

June 17, 1958

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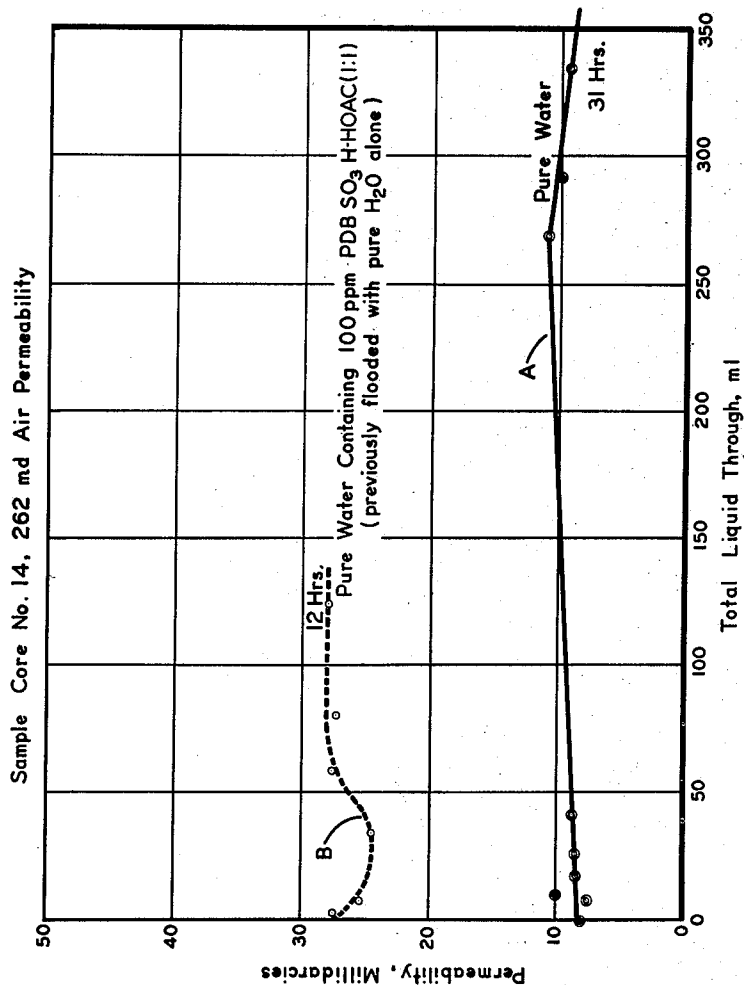
2,839,466

FLOODING COMPOSITION

Filed March 30, 1955

4 Sheets-Sheet 1

FIG. 1



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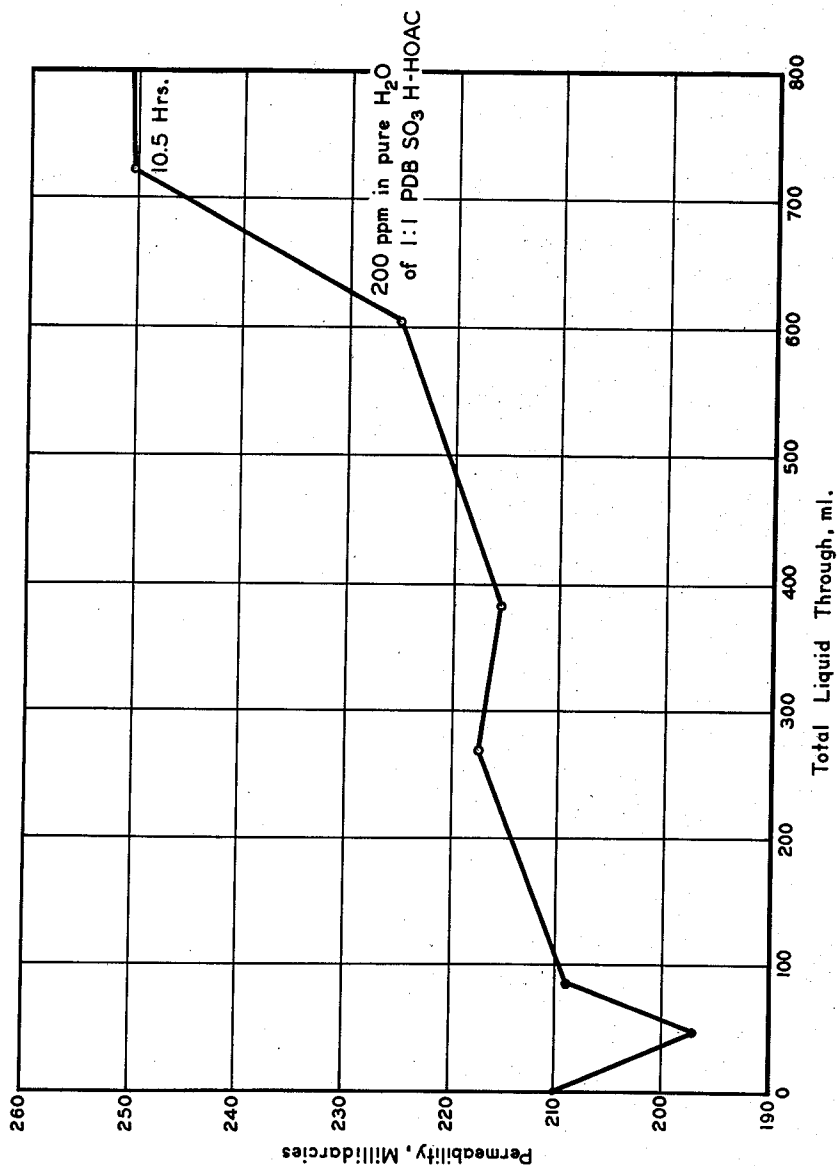
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FIG. 2



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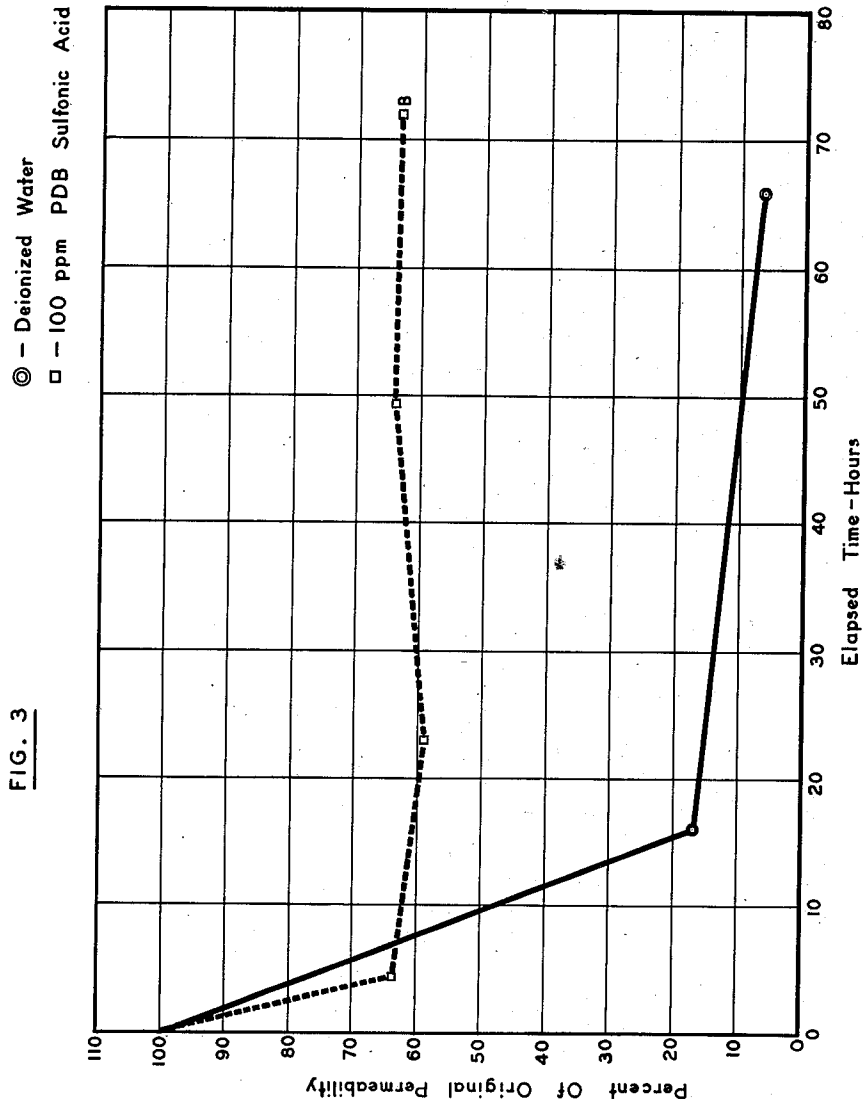
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FLOODING COMPOSITION

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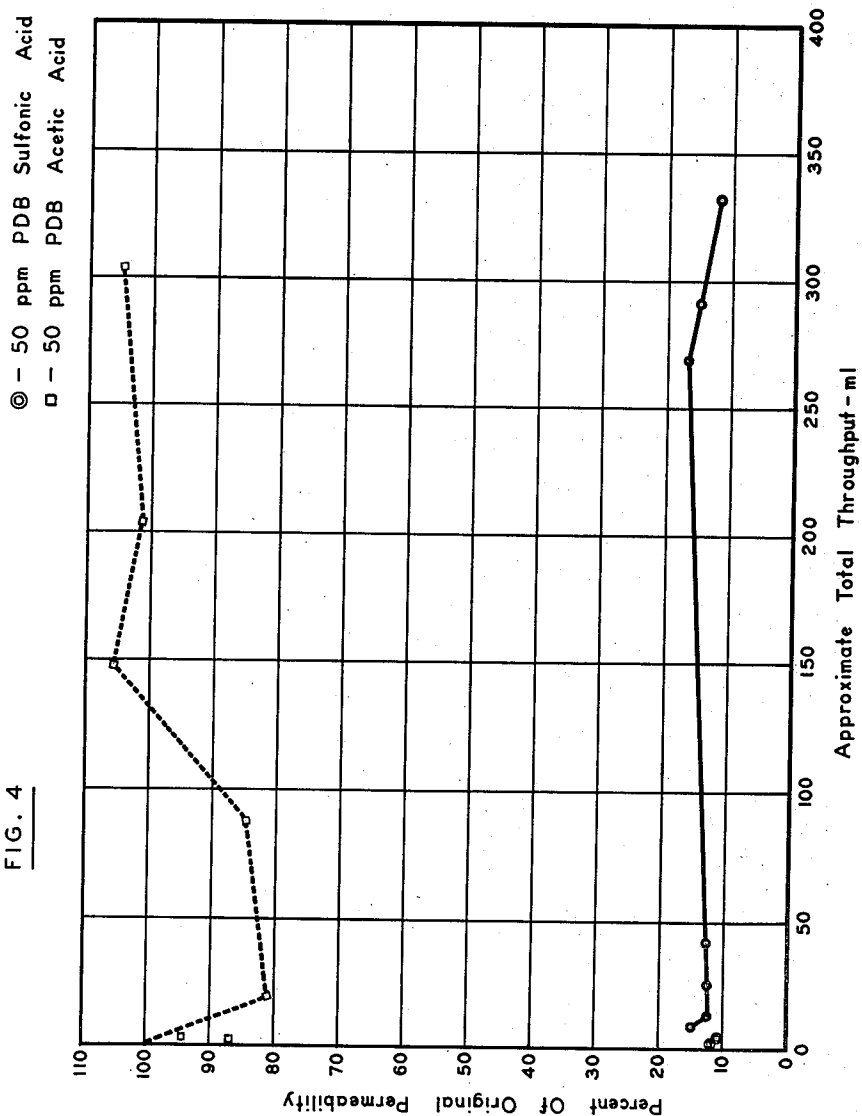
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FIG. 4



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FLOODING COMPOSITION

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Application March 30, 1955, Serial No. 498,040

5 Claims. (Cl. 252—8.55)

This invention relates to the recovery of oil from subterranean oil sands and oil-bearing strata by secondary flooding operations after depletion of primary production. More particularly this invention relates to an improved flood water composition for flooding clay-containing petroleum formations.

It is well known that oil-producing formations containing clays, such as the bentonites, undergo a marked decrease in injection rates when flooded with fresh water; i. e., water containing up to about 10,000 parts per million total solids. Because of the presence of such clays in the oil-bearing formation, it becomes impossible to maintain adequate injection rates of fresh water for the production of oil therefrom.

We have found that efficient injection rates can be maintained by the use of flood water containing an alkyl aromatic sulfonic acid having a molecular weight of at least about 400. A more preferred alkyl aromatic sulfonic acid is one that has a molecular weight of not less than about 440. Since such sulfonic acids have only a very limited solubility in water, improved results are obtained when a water soluble carboxylic acid is used in conjunction with the sulfonic acid. Suitable carboxylic acids are those which do not form an insoluble salt with the alkaline earth metals, such as calcium, barium, magnesium, etc. Preferred carboxylic acids are the aliphatic acids containing not more than 4 carbon atoms as follows: formic, acetic, propionic, and butyric acids. Other suitable carboxylic acids include lactic, maleic, gluconic, and salicylic acids. In no case should the carboxylic acid contain more than about 7 carbon atoms, otherwise, it will be rather insoluble in water. As to the amount of the sulfonic acid used, that may vary from about 25 to 200 parts per million of the fresh water. A more preferred range is 50 to 100 parts per million. Generally the amount of the carboxylic acid used is within the same range as the sulfonic acid. Obviously greater quantities of the sulfonic acid and also the carboxylic acid could be used; however, such excessive use imparts no beneficial effect and does increase the cost.

A preferred sulfonic acid is that produced by sulfonating the detergent alkylate sometimes called polydodecylbenzene which consists of monoalkyl benzenes and dialkyl benzenes in the approximate ratio of 2:3. Its typical physical properties are as follows:

Specific gravity at 38° C.	0.8649
Average molecular weight	365
Percent sulfonatable	88
A. S. T. M.—D-158 Engler:	
I. B. P.	°F. 647
5	°F. 682
50	°F. 715
90	°F. 760
95	°F. 775
F. B. P.	°F. 779
Refractive index at 23° C.	1.4900

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Viscosity at:

—10° C.	centipoises	2800
20	do	280
40	do	78
80	do	18
Aniline point	°C.	69
Pour point	°F.	—25

As pointed out above sulfonic acids having a molecular weight greater than 400 are suitable. Such sulfonic acids in addition to the polydodecylbenzene sulfonic acid described above include the mahogany sulfonic acids produced by sulfuric acid treatment of lube stock petroleum fractions and the sulfonic acids of the naphthenic and aromatic furfural extracts of petroleum distillate oils. Our experiments have demonstrated that sulfonic acids having a molecular weight of less than 400 are less than 50 percent as effective as the sulfonic acids of the preferred range.

Broadly stated, our invention comprises an improved water flooding composition for pressure depleted petroleum reservoirs consisting of water containing not more than about 10,000 parts per million of dissolved solids to which has been added from about 25 to about 200 parts per million of alkyl aromatic sulfonic acid and a water-soluble carboxylic acid in approximately the same amount, namely, 25 to 200 parts per million.

In order to disclose more clearly the nature of the present invention and the advantages thereof, reference will hereinafter be made to certain specific embodiments which illustrate the flexibility of the hereinafter described process. It should be clearly understood, however, that this is done solely by way of example and not to be construed as a limitation upon the spirit and scope of the appended claims.

Core samples measuring $\frac{3}{4}$ of an inch in diameter and from one to two inches in length were tested under flooding conditions at about a pressure drop of about 7 inches of mercury through the core. A relatively simple apparatus provided means for mounting formation core samples so that continuous flooding or passing of liquids through the core could be maintained under constant conditions. The permeability in millidarcies was determined from the liquid flow in milliliters per second in conjunction with the viscosity of the liquid, length of core in centimeters, cross-sectional area of the core, and pressure drop through the core by means of the following equation:

$$K = \frac{1000Q\mu}{\Delta P} L/A$$

wherein

K=permeability in millidarcies

Q=liquid flow, ml./sec.

55 μ =viscosity of liquid, centipoises

L=length of core, cm.

A=cross-sectional area of core, cm.² ΔP =pressure drop through core in atmospheres

Example 1

A non-saline water was flowed through a clay-containing core sample having an air permeability of 262 md. for a period of 30 hours. The permeability of the core throughout the flow period remained at approximately 10 md., which is shown in Figure 1 as curve A wherein permeability versus liquid throughput is plotted.

Example 2

The water-flooded core sample of Example 1 was then subjected to flow flooding with a composition consisting of the same non-saline water containing 50 p. m. each of polydodecylbenzene sulfonic acid and acetic acid. In

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this case the permeability of the core to the liquid rose to about 28 md., dropped off for a short period, and then rose again to a constant value of about 28 md. The results are represented by curve B of Figure 1 wherein permeability versus liquid throughput is plotted.

Example 3

A core sample having an air permeability of 420 md. was flow-flooded with a non-saline water composition containing 100 p. p. m. each of polydodecylbenzene sulfonic acid and acetic acid. The initial permeability was 210 md., dropped off momentarily to recover, and rose steadily thereafter to an apparent steady rate of about 250 md. as is illustrated in Figure 2.

Example 4

In this example a core sample was flooded with a non-saline water plus 100 p. p. m. of polydodecylbenzene sulfonic acid and with water alone. When the core was flooded with water alone, the permeability soon dropped to less than 10 percent of the original permeability as is shown in Figure 3. In that case where the saline water plus the polydodecylbenzene sulfonic acid was used, the permeability dropped to about 60 percent of the original permeability and remained at that value. These data are also plotted in Figure 3 as curve B.

Example 5

A core sample very similar to that used in Example 4 was flooded with a composition consisting of the non-saline water containing 50 p. p. m. sulfonic acid and 50 p. p. m. of acetic acid. For comparison purposes the core was also flooded with non-saline water alone. Where a non-saline water was used alone, permeability dropped to about 10 percent of the original permeability while the core water-flooded with the water containing the sulfonic acid and the acetic acid showed a permeability of about 100 percent of the original permeability. These results are graphically illustrated in Figure 4.

Similar experiments were made in accordance with Example 4 with the exception that the following acids were substituted for the acetic acid: formic, propionic, butyric, maleic, gluconic acids. The results using these acids were very similar to that obtained using acetic acid.

What is considered new and inventive is defined in the hereunto appended claims, it being understood, of course, that equivalents known to those skilled in the art are to be construed as within the scope and purview of the claims.

Accordingly, applicants claim:

1. A flooding process for recovering oil from a subterranean oil-bearing formation which consists in flooding said formation with an aqueous composition comprising water as the major component having incorporated therein 25 to 200 p. p. m. of an alkaryl sulfonic acid which has a molecular weight of not less than 400 and 25 to 200 p. p. m. of a water soluble carboxylic acid containing from 1 to 7 carbon atoms, characterized further in that the alkaline earth metal salt of said carboxylic acid is water soluble.

2. A flooding process for recovering oil from a subterranean oil-bearing formation which consists in flooding said formation with an aqueous composition comprising water as the major component having incorporated

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therein 50 to 100 p. p. m. of an alkaryl sulfonic acid which has a molecular weight of not less than 400 and 50 to 100 p. p. m. of a water soluble carboxylic acid containing from 1 to 7 carbon atoms, characterized further in that the alkaline earth metal salt of said carboxylic acid is water soluble.

3. A flooding process for recovering oil from a subterranean oil-bearing formation which consists in flooding said formation with an aqueous composition comprising water as the major component having incorporated therein 25 to 200 p. p. m. of an alkaryl sulfonic acid produced by sulfonating a mixture of monoalkylbenzene and dialkylbenzenes in the approximate ratio of 2:3, characterized in that the mixture of said alkylbenzenes have the following physical properties:

Specific gravity at 38° C.	0.8649
Average molecular weight	365
Percent sulfonatable	88
A. S. T. M.—D-158 Engler:	
I. B. P.	°F. 647
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Refractive index at 23° C.	1.4900
Viscosity at:	
—10° C.	centipoises 2800
20	do 280
40	do 78
80	do 18
Aniline point	°C. 69
Pour point	°F. -25

and 25 to 200 p. p. m. of a water soluble carboxylic acid containing from 1 to 7 carbon atoms, characterized further in that the alkaline earth metal salt of said carboxylic acid is water soluble.

4. A flooding process for recovering oil from a subterranean oil-bearing formation which consists in flooding said formation with an aqueous composition comprising water as the major component having incorporated therein 25 to 200 p. p. m. of an alkaryl sulfonic acid which has a molecular weight of not less than 400 and 25 to 200 p. p. m. of an aliphatic acid containing not more than 4 carbon atoms characterized further in that the alkaline earth metal salts of said acid are water soluble.

5. A flooding process for recovering oil from a subterranean oil-bearing formation which consists in flooding said formation with an aqueous composition comprising water as the major component having incorporated therein 25 to 200 p. p. m. of an alkaryl sulfonic acid which has a molecular weight of not less than 400 and 25 to 200 p. p. m. of acetic acid.

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