

United States Patent [19]

Siess, Jr.

[11] 3,782,472

[45] Jan. 1, 1974

[54] **STEAM INJECTION OF OIL FORMATIONS**

[75] Inventor: **Charles P. Siess, Jr., St. Louis, Mo.**

[73] Assignee: **Petrolite Corporation, Wilmington, Del.**

[22] Filed: **Mar. 20, 1967**

[21] Appl. No.: **624,133**

[52] U.S. Cl. **166/303**

[51] Int. Cl. **E21b 43/24**

[58] Field of Search 166/40, 39, 11, 302,
166/303, 272; 252/344

[56] **References Cited**

UNITED STATES PATENTS

2,499,365	3/1950	De Groote et al.....	252/344 X
2,589,200	3/1952	Monson	252/344
2,944,983	7/1960	De Groote et al.....	252/344

2,944,984	7/1960	De Groote et al.....	252/344
2,944,985	7/1960	De Groote et al.....	252/344

OTHER PUBLICATIONS

Rhorback, "New Additive Promises Revised Steam-Stimulation Economics," The Oil and Gas Journal, October 10, 1966, pp. 207-209.

Primary Examiner—Stephen J. Novosad

Attorney—Sidney B. Ring

[57]

ABSTRACT

In the process of stimulating the production of petroleum from underground formations by treating the formation with steam, including steam flooding and the "huff and puff" steam soak techniques, the improvement which is characterized by the use of demulsifiers in conjunction with steam.

12 Claims, No Drawings

STEAM INJECTION OF OIL FORMATIONS

In general, this invention relates to the steam treatment of oil formations.

In one embodiment, this invention relates to the production of oil from underground formations and pertains more particularly to methods for treating oil-bearing formations with steam through an injection well to reduce the viscosity of oil in the formation and drive it to a producing well in communication with the same formation (also referred to as "steam flooding"), said process being characterized by the use of demulsifiers with steam.

In another embodiment, the term "steam treatment" also includes the process of steam and/or hot water injection, soaking and production return from the same well which is commonly referred to as the "huff and puff" or steam soak technique in petroleum production. With this method one well serves both for the injection of steam or hot water and also for the production of the crude petroleum. The stimulation mechanism of steam treating consists primarily of transferring heat to the crude, reducing its viscosity and promoting flow to the well bore.

The producing formations of many oil fields contain low-gravity oil whose viscosity is high enough to prevent easy flow of the oil through the formation and into a well. In some fields of this type, steam flooding of the formation is carried out through one or more injection wells in order to reduce the viscosity of the production fluid and drive the heated oil to adjacent wells in the same field through which it is produced to the surface.

All secondary recovery operations are in essence a balance between cost and the value of production. Since secondary production must compete with primary production, it is essential that the test of the market place must be met. Thus, the costs of secondary recovery must be minimized.

One of the main expenses in steam treating is the cost of creating energy in the form of steam and transferring this energy to the oil by injection into the formation. Steam reduces the viscosity of the oil and/or drives the oil toward the producing well. Oil contains natural emulsifiers, which under proper conditions, tend to form emulsions. When such emulsions are formed, the viscosity of the produced oil is increased by a secondary phenomenon which negates the primary purpose of steam recovery which is to lower the viscosity of the oil.

In addition to increasing viscosity, the formation of emulsions tends to create barriers which prevent the transfer of heat from steam to oil.

I have now discovered that the efficiency of steam treating, including steam flooding and soaking, can be enhanced by injecting demulsifiers in the steam treatment of formations to prevent the formation of emulsions in situ with resultant advantages.

I have further discovered that a class of demulsifiers is most effective in a steam flooding system — namely amino-containing demulsifiers.

A wide variety of surface active compounds have been used for breaking crude-oil emulsions and the number of actual compounds and compositions disclosed for this purpose runs into the thousands. They range from simple soaps, sulfates, and sulfonates to complex products of uncertain structure defined by the methods of preparation. They include anionic, cationic, ampholytic, and non-ionic agents, and mixtures

of the different major classes of surface active agents. They range in properties from low molecular weight compounds to polymeric products. Among these materials are the relatively simple sulfated and sulfonated compounds such as the Teepols, polyalkylbenzenesulfonates, and the sulfonated simple terpenes. Petroleum sulfonates such as the mahogany and green sulfonates have also been used successfully both alone and in conjunction with simple nonionic detergents. Among the most versatile and successful emulsion breakers for crude petroleum are the organic amine salts of mahogany sulfonates and alkylaromaticsulfonates. Both the simple amines and long-chain or complex amines of high surface activity have been used in this connection. The carboxylic acid soaps both alone and in conjunction with auxiliaries have been successful in resolving crude oil emulsions of certain types. Simple nonionic surfactants of the polyethenoxy type, as well as the polymeric ester types of nonionics have been employed as emulsion breakers. A relatively large number of cationic surfactants are effective crude petroleum emulsions breakers. Among these materials are the long-chain fatty imidazolines, the polymerized amino alcohols, amine derivatives of chlorinated paraffin, as well as more complex amine derivatives. Among the ampholytic surfactants, the aspartic esters are stated to be good demulsifying agents, and crude oil emulsions have also been broken by aminated petroleum sulfonates.

The diversity of surfactants employed as demulsifiers is illustrated by the following list of patents describing such demulsifiers which is presented for purposes of illustration and not of limitations. They are by reference incorporated into this application as if part hereof: 2,499,365; 2,695,882; 2,695,885-6-7-8-9-90-91; 2,695,917; 2,695,883-4; 2,695,909; 2,671,762; 2,457,735; 2,492,473; 2,540,437; 2,646,404; 2,653,135; 2,653,137; 2,653,136; 2,543,223; 2,443,273; 2,427,326; 2,562,878; 2,557,081; 2,615,853; 2,422,177; 2,442,073-4-5-6-7; 2,646,405-6; 2,589,198-9; 2,589,200-1; 2,407,895; 2,425,175; 2,472,573-4; 2,435,810; 2,454,382; 2,943,071; 2,950,310; 2,950,313; 1,944,021, etc.

Widely used examples of demulsifiers are the oxalkylated resins of U.S. Pat. No. 2,499,365, the polyesters of the type described in U.S. Pat. No. 2,563,878, and the sulfates and sulfonates of the type described in U.S. Pat. No. 1,944,021. These are by reference incorporated herein as if part hereof.

Although a wide variety of demulsifiers useful in preventing or breaking petroleum emulsions are well known, it is similarly known that a large repertoire of demulsifiers must be available from which to select a specific demulsifier which will work most effectively in each specific area or well.

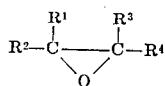
This is particularly true of steam treating since the demulsifier must not only be able to prevent or break the emulsion of a highly viscous oil (in which systems steam flooding is usually employed) but must also be stable enough to withstand the extreme conditions which are imposed on the demulsifier in which degradation of the demulsifier occurs due to thermal degradation, hydrolysis, etc., so as to render it ineffective. Although a wide variety of demulsifiers can be employed in steam treating (such as those specified above) which are capable of withstanding extreme conditions and are effective therein, I have particularly found that a certain class of demulsifiers is most effective

3

tive in steam treating. These may be generally described as amine-derived demulsifiers, of which the preferred types are oxyalkylated amines.

When the compositions of this invention are oxyalkylated they yield products having —OA—_n units attached to the base oxyalkylatable unit.

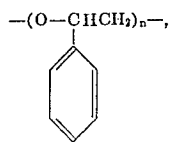
$(\text{OA})_n$ is derived from any suitable α, β alkylene oxide, for example, alkylene oxides of the formula



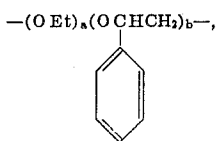
where $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ are hydrogen or a substituted group, such as alkyl, cycloalkyl, aryl, etc., for example ethylene oxide, propylene oxide, butylene oxide, amylene oxide, octylene oxide, styrene oxide, methylstyrene oxide, cyclohexene oxide (where R^1 and R^3 are joined to form a ring), etc.

Equivalents of alkylene oxides can also be employed, for example alkylene carbonates, i.e., ethylene carbonate, propylene carbonate, butylene carbonate, etc. In addition alkylene oxides of the glycidic, methyl glycidic, etc. type and their equivalents can also be employed.

$(\text{OA})_n$ denotes (1) homo units for example —(OEt)—_n , —(OPr)—_n , —(OBu)—_n , —(O Octyl)—_n ,

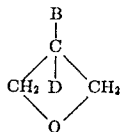


etc., (2) block units, $\text{—(OEt)}_a\text{—(OPr)}_{bb}\text{—}$, $\text{—(OEt)}_2\text{—(OBu)}_b\text{—}$, $\text{—(OPr)}_a\text{—(OEt)}_b\text{—(OPr)}_c\text{—}$, $\text{—(OEt)}_a\text{—(OPr)}_b\text{—(OBu)}_c\text{—}$,



etc. where $a+b+c=n$; (3) hetero units containing random mixtures of more than one oxide $(\text{OEt—OPr})_n$, $(\text{OPr—OBu})_n$, $(\text{OEt—OBu})_n$, wherein the ratio of each oxide to the other is for example 1-99 to 99-1; (4) hetero-homo units for example $(\text{EtO})_a(\text{EtO—PrO})_b$, $(\text{EtO})_a(\text{PrO})_b(\text{EtO—PrO})_c$, $(\text{EtO—PrO})_a(\text{BuO})_b$, etc.

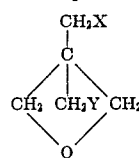
In addition, derivatives of $(\text{OA})_n$ can be derived from an oxetane (e.g., $\alpha\text{—}\gamma$ alkylene oxides) for example those of the formula



where B and D are hydrogen or a substituted radical, for example alkyl, aryl, cycloalkyl, alkenyl, aralkyl, etc.

In addition, B and D can be substituted such as where the oxetane is derived from pentaerythritol and derivatives thereof. Examples of such oxetanes can be found in the American Chemical Society Monogram "The Pentaerythritols" by Berlow et al. (Reinhold 1958), chapter X. Preferred embodiments of such pentaerythritol-derived oxetanes include those of the formula

4



where X and Y are halogen, cyano, hydroxy and alk-oxy.

Since the products of this invention may be block polymers containing blocks or segments of alkylene oxide units which are added sequentially, oxyalkylation is in essence a stepwise procedure. For the sake of simplicity of presentation, the invention will be illustrated by employing as a base oxyalkylatable compound $\text{R}'\text{H}$ and by employing only ethylene, propylene, and butylene oxides with the understanding that other hydrophobe oxides can be used in place of propylene and butylene oxides such as amylene oxide, octylene oxide, styrene oxide, oxetanes, etc. These are shown in the following table.

TABLE I
STEP I

1. $\text{R}'(\text{EtO})_n\text{H}$
 2. $\text{R}'(\text{PrO})_n\text{H}$
 3. $\text{R}'(\text{BuO})_n\text{H}$
 4. $\text{R}'(\text{MO})_n\text{H}$
 5. $\text{R}'(\text{PrO—BuO})_n\text{H}$
- MO = mixed EtO—PrO

STEP II

Reaction of the Step I product with one of the five oxides or mixtures employed in Step I, which oxide had not been reacted in the immediately preceding step. For example:

6. $\text{R}'(\text{EtO})_n(\text{PrO})_m$
7. $\text{R}'(\text{EtO})_n(\text{BuO})_m\text{H}$
8. $\text{R}'(\text{EtO})_n(\text{MO})_m\text{H}$
9. $\text{R}'(\text{EtO})_n(\text{PrO—BuO})_m\text{H}$
10. $\text{R}'(\text{PrO})_n(\text{EtO})_m$
11. $\text{R}'(\text{PrO})_n(\text{BuO})_m$
12. $\text{R}'(\text{PrO})_n(\text{MO})_m$
13. $\text{R}'(\text{PrO})_n(\text{PrO—BuO})_m\text{H}$
14. $\text{R}'(\text{BuO})_n(\text{EtO})_m\text{H}$
15. $\text{R}'(\text{BuO})_n(\text{PrO})_m\text{H}$
16. $\text{R}'(\text{BuO})_n(\text{MO})_m\text{H}$
17. $\text{R}'(\text{BuO})_n(\text{PrO—BuO})_m\text{H}$
18. $\text{R}'(\text{MO})_n(\text{EtO})_m\text{H}$
19. $\text{R}'(\text{MO})_n(\text{PrO})_m\text{H}$
20. $\text{R}'(\text{MO})_n(\text{BuO})_m\text{H}$
21. $\text{R}'(\text{MO})_n(\text{PrO—BuO})_m\text{H}$
22. $\text{R}'(\text{PrO—BuO})_n(\text{EtO})_m\text{H}$
23. $\text{R}'(\text{PrO—BuO})_n(\text{PrO})_m\text{H}$
24. $\text{R}'(\text{PrO—BuO})_n(\text{BuO})_m\text{H}$
25. $\text{R}'(\text{PrO—BuO})_n(\text{MO})_m\text{H}$

STEP III

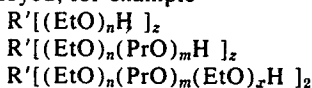
The products of Step II can be reacted with one of the five epoxides or mixture of oxides which had not been reacted in the immediately preceding step, i.e., either EtO, PrO, BuO, MO, or PrO—BuO, with the

above exclusion as to the epoxide just reacted. This will be illustrated as follows:

26. $R'(\text{EtO})_n(\text{PrO})_m(\text{EtO})_x\text{H}$
27. $R'(\text{EtO})_n(\text{PrO})_m(\text{BuO})_x\text{H}$
28. $R'(\text{EtO})_n(\text{PrO})_m(\text{MO})_x\text{H}$
29. $R'(\text{EtO})_n(\text{PrO})_m(\text{PrO}-\text{BuO})_x\text{H}$
30. $R'(\text{EtO})_n(\text{BuO})_m(\text{EtO})_x\text{H}$
31. $R'(\text{EtO})_n(\text{BuO})_m(\text{PrO})_x\text{H}$
32. $R'(\text{EtO})_n(\text{BuO})_m(\text{MO})_x\text{H}$
33. $R'(\text{EtO})_n(\text{BuO})_m(\text{PrO}-\text{BuO})_x\text{H}$
34. $R'(\text{EtO})_n(\text{MO})_m(\text{EtO})_x\text{H}$
35. $R'(\text{EtO})_n(\text{MO})_m(\text{PrO})_x\text{H}$
36. $R'(\text{EtO})_n(\text{MO})_m(\text{BuO})_x\text{H}$
37. $R'(\text{EtO})_n(\text{MO})_m(\text{PrO}-\text{BuO})_x\text{H}$
38. $R'(\text{EtO})_n(\text{PrO}-\text{BuO})_m(\text{EtO})_x\text{H}$
39. $R'(\text{EtO})_n(\text{PrO}-\text{BuO})_m(\text{PrO})_x\text{H}$
40. $R'(\text{EtO})_n(\text{PrO}-\text{BuO})_m(\text{BuO})_x\text{H}$
41. $R'(\text{EtO})_n(\text{PrO}-\text{BuO})_m(\text{MO})_x\text{H}$
42. $R'(\text{PrO})_n(\text{EtO})_m(\text{PrO})_x\text{H}$
43. $R'(\text{PrO})_n(\text{EtO})_m(\text{BuO})_x\text{H}$
44. $R'(\text{PrO})_n(\text{EtO})_m(\text{MO})_x\text{H}$
45. $R'(\text{PrO})_n(\text{EtO})_m(\text{PrO}-\text{BuO})_x\text{H}$
46. $R'(\text{PrO})_n(\text{BuO})_m(\text{EtO})_x\text{H}$
47. $R'(\text{PrO})_n(\text{BuO})_m(\text{PrO})_x\text{H}$ etc.

Step IV involves the oxyalkylation of the products of Step III. Step V involves the oxyalkylation of Step IV. Further oxyalkylations involve Steps VI-X of higher.

Although the above represent compounds having only one oxyalkylatable group, compounds having a plurality of oxyalkylatable groups can also be employed, for example



etc.

where z represents the number of oxyalkylatable groups, for example 2, 3, 4, etc.

The following are non-limiting examples of oxyalkylatable amines that may be oxyalkylated to yield suitable demulsifiers:

- n-Butyl amine — Furfurylamine
- Dibutyl amine — Dodecylamine
- 2-ethylhexyl amine — Monoethanolamine
- Di(2-ethylhexyl) amine — Diethanolamine
- Monoisopropanolamine — N-methyl ethanolamine
- Diisopropanolamine — N-ethyl ethanolamine
- Methyl isopropanolamine — N-Amylamine
- Butyl isopropanolamine — Di-n-amylamine
- Hexylamine — Sec-amylamine
- Diethylamine — N-ethylbutylamine
- Heptylamine — 2-amino-4-methylpentane
- Octylamine — 4-amino-o2-butanol
- Dioctylamine — 5-isopropylamino-1-pentanol
- Decylamine — N-butylaniline

Similarly, secondary high molecular weight aliphatic amines known as Armeen 2C and Armeen 2HY can be used.

Also, high molecular weight aliphatic amines known as Armeen 10, Armeen 16D, Armeen HTD, Armeen 18D, and Armeen CD can be used.

Suitable amines having an aromatic ring include alpha-methylbenzylamine and alpha-methylbenzylmonoethanolamine.

Other amines include:

- 2-amino-2-methyl-1-propanol
- 2-amino-2-methyl-1,3-propanediol
- 2-amino-2-ethyl-1,3-propanediol

3-amino-2-methyl-1-propanol

2-amino-1-butanol

3-amino-2,2-dimethyl-1-propanol

2-amino-2,3-dimethyl-1-propanol

5 2,2-diethyl-2-amino ethanol

2,2-dimethyl-2-amino ethanol

3-amino-1,2-butanediol

4-amino-1,2-butanediol

2-amino-1,3-butanediol

10 4-amino-1,3-butanediol

2-amino-1,4-butanediol

3-amino-1,4-butanediol

1-amino-2,3-butanediol

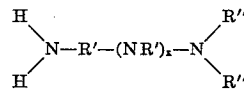
Tris-(hydroxy methyl) amino methane

15 Amines having ring structures of course include aniline, diphenylamine, cyclohexylamine, dicyclohexylamine, and various comparable amines with alkyl substituents in the ring.

A monoamine compound can be cyclic or non-cyclic.

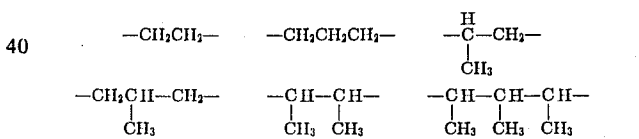
20 Those which are cyclic may be heterocyclic as in the case of morpholine and its derivatives or oxazolines which may be regarded as derivatives of N-acyl-2-amino-ethanols. This would apply where instead of being a derivative of monoethanolamine the oxazoline was a derivative of a low molal acid or a high molal acid and 2-amino-2-methyl-1,3-propanediol.

One may use polyamines corresponding to the formula

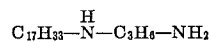


$X=0$, or greater (for example 1-10 or greater)

35 in which R'' is hydrogen, alkyl, cycloalkyl, aryl, or aralkyl and R' is a divalent radical such as

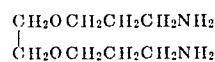


45 Examples of suitable amines include: Ethylenediamine Diethylenetriamine Triethylenetetramine Tetraethylenepentamine Propylenediamine Dipropylenetriamine Tripropylenetetramine Butylenediamine Aminoethylpropylenediamine Aminoethylbutylenediamine



55 Other polyamines in which the nitrogen atoms are separated by a carbon atom chain having 4 or more carbon atoms include the following: Tetramethylenediamine, pentamethylenediamine, and especially hexamethylenediamine.

60 Other suitable amines are exemplified by ethylene-bisoxypopylamine,



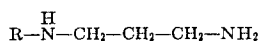
65 and derivatives obtained by treating ethylenebisoxypopylamine with 1, 2, 3, or 4 moles of ethylene oxide, propylene oxide, butylene oxide, or the like.

Other compounds including those having cyclic structures include piperazine, and the corresponding derivatives obtained by treating piperazines with alkylene oxides. The same applies to substituted piperazine such as the 2,5-dimethylpiperazine.

As to mono-substituted dialkanol piperazine see U.S. Pat No. 2,421,707, dated June 3, 1947, to Malkemus.

Another example of polyamine which may be employed as a reactant is the kind described as "Duomeens."

Duomeen is a trademark designation for certain diamines. Duomeens have the following general formula:

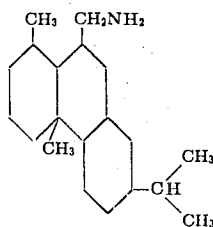


R is an alkyl group derived from a fatty acid or from the mixed fatty acids as obtained from certain oils. The specific Duomeen and the source of the radical R are as follows:

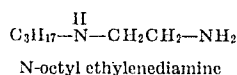
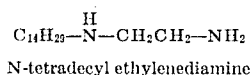
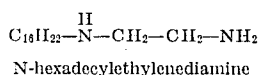
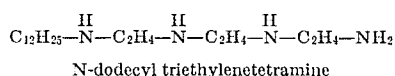
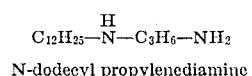
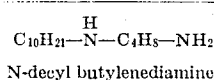
Duomeen 12—R=lauric

Duomeen C—R=Coconut oil fatty acid

Similarly, a comparable diamine, presumably obtained from Rosin Amine D and acrylonitrile, can be prepared. The structure of Rosin Amine D is as follows:

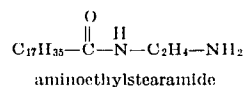
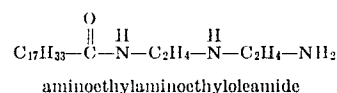
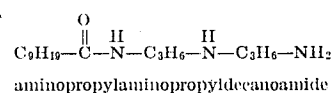
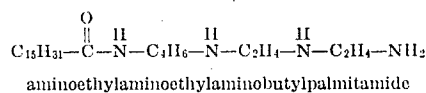
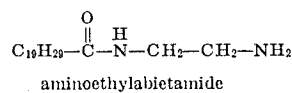
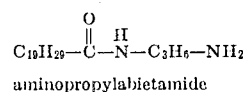
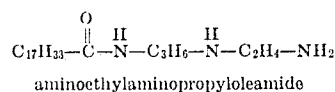


Polyamines from monoamines and cyclic imines, such as ethylene imine.

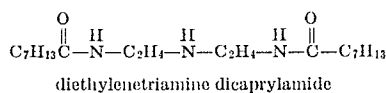
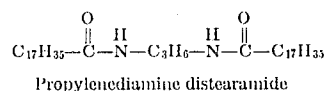


It is to be noted that all the above examples show high molal groups, i.e., eight carbon atoms or more. The same derivatives in which methyl, ethyl, propyl, butyl, amyl, acryl groups, or the like, appear instead of octyl, decyl, etc., are equally satisfactory.

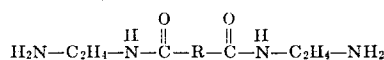
Suitable amides derived from amines of the kind described previously are suitable as reactants for the present purpose. Such amides are shown as follows:



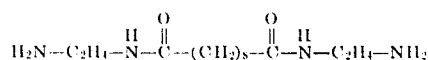
Diamides may be obtained from polyamines and 2 moles of acid.



Polyamides are derived from polycarboxy acids as well as monocarboxy acids. Thus it is possible to get polyamides by using acids containing more than one carboxyl group, as illustrated in the following examples:

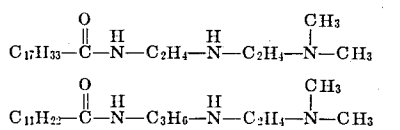


R(COOH)₂ = Emery dimeric acid available commercially and said to be dilinoleic acid.



Amino amides can be obtained from polyamides in which there is a terminal tertiary amine radical having a basic nitrogen atom. Another procedure involves the

production of an amino amide from a polyamine in which the terminal radicals are either primary or secondary followed by alkylation of the amide so as to convert the residual terminal radical into a basic tertiary amine radical. Another procedure is to use a secondary amine, such as dibutylamine or dihexylamine, and react stepwise with ethylene imine or propylene imine. The polyamine so obtained contains a basic tertiary amino radical. The acylation of such a polyamine results in an amino amide which will form complexes comparable to those obtained from a basic tertiary amine. Examples of such amino amides are as follows:



It is to be noted that all the above examples show high molal groups, i.e., seven carbon atoms or more. The same derivatives in which methyl, ethyl, propyl, amyl, butyl, hexyl groups, or the like, appear instead of groups having 9, 17, 19 carbon atoms or the like, are equally satisfactory.

This process is practiced by employing a small proportion of demulsifier which is sufficient to effect the desired results of enhancing the efficiency of steam treating such as from about 5 to 1000 ppm, or more, for example about 10 to 750 ppm, such as about 20 to 500 ppm, but preferably about 40 to 100 ppm. Larger or smaller amounts may be employed by the most effective amounts consistent with cost should determine the specific demulsifier and the amount employed.

The following examples are presented for purposes of illustration and not of limitation.

EXAMPLES

A constant stream of steam was injected into a sample of crude for a specified period of time (30 minutes). The rate steam condensate separated from the crude and the moisture content of the oil, as determined by centrifugation, was measured. The following demulsifiers when tested gave improved results.

TABLE II
Amino-Containing Demulsifiers

Ex.	Demulsifier Type	Composition Molar Ratio of Alkylene Oxides Based on 1 Mole of Starting Material
1	Oxyalkylated tris (hydroxymethyl) amino methane (Tris)	Tris + 5 EtO + 30 PrO
2	do. (HOCH ₂) ₃ CNH ₂	Tris + 75 PrO + 35 EtO
3	do.	Tris + 2 EtO + 10 PrO
4	do.	Tris + 4 EtO + 8 BuO
5	Oxyalkylated Polyalkylene Polyamines	Triethylene tetramine + 10 EtO + 50 PrO
6	do.	Triethylene tetramine + 20 PrO + 5 EtO
7	do.	Diethylenetriamine + 14 EtO + 30 PrO
8	do.	Tetraethylenepentamine + 7 EtO + 35 PrO
9	Oxyalkylated Polymerized Alkanolamine	Heat Polymerized Triethanolamine +2 EtO + 10 PrO
10	do.	Acylatd (oleic) heat polymerized triethanol amine + 5 EtO + 15 PrO
11	do.	Heat Polymerized

12	Oxyalkylated	Triethanolamine + 25 PrO + 5 EtO P-tert-butylphenol-formaldehyde resin (approximately 5-6 phenolic units) +1 diethanolamine + 1.5 EtO
13	amine-modified Phenol-aldehyde Resins do.	p-tert-amylphenol-formaldehyde resin (approx. 5-6 phenolic units) + 1 morpholine + 2 EtO + 10 PrO
14	do.	p-tert-butylphenol-formaldehyde resin (approx. 5-6phenolic units) + 1-diethylamine + 1 EtO + 15 PrO

In addition to the amino-containing demulsifiers, other demulsifier types can also be employed, of which the following are non-limiting examples:

TABLE III
Non-Amino-Containing Demulsifiers

Ex.	Emulsifier Type	Composition - Molar Ratio of Alkylene Oxides Based on one Mole of Starting Material
1	Oxyalkylated Phenol- Aldehyde Resins	P-tert-butyl phenol-formaldehyde resin (approx. 5-6 phenolic units) 6 EtO +5 EtO
2	do.	p-tert-butylphenol-formaldehyde resins (approx. 5-6 phenolic units) + 3 EtO
3	do.	Same Resin + 8 EtO + 6 PrO
4	do.	p-phenyl-phenol-formaldehyde resin (approx. 5-6 units) + 3 EtO + 3 PrO
5	Oxyalkylated Phenolic Compounds	p-tert-butylphenol + 4 EtO
6	do.	P-tert-butylphenol +10 EtO +8 PrO
7	Oxyalkylated alcohols	Lauryl Alcohol +8 EtO
8	do.	Octanol + 8 EtO + 4 PrO
9	do.	Octadecanol + 20 PrO + 15 EtO
10	Sulfates of Oxyalkylate Resins	The sulfated product of Ex. 1
11	Sulfates of Oxyalkylated alcohols	The sulfated product of Ex. 7
12	Sulfates of Oxyalkylated Phenols	The sulfated product of Ex. 5
13	Polyesters of Alkyleneether Glycols	Polypropyleneether glycol 2000 MW + diglycolic acid (1M/1.1M)
14	do.	Polypropyleneether glycol 2000 MW + phthalic acid (1M/1.1M)

The stability of the demulsifiers were tested by the following procedures:

A 2% water solution of a demulsifier was placed in a small oxygen-free bomb and heated to 700°F. for up to 30 days. Deterioration was measured by infra-red analysis after various periods -- 1, 7 and 30 days. This test is unusually severe since steam temperatures are usually only about 500°F which are soon reduced to the formation temperature which is only about 400°-450°F.

In general, amino-containing demulsifiers were comparatively stable. In fact, oxyalkylated tris-(hydroxymethyl) amino-methane exhibited no deterioration even after 30 days. Because of their unusual stability, oxyalkylated amino compositions are preferred, including oxyalkylated hydroxylamines, and most preferably hydroxyl-alkyl amino-alkanes, as exemplified by tris(hydroxyalkyl) amino-alkanes. A most preferred embodiment is tris-(hydroxymethyl) amino-alkanes wherein the alkane group is methane, ethane, etc.

The following patents describe specific demulsifiers which are particularly stable according to this test.

11

1. U.S. Pat. Nos. 2,944,983, and 2,944,984 which relate to oxyalkylated tris(hydroxymethyl) amino-alkanes such as methanes, ethanes, etc.

2. U.S. Pat. No. 2,944,985 which relates to oxyalkylated polyamines such as triethylenetetramine.

3. U.S. Pat. Nos. 2,247,573, 2,468,181, 2,589,199, 2,589,200 and 2,589,201 which relate to polymerized alkanol amine and derivatives thereof.

4. U.S. Pat. Nos. 2,771,454, 2,854,414, 2,854,415, 2,854,416, etc., which relate to oxyalkylated amine-modified phenol-aldehyde resins.

Where a demulsifier is employed which is not amino-containing, such as a non-amino containing oxyalkylates, then this demulsifier may be employed in conjunction with the amine, for example, those described above. In certain instances it may be advantageous to blend these demulsifiers with other surfactants, such as other demulsifiers.

FIELD TESTS

EXAMPLE A

A steam flood on a California crude was run employing about 100 ppm in the steam of oxyalkylated tris(hydroxymethyl) amino-methane (1M Tris + 75 MP₂O + 35 MetO). The producing wells in the steam flood area produced an average of an additional 13 more barrels than was produced without demulsifier over the period of the test.

EXAMPLE B

Similar treatment with "huff and Puff" Steam soaking (10 days steam soak) of these wells also gave improved results, with a 50 to 100 percent improvement in production over the period of the test (3-4 months production cycle).

EXAMPLE C

A modification of the above "Huff and Puff" procedure was also run. The steam flood was enhanced by injecting the demulsifier dissolved in oil into the formation through the producing well even though no demulsifier was injected in the steam treatment. Production was doubled as compared to steam treatment without demulsifier.

EXAMPLE D

Another modification was to use the demulsifier in the steam injection as well as the demulsifier injected into the producing well just before production is started, with enhanced results.

EXAMPLE E

This example is presented for purposes of illustrating a steam soak "Huff and Puff" operation. The steam injection as water in BPD is between 950 and 1000 bbls. The injection period varied between 10 and 14 days. The wells are then allowed to soak for 5 to 7 days or until the surface pressure on the closed-in well reaches a constant value. Production accumulation figures on the well from a formation called "light oil zone" producing 13.4° API oil as follows:

DATA PRIOR TO DEMULSIFIER USE

Cycle	Length of Steaming Cycle days	Length of Production Cycle months	Bbls. of Oil produced	Injection Pressure pounds	Injection Rate GPM
1	10	4	4300	750	34

12

2	10	2 1/2	2160	725	34
3	15	5	3760	425	166
4	14	9	—	650	31

After demulsifier was employed on this well at a rate of one quart 50% of active material per 100 B/D of water injected as steam, the following data was obtained.

The demulsifier employed was a mixture of the products of (1) of Table II, Ex. 2 and (2) Table III, Ex. 13. 75 parts by weight of (1) and 25 parts of (2).

DATA AFTER DEMULSIFIER USE

Cycle	Length of Steaming Cycle days	Length of Production Cycle months	Bbls. of Oil Produced	Injection Pressure pounds	Injection Rate GPM
1	10	3 1/2	3490	675	35
2	15	3 1/2	4320	700	30
3	12	7	10,080	525	31
4	13	3	—	425	31

Thus, the use of demulsifier in steam techniques enhanced production.

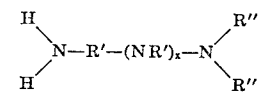
As is quite evident, other demulsifiers are known or will be constantly developed which could be useful in this invention. It is, therefore, impossible to attempt to describe the invention in its broader aspects in terms of specific names of demulsifiers used as it would be too voluminous and unnecessary since one skilled in the art could by following the procedures described herein select the proper agent. This invention lies in the use of demulsifiers and the physical form thereof used in carrying out this invention and their individual composition is important only in the sense that their properties can effect this function. To precisely define each specific chemical composition useful as a demulsifier in light of the present disclosure would merely call for knowledge within the skill of the art in a manner analogous to a mechanical engineer who prescribes, in the construction of a machine, the proper materials, and the proper dimensions thereof. From the description in this specification and with the knowledge of a chemist, one will know or deduce with confidence the demulsifier suitable for this invention. In analogy to the case of a machine wherein the use of certain materials of construction or dimensions of parts would lead to no practical useful result, various materials will be rejected as inapplicable where others would be operative. One can obviously assume that no one will wish to make a useless composition or will be misled because it is possible to misapply the teachings of the present disclosure in order to do so. Thus, any suitable demulsifiers that can perform the function stated herein can be employed.

The above paragraph applies with particular emphasis on amino-containing demulsifiers.

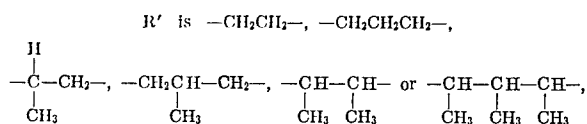
Having thus described my invention what I claim as new and desire to obtain by Letters Patent is

1. A process of injecting steam into a subsurface oil-producing formation to stimulate oil production which is characterized by the use of a demulsifier in conjunction with steam, said demulsifier being selected from the group consisting of

1. oxyalkylated secondary amines,
2. oxyalkylated hydroxyalkyl amino-alkanes,
3. oxyalkylated polyamines of the formula

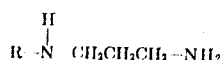


in which R' is hydrogen, alkyl, cycloalkyl, aryl, or aralkyl and



and x is 1-10,

4. oxyalkylated polyamines of the formula



in which R is an alkyl group derived from a fatty acid or from mixed fatty acids,

5. oxyalkylated ethylene-bisoxypyrrolamine,
6. oxyalkylated N-dodecyl triethylenetetramine,
7. oxyalkylated N-decyl butylenediamine,
8. amino amides,
9. oxyalkylated polymerized alkanolamines, and (10) 25
oxyalkylated amine-modified phenolaldehyde resins.
2. The process of claim 1 where the demulsifier is an oxyalkylated hydroxyalkyl aminoalkane.
3. The process of claim 2 where the demulsifier is an oxyalkylated tris (hydroxyalkyl) aminoalkane.
4. The process of claim 3 where the demulsifier is an oxyalkylated tris aminomethane.

5. The process of claim 4 where the tris (hydroxymethyl) aminomethane is oxyalkylated with ethylene oxide, propylene oxide, or a mixture of ethylene oxide and propylene oxide.

5 6. The process of claim 5 where the tris (hydroxymethyl) aminomethane is oxyalkylated with a mixture of ethylene oxide and propylene oxide.

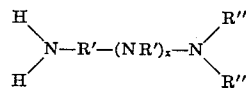
7. The process of claim 6 where the mole ratio of tris (hydroxymethyl) aminomethane to ethylene oxide to propylene oxide is 1:5:30.

8. The process of claim 6 where the mole ratio of tris (hydroxymethyl) aminomethane to ethylene oxide to propylene oxide is 1:35:75.

9. The process of claim 6 where the mole ratio of tris (hydroxymethyl) aminomethane to ethylene oxide to propylene oxide is 1:2:10.

10. The process of claim 4 where the tris (hydroxymethyl) aminomethane is oxyalkylated with a mixture of ethylene oxide and butylene oxide, the mole ratio of the tris (hydroxymethyl) aminomethane to ethylene oxide to butylene oxide being 1:4:8.

11. The process of claim 5 where the demulsifier is an oxyalkylated polyamine of the formula



12. The process of claim 1 where the demulsifier is an oxyalkylated polymerized alkanolamine.

* * * * *

35

40

45

50

55

60

65