid to effect this neutralization.

The reagent is preferably employed in the form of an aqueous dispersion, although sometimes favorable results are obtained merely by introducing the undiluted reagent into the well whose productivity is to be improved. In some of such cases, undoubtedly, there is produced, in the well bore or in the formation, an aqueous dispersion of the reagent, from water present in such bore or

such formation. Production of an aqueous dispersion from my reagent and water is accomplished almost spontaneously on mixing the two, in most cases. I greatly prefer to employ the reagent in the form of an aqueous dispersion, because in that manner the two components are prevented from separating from each other before the reagent can become effective to remove the deposit of organic materials.

The present reagent has certain advantages over other reagents which have been suggested for the same purpose. For example, the present reagent has been found to be quite stable in the presence of fairly saline water and in the presence of fairly hard water, over a period ranging from at least several hours to at least several days. Reagents like those of U. S. Patent No. 1,892,205, to De Groote, dated December 27, 1932, which include sulfonated saponifiable oil, react with hard water to produce insoluble precipitates of such sulfonated saponifiable oil; and such constituents of such reagents are "salted out" by saline waters. The present reagent, in contrast, is unaffected by waters of appreciable salinity and/or hardness. In fact, as stated above, I have made it into aqueous dispersions of good stability, using such waters.

It is also noteworthy that my present reagent is useful in the presence of acids. It may therefore be applied satisfactorily to wells that have been acidized by the use of hydrochloric or hydrofluoric or other acids. The reagents of the above-mentioned Patent No. 1,892,205 would react with such acidizing acids to liberate free sulfonated fatty acids, which would either be water-insoluble per se, or else would readily become water-insoluble on hydrolysis and loss of their acid sulfate radical. The present reagent would be quite stable in the presence of such acidizing acids.

I prefer to employ a considerable excess of acylated aminoalcohol over what would be exactly required to effect dispersion of the water-insoluble organic liquid in water. Such excess further prevents any separation of the phases, enhancing the stability of the dispersion to such an extent that it will remain stable for at least several hours. The excess of acylated aminoalcohol also acts to lower the surface tension of the whole reagent, because of which the reagent exhibits a marked penetrating effect. In this way, it is carried into the crevices and irregularities of the deposit, weakening the bond between the deposit of organic materials and the supporting wall.

The proportions of oil solvent and acylated aminoalcohol may be varied within wide limits. For example, I have prepared my reagent in one form in which it contained 4 parts of acylated aminoalcohol to 1 part of oil solvent. I have likewise prepared it in a form in which it contained 4 parts of oil solvent to 1 part of acylated aminoalcohol. Both forms were relatively stable, and did not separate appreciably into their components, on standing for protracted periods of time. I have likewise prepared my reagent in a form in which it contained 9 parts of acylated aminoalcohol and 1 part of oil solvent; and in a form in which it contained 1 part of acylated aminoalcohol and 9 parts of oil solvent. I have thereby determined that use of the acylated aminoalcohol and the oil solvent within the range of proportions, 9:1 and 1:9, is practicable, in producing my reagent. Therefore, I do not wish to be limited to the exact proportions of ingredients recited in the following example, or to those spe-

cific ingredients recited, the example given being merely illustrative.

As a preferred example of reagent, I employ a 20% dispersion of the preferred acylated amino-alcohol mentioned above, in aromatic petroleum solvent, including 2% of concentrated acetic acid in the finished reagent. I prefer to employ this reagent in the form of a dilute aqueous dispersion, of about 5% concentration. Sometimes aqueous dispersions containing as little as 1% of the reagent are fully effective. Sometimes it is desirable to introduce the reagent in the form of a more concentrated aqueous dispersion, as when additional water is expected to be encountered in the well bore or the surrounding formation. The reagent may even be introduced in undiluted form, although, as stated above, I prefer not to use it in this form.

From the foregoing, it will be understood that my invention, broadly stated, consists in subjecting a deposit of organic materials of the kind mentioned to the action of a reagent of the kind described. It should be understood that while my reagent includes, as an indispensable ingredient, a constituent which might constitute a wax solvent, it does not commonly operate completely to dissolve or completely to disperse any waxy organic deposit to which it may be applied in the practice of my invention. Of course, a minor portion of such deposit may be truly dissolved or dispersed by the reagent; but the usual fact is that the deposit is dislodged and brought to a trap or tank that can be more readily cleaned of the organic materials. The same statement applies to other types of organic matter which are found in such deposits. The reagent is usually applied in such small and economical amounts that it could not dissolve completely, or even satisfactorily, the organic deposit to which its action is directed. Its manner of operation is uncertain; but its effects are frequently striking. Well productivity usually increases promptly. Line pressures which have increased with deposition of the organic matter drop to normal within a short time; and sometimes sizeable chunks of the dislodged deposit are observed in open flows from wells or lines, or on screens inserted into such flows for purposes of observation.

My reagent may be applied in a large number of different ways, depending upon the character of the organic material deposit it is desired to remove and on the location of such deposit. If the productivity of a well has declined to undesirably low levels and the clogging deposit is found at the formation, it may be preferable to introduce the reagent, either in undiluted form, or as an aqueous dispersion, into the fluids being produced from the well, and then tie the tubing back into the casing of the well, and circulate the fluids being produced. In this manner chemicalized well fluids are passed over the deposit for a period of from several hours to several days, usually with a striking improvement in well productivity when circulation is stopped and normal production of the well is resumed.

Sometimes the deposit is located at some higher or lower level in the tubing. For example, passage of the well fluids past a point in the well which lies opposite a water sand may produce a deposit at that point, because such a water sand commonly represents a point of cooling. In treating tubing deposits, the circulation method above may be practised. However, in some instances, it is possible to introduce the reagent in undiluted or diluted form into the tubing at

the well head by unscrewing the stuffing box. (Usually the tubing does not stand entirely full of fluid, because of slight leakage past the pump.) If the reagent is introduced as an aqueous dispersion, it will settle relatively slowly down through the oil in the tubing until it reaches the deposit. After introducing the reagent in any desirable manner, it may be allowed to stand in the tubing for any desired period of time before the well is replaced on production. In some instances it is preferred to pump the well intermittently for very short periods of time, so as to pick up the reagent and lift it above the deposit, letting it settle down past the deposit again during the next idle period.

Where the organic deposits in question occur in flow lines, the reagent may be introduced and allowed to "soak" the deposit. Thereafter, normal production may be resumed; and the dislodged deposit flushed from the line by the flow of well fluids. In other instances, gas pressure is put on the soaked line, and the deposit flushed out in that manner. Sometimes, introduction of a dilute aqueous dispersion of the reagent is effected intermittently, and the deposit progressively removed. Or the reagent may be introduced in a continuous fashion, if desired.

In the case of pipe lines, the diameter of the pipe and the length of the line make it necessary to apply the reagent in the most economical fashion possible. In such cases, I have found that very dilute aqueous dispersions are useful, e. g., of 1% concentration or sometimes even less. Soaking of the line, i. e., merely introducing reagent dispersion into it and allowing the line to lie idle for a period of time, is practicable. Sometimes I prefer to prepare a relatively large volume of dilute aqueous dispersion in a tank at some convenient location at one end of the pipe line, and interrupt the pumping of oil only long enough to switch to the solution tank and pump the volume of reagent dispersion into the line. Then the pumping of oil is resumed, and the liquid cylinder of reagent dispersion is thereby moved across the face of the deposit in the line, over the whole length of line. If desired, the direction of pumping may be reversed when such liquid cylinder of reagent dispersion reaches the opposite end of the line; and a second, or even a third pass or more may be made, of reagent dispersion over the deposit in the line.

Where deposits have been allowed to accumulate over a considerable period of time, they may be of such proportions that application of a normal amount of my reagent would produce sloughing of sufficient of the deposit to plug the conduit further downstream, by forming a bridge with undislodged deposit at that point. In such instances, I prefer to proceed more cautiously, introducing successive small portions of reagent and successively dislodging portions of the deposit sufficiently small to pass freely through the limited freeway in the conduit.

Merely introducing my reagent into an area containing a deposit, so the reagent contacts the deposit, is sometimes sufficient to cause the removal of the latter. Sometimes agitation of the reagent at the face of the deposit greatly accelerates removal of the latter. Any suitable agitation means may be employed in such instances.

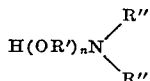
Because there are so many conditions under which such organic deposits may occur, it is difficult to give any preferred procedure for applying my reagent. The foregoing descriptions have covered instances where such deposits were to

be removed from the face of the formation, the well tubing or casing, flow lines, and pipe lines. They may be taken as preferred methods of operating the process for the respective conditions outlined. All of them are exemplary only. The process may be varied as conditions may require. In all cases, the process consists broadly in the application of my reagent to the organic deposits described above.

Application of my reagent upstream in any system, as, for example, into a well, results in an attack on any such organic deposits further downstream. For example, wax or similar deposits, in traps and tanks, are freed and usually flowed out of such vessels in subsequent operation of the system. In the case of tanks, I have found that waxy tank bottoms may sometimes be removed by introducing my reagent into the tank containing such deposits and allowing the whole to soak for any desired period of time. The deposit is thereby made more free and more readily removable. Removal of deposits of organic matter from oil production equipment, such as traps and tanks and the like, is obviously contemplated by my process.

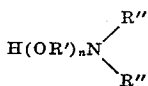
Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A process for removing deposits of organic matter from oil wells, flow lines, and pipe lines, which consists in the application thereto of a reagent comprising a mixture of (a) an acylated derivative of a basic aminoalcohol of the formula:



said derivative being such that there is at least one occurrence of the radical RCO, which is the acyl radical of a monocarboxy detergent-forming acid having at least 8 and not more than 32 carbon atoms; the amino nitrogen atom is basic; R'' is a member of the class consisting of alkanol radicals, aminoalkanol radicals, and polyaminoalkanol radicals, in which polyaminoalkanol radicals the amino nitrogen atoms are united by divalent radicals selected from the class consisting of alkylene radicals, alkyleneoxyalkylene radicals, hydroxyalkylene radicals, and hydroxyalkyleneoxyalkylene radicals, and all remaining amino nitrogen valences are satisfied by hydroxyalkyl radicals, including those in which the carbon atom chain is interrupted at least once by an oxygen atom; R' is an alkylene radical having at least 2 and not more than 10 carbon atoms; and *n* is a small whole number varying from 1 to 10; RCO being a substituent for a hydroxyl hydrogen atom; and the molecular weight of said compound being at least 273 and not over 4,000; said amino compound being selected from the class consisting of the anhydro base, the hydrated base, and salts; and (b) a water-insoluble oil solvent; the proportions of (a) and (b) lying between 1 to 9 and 9 to 1.

2. A process for removing deposits of organic matter from oil wells, flow lines, and pipe lines, which consists in the application thereto of a relatively stable aqueous dispersion of a reagent comprising a mixture of (a) an acylated derivative of a basic aminoalcohol of the formula:



said derivative being such that there is at least one occurrence of the radical RCO, which is the acyl radical of a monocarboxy detergent-forming acid having at least 8 and not more than 32 carbon atoms; the amino nitrogen atom is basic; R'' is a member of the class consisting of alkanol radicals, aminoalkanol radicals, and polyaminoalkanol radicals, in which polyaminoalkanol radicals the amino nitrogen atoms are united by divalent radicals selected from the class consisting of alkylene radicals, alkyleneoxyalkylene radicals, hydroxyalkylene radicals, and hydroxyalkyleneoxyalkylene radicals, and all remaining amino nitrogen valences are satisfied by hydroxyalkyl radicals, including those in which the carbon atom chain is interrupted at least once by an oxygen atom; R' is an alkylene radical having at least 2 and not more than 10 carbon atoms; and *n* is a small whole number varying from 1 to 10; RCO being a substituent for a hydroxyl hydrogen atom; and the molecular weight of said compound being at least 273 and not over 4,000; said amino compound being selected from the class consisting of the anhydro base, the hydrated base, and salts; and (b) a water-insoluble oil solvent; the proportion of (a) and (b) lying between 1 to 9 and 9 to 1.

3. The process of claim 2, wherein the aminoalcohol contains more than one basic amino nitrogen atom.

4. The process of claim 2, wherein the aminoalcohol contains at least 2 and not more than 4 basic amino nitrogen atoms.

5. The process of claim 2, wherein the aminoalcohol contains at least 2 and not more than 4 basic amino nitrogen atoms and at least one free hydroxyl radical.

6. The process of claim 2, wherein the aminoalcohol contains at least 2 and not more than 4 basic amino nitrogen atoms and a plurality of free hydroxyl radicals.

7. The process of claim 2, wherein the aminoalcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical.

8. The process of claim 2, wherein the aminoalcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical in a position other than part of the divalent linking radical which unites RCO with the nearest basic amino nitrogen atom.

9. The process of claim 2, wherein the aminoalcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical in a position other than part of the divalent linking radical which unites RCO with the nearest basic amino nitrogen atom; and wherein RCO is a higher fatty acid acyl radical.

10. The process of claim 2, wherein the aminoalcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical in a position other than part of the divalent linking radical which unites RCO with the nearest basic amino nitrogen atom; and wherein RCO is a higher fatty acid acyl radical having 18 carbon atoms.

11. The process of claim 2, wherein the aminoalcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical in a position other than part of the divalent linking radical which unites RCO with the nearest

basic amino nitrogen atom; and wherein RCO is an unsaturated higher fatty acid acyl radical having 18 carbon atoms.

12. The process of claim 2, wherein the amino-alcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical in a position other than part of the divalent linking radical which unites RCO with the nearest basic amino nitrogen atom; and wherein RCO, occurring only once, is an unsaturated higher fatty acid acyl radical having 18 carbon atoms.

13. The process of claim 2, wherein the amino-alcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical in a position other than part of the divalent linking radical which unites RCO with the nearest basic amino nitrogen atom; wherein RCO, occurring only once, is an unsaturated higher fatty acid acyl radical having 18 carbon atoms; and wherein the value of n is unity.

14. The process of claim 2, wherein the amino-alcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical in a position other than part of the divalent linking radical which unites RCO with the nearest basic amino nitrogen atom; wherein RCO, occurring only once, is an unsaturated higher fatty acid radical having 18 carbon atoms; and wherein the value of n is unity and R' is an alkylene radical having at least 2 and not more than 3 carbon atoms.

15. The process of claim 2, wherein the amino-alcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical in a position other than part of the divalent linking radical which unites RCO with the nearest basic amino nitrogen atom; wherein RCO, occurring only once, is an unsaturated higher fatty acid acyl radical having 18 carbon atoms; wherein the value of n is unity and R' is an alkylene radical having at least 2 and not more than 3 carbon atoms; and wherein the molecular weight is less than 1,000.

16. The process of claim 2, wherein the amino-alcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical in a position other than part of the divalent linking radical which unites RCO with the nearest basic amino nitrogen atom; wherein RCO, occurring only once, is a ricinoleyl radical; wherein the value of n is unity and R' is an alkylene radical having at least 2 and not more than 3 carbon atoms; and wherein the molecular weight is less than 1,000.

17. The process of claim 2, wherein the amino-alcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical in a position other than part of the divalent linking radical which unites RCO with the nearest basic amino nitrogen atom; wherein RCO, occurring only once, is an oleyl radical; wherein the value of n is unity and R' is an alkylene radical having at least 2 and not more than 3 carbon atoms; and wherein the molecular weight is less than 1,000.

18. The process of claim 2, wherein the amino-alcohol contains at least 2 and not more than 4 basic amino nitrogen atoms, a plurality of free hydroxyl radicals, and at least one ether radical in a position other than part of the divalent linking radical which unites RCO with the nearest basic amino nitrogen atom; wherein RCO, occurring only once, is a linoleyl radical; wherein the value of n is unity and R' is an alkylene radical having at least 2 and not more than 3 carbon atoms; and wherein the molecular weight is less than 1,000.

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The following references are of record in the file of this patent:

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Number	Name	Date
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