

United States Patent

[11] 3,612,178

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- [21] Appl. No. **867,500**
- [22] Filed **Oct. 20, 1969**
- [45] Patented **Oct. 12, 1971**

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Attorney—Robert W. B. Dickerson

[54] **METHOD OF RECOVERING OIL USING FLOW
STIMULATING SOLUTION**
3 Claims, 7 Drawing Figs.

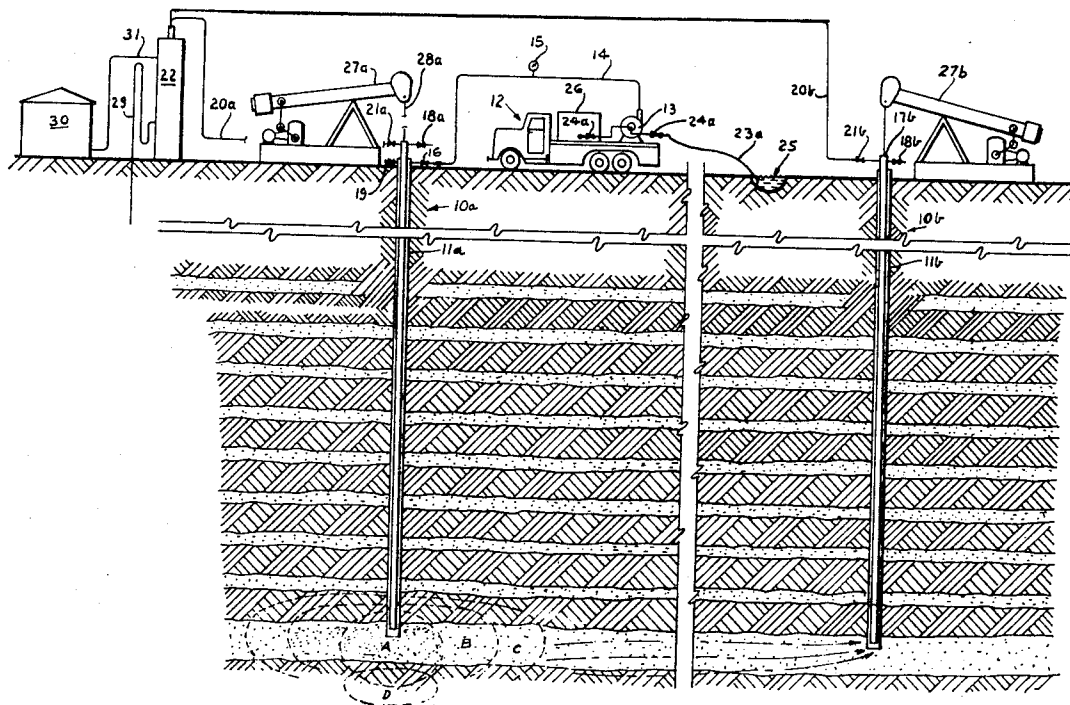
- [52] U.S. Cl. **166/267,**
166/275, 166/305 R, 208/181
- [51] Int. Cl. **E21b 43/22**
- [50] Field of Search 166/267,
273-275, 305 R; 252/8.55 D

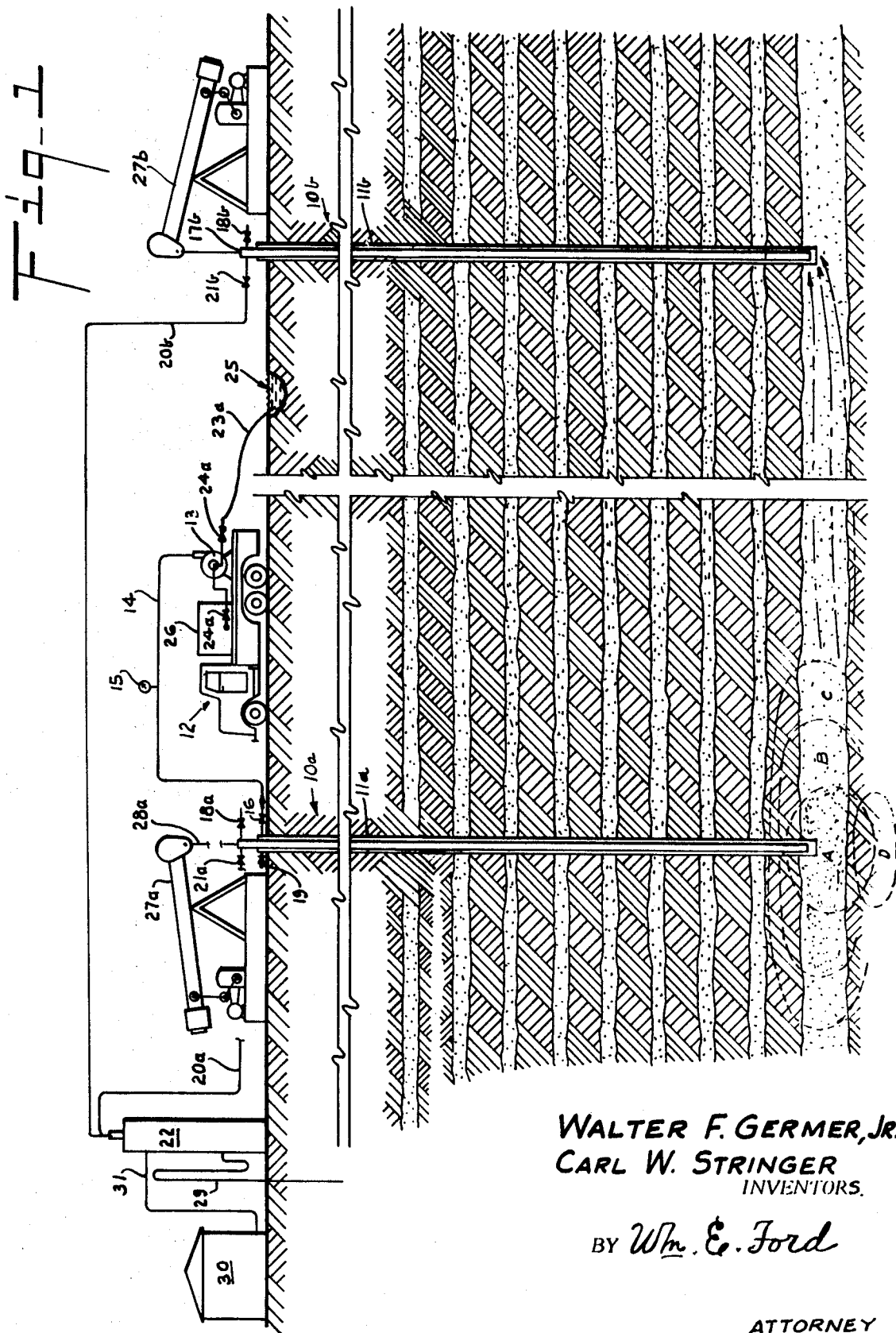
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ABSTRACT: The disclosure of a flow-stimulating liquid solution and methods of use is based primarily on the combination of a linear alkyl sulfonate as a detergent and penetrant, serving as a special carrier for a lauric amide emulsifier to draw oil into emulsion and for a phosphate, as sodium phosphate, to draw water into emulsion. A preservative may be added, as a formaldehyde, as to inhibit deterioration due to bacteria, or other factors. Also when in the course of usage, it may be desirable to quicken the setting action, as by clarifying a floated emulsion, a base, as sodium hydroxide, may be added as a stimulant to break the emulsion. The solution may be used in recovering oil from an oil-bearing formation, or in reclaiming contaminated or used oil.





TEST No.	C.C. OIL	TYPE OF OIL	C.C. OF H ₂ O	SOLUTION C.C. OF NaOH	% NaOH (wt) IN H ₂ O	C.C. OF LIME	% IND LIME BY VOLUME	TIME TO END EMULSION C.C. (SAND) (WELL)	COLOR GRADE LOWER LAYER	No. LAYERS AFTER SEP.	H ₂ O TYPE
1	5	CRUDE	20	1	10	1%		3	4	2	SALT
2	10	CRUDE	20	1	20	1%		3	5	2	SALT
3	30	CRUDE	40	1	20	1%		4	7	2	SALT
4	10	REFINED	50	1	20	1%		1	3	2	TAP
5	20	REFINED	50	5	20	1%		2	4	2	TAP
6	20	REFINED	50	10	20	4%		2	3	2	TAP
7	10	CR. CASE	50	10	20	4%		5	4	3	SALT
8	30	CR. CASE	50	7	20	2%		10	8	3	TAP
9	35	CR. CASE	50	20	20	10%		10	9	3	TAP
10	10	CRUDE	50	7	10	1%		5	8	3	SALT
11	20	CRUDE	50	9			2%	30	100	3	SALT
12	26	CRUDE	500	10	30	1%	2%	30	100	3	SALT

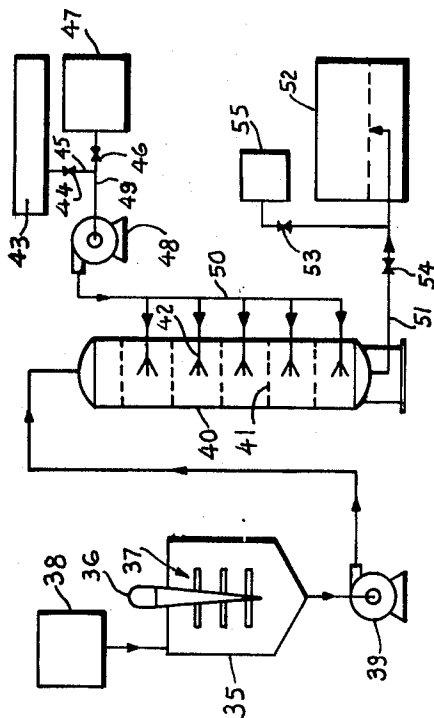


Fig. 4

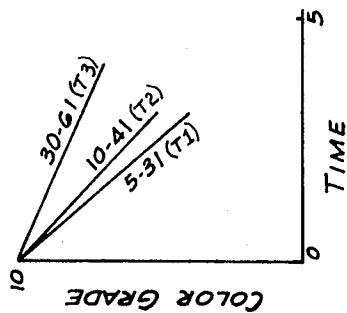


Fig. 3A

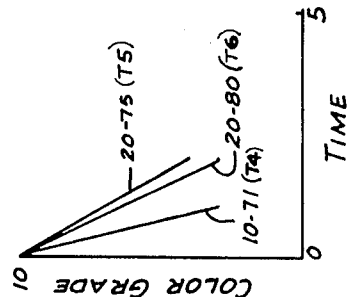


Fig. 3B

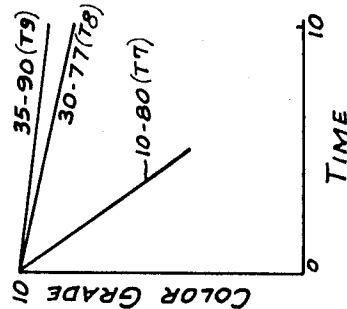


Fig. 3C

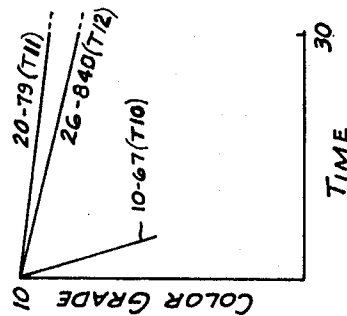


Fig. 3D

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METHOD OF RECOVERING OIL USING FLOW STIMULATING SOLUTION

For a long number of years large volumes of oil have thickened down in the earth and have grown too viscous to flow easily, with the consequence that the pumps are unable to obtain recovery of much of this viscous oil which has not been produced by conventional means. Annually millions of dollars are spent on various treatments as "acidizing," "fracturing," and in other steps all designed to stimulate the flow of petroleum products in wells which are initially or which have become of low productivity.

Also, much waste could be reclaimed or recovered in the form of petroleum products or byproducts if the heavy, viscous or substantially solidified discard of petroleum products could be reclaimed or recovered as purified oil, the discard of crankcase oil being only one of many examples.

Additionally, the circulating fluid or drilling mud circulated down the drill stem and up the annulus therearound in the rotary method of drilling wells, as oil and gas wells, could be improved by the introduction therein of an additive of some viscosity, and lubricating action, advantageous to circulate the drilling mud at least in part in a state of emulsion (as a less costly oil base mud).

Another specific use arises in the disposition of water produced with oil, as from a multiplicity of wells, where it may be required that the water thus produced is pumped back into a common disposal well designated for this purpose. In such case a special flow-stimulating solution is needed and can well serve as an agent introduced into the disposal well to bring into emulsion any oil or other matter introduced into the disposal well with the water to be disposed of therein.

The solution may thus serve to bring into a state of emulsion and cut away any film or other matter previously carried into the disposal well with the disposed water, to clog or otherwise settle an oil film on the formation surrounding the waters of disposal, thus to limit the expansion of the disposal area, as more disposal water may demand; in such cases the generally intended bounds of the disposal area may be said to be circumscribed or "packed in," whereby the solution of this invention may break the dam or circumscription of this predetermined area by bringing the film or other damming material into emulsion to open up paths and areas through which the volume of the disposal area may be expanded.

Also, in cases where the oil in the casing annulus of any respective oil well may stand above the highest casing perforation, or where the oil at the bottom of the well bore may fall below the bottom of the well tubing; in either case the respective wells may require "flooding" so that water introduced down a separate, nearby well bore may pass through the formation, or paths therein, to carry oil to respective well bore bottom areas. Thus, in the first case, the oil again stands with bottom of oil layer in casing annulus below the highest casing perforation, or in the second case the oil level may rise to at least the level of the bottom of the well tubing; and in both cases oil production may be resumed. The introduction of the solution of this invention into the "flooding" water employed to restore the oil to the respective production levels will result in emulsification of oil to flow more readily and quantitatively, as carried by the "flooding" water, to the respective well bore bottom area involved.

Further, it is known that oil producers consider it a good omen when a well "pulls vacuum" or sucks downwardly tending to draw air or fluid down into the well bore. This indicates that whatever liquid, as water, that may have been resisted by pressures down in the well, by hydrostatic and/or by the stopped up outlets through the formation, no longer encounters such resistance, and that the water and/or other liquids at the bottom of the well bore have broken through into, or have otherwise passed into low-resistance areas indicative of the opening up of new areas, as of potential oil production.

The chemicals hereinabove described in association may be asserted to have been arrived at to substantiate the various objects set forth for the invention, as follows:

It is a primary object of the invention to provide a flow-stimulating solution, which in its usages, is comprised of at least a linear alkyl sulfonate, as a detergent and penetrant, a lauric amide emulsifier to draw oil into emulsion, and a phosphate or sulfate as sodium phosphate as an emulsifier to draw water into emulsion.

It is another object of the invention to provide a flow-stimulating solution of this class, and method of its use, whereby it is specifically adapted to penetrate into oil well perforations, fissures, crevices and formation strata with rapidity to draw matter encountered into emulsion, thereby opening up flow of material, as oil products, from beyond the locality of emulsification.

It is another and further object of the invention to provide a flow-stimulating solution and methods of its use, in which the solution may be introduced with "flooding" water through a bore adjacent to an oil well, to emulsify oil in the area around and below the bottom of such oil well, where the lower oil level in the casing annulus stands above the highest perforation in the lower portion of the casing, or where the upper oil level stands below the bottom of the well tubing. In either case, the stimulation of oil flow by the solution can "prime" the aforesaid oil well to resume oil production, respectively, by "bubbling" oil upwardly to lower the casing annulus lower oil level below the highest perforation, or by raising the oil level in the bottom of the well to at least the level of the bottom of the well tubing.

It is an additional object of the invention to provide a flow-stimulating solution of this class, and method of its use, whereby it is specifically adapted to draw viscous and solidifying petroleum products discard into emulsion, whereby the emulsion, when clarified, results in a recoverable liquid layer over a carrying liquid layer, as water.

It is a further object of the invention to provide a flow-stimulating solution of this class, and method of its use, whereby it is adapted to be introduced into a water disposal well, as for a multiplicity of wells which have produced water with the oil, the solution bringing deposits upon the disposal well formation into emulsion, thereby unclogging the formation to permit enlargement of the water disposal area.

It is yet another object of the invention to provide a flow-stimulating solution and methods of its use, in which the relatively low cost of the solution, (approximately less than \$5.00 per gallon), suggests the employment of the solution in a vast number of operations in extension of, or replacing expensive "acidizing" or "fracturing" operations, with the flow stimulation attained being suggested as greatly in excess of the flow stimulation currently obtained by conventional service processes.

As the emulsified oil is produced or recovered with the water carrying it, often some period of time may elapse before the produced or recovered volume separates and settles into liquid layers, oil, lighter and on top, and the other heavier liquid products, as the resultants from the solution, being in a lower layer. It was found that sodium hydroxide provided a most applicable settling or separation agent to enhance the clearing of the products in the settling or separation tank. This enhancement could be appreciable, contributing greatly in reducing the overall time from onset of first treatment steps toward production or recovery, and the time when the layer of oil could be drawn off from the separator as a merchantable product.

Premises considered, it thus should become another and most important object of the invention to provide a settling or separation agent, and methods of its use, whereby the settling or separation of emulsified oil and the means carrying it can be affected in the shortest time possible, sodium hydroxide and other related products being suggested as adapted for this purpose.

The accompanying chart, graph, diagrams and drawings, are illustrative of specific examples, tests, and apparatus that may be employed in a specific usage; such drawings being described, as follows:

FIG. 1 is an elevational view, part is section and partially diagrammatic, illustrative of a specific example of the employment of the invention to increase the rate of oil flow in an oil well, and in a plurality of oil wells.

FIG. 2 is a chart of various tests made upon various petroleum products which could be the subject matter for reclamation and recovery, times required for layer separation from emulsification, agency, and relative clarity of the layer below the oil being listed.

FIGS. 3A, 3B, 3C and 3D are graphs of tests performed in support of the efficacy of the solution in bridging various reclamation crude, crankcase and refined oil into emulsion and into a separate, different density layer above a supporting liquid layer.

FIG. 4 is a view, partially elevational, and partially diagrammatic, and is illustrative of apparatus employable with the solution, as in the recovery or reclamation of petroleum products of any type from soiled, used or contaminated status.

In the process of arriving at the aforesaid solution, it was found that the requirement of a predominating translator, penetrant and breakthrough agent could best be supplied by a linear alkyl sulfonate, primarily, $C_3H_7SO_3$ being the least expensive.

Lauric super amide, $C_{24}H_{44}NO_2$, was selected as the best and relatively inexpensive type of oil attracting emulsifier to draw the oil encountered into an emulsion. Also, still slightly less expensive and almost equally effective lauric amide, $C_{12}H_{25}$ emulsion.

Then a phosphate, as Na_2PO_4 , was selected as the best emulsifier to draw water, the ever present and main carrier for the solution, into an emulsion. Also, it was considered that a sulfate, as Na_2SO_4 , might serve for the purpose of drawing water with almost equal efficacy.

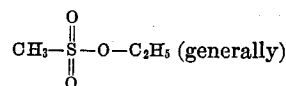
Having arrived at the hereinabove described components for an oil flow stimulant or reclamer, as well as a purification agent and circulating fluid or drilling mud additive, it was then found best, although not compulsory, to add a preservative as formaldehyde, C_2H_4O , or as paraformaldehyde, C_4H_6O . Also other preservatives.

With the components of the reclamer and purification agent selected with full consideration of the objects to be accomplished, the proportions of each ingredient were then studiously selected. Thus, considering that a large part of the work to be accomplished would consist of pioneer or initial contact work of coming in contact with the paraffin and sticky materials interposed in front of the oil to be recovered, or interposed upon or over a petroleum product to be purified and reclaimed, it was decided that a linear alkyl sulfonate should comprise the largest portion of the solution or say approximately 82 percent by volume. Then as lauric amide has less potency in action comparable to hygroscopic action to bring oil into emulsion, than a phosphate, as Na_2SO_4 would have in bringing water into emulsion, it was decided that some considerable more lauric amide would be required as an emulsification agent than the more concentrated acting phosphate. Thus it was decided that the remaining percentages of the solution might be divided, 15 percent lauric amide, by volume, 3 percent Na_2PO_4 .

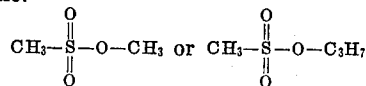
In problems involving the emulsification of lighter oils, the proportions of the linear alkyl sulfonate could be decreased to say 75 percent, since not too much detergent action would be required brought into emulsion in accordance with the aforesaid increase in availability of oil. Thus in such a case, the solution could be comprised of say 75 percent linear alkyl sulfonate, 20 percent lauric amide, and 5 percent of the phosphate.

In cases involving the emulsification of heavy, more viscous oils, as from low-producing wells, or from industrial usages under reclamation, the proportions of the linear alkyl sulfonate could be increased above the 82 percent initial or average selection, as to say 88 percent. Correspondingly, the emulsifiers could be decreased to say 10 percent lauric amide and 2 percent of the phosphate.

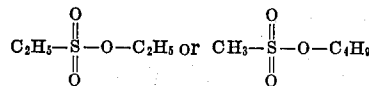
The linear alkyl sulfonate detergent, obviously nonionic, having excellent properties of penetration, has structural formulas, as follows:



But some:

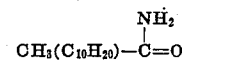


Also:

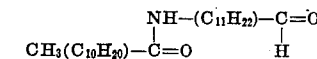


The first form $C_3H_7SO_3$ being available and relatively inexpensive, was recommended for first usage.

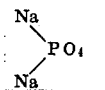
Lauric amides include lauric superamides as a variation under the generic designation, and the superamide form was available, having some increased potential for producing emulsification of oil, and being almost as readily available and only slightly more expensive than the simpler lauric amide form. The lauric amide form has structural formula:



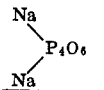
whereas, the lauric superamide has structural formula:



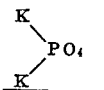
The sodium phosphate, an emulsifier with great propensity for drawing water into emulsion, was also available at relatively low cost, having structural formula:



Also sodium tetrphosphate:

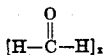
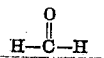


which has an indefinite structural representation. While potassium phosphate, also available but at slightly greater expense, and probably more expensive, had structural formula:

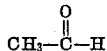


Other phosphates could also serve, but would cost more.

Any number of preservatives could have been used, and formaldehyde, a well known, commercially available product, was employed, with structural formula:



Paraformaldehyde also was available and suggested. Also acetaldehyde:



As a first specific example, a well in Caldwell County, Tex., was obtained for test, the well being designated POM 2, which had been drilled to a depth of 2,500 feet approximately 3 years previously, the casing having been perforated at eight successively spaced-apart levels of strata. The well had not flowed oil very long under its own pressure, and had been "on pump" for approximately two years, with production having decreased down to approximately 2½ barrels per day. The well pump at the top of the well had been disconnected from the pumping string in the well tubing and the well casing had been closed at the top, as indicated diagrammatically in FIG. 1.

The suction conduit from the Halliburton truck pump was first placed to draw water from the San Marcos river, pH 7, whereas the water in the well under test was pH 6.6. One thousand barrels of the river water was then introduced into the test well, as measured and recorded with the conventional Halliburton truck carried apparatus for this purpose. The gauge on the truck indicated that the first 500 barrels of this water was introduced in about 15 minutes at approximately 1,200 p.s.i., after which the pressure indicated a drop down to about 800 p.s.i. which it maintained during a second 25 minute period while the second 500 barrels of water was introduced into the well. The purpose of first adding this 1,000 barrels of water was to insure that the pH factor of that water, into which the solution comprising the invention was later to be added, would be at a satisfactory neutral or near neutral pH factor approximating pH7. The solution in amount of approximately 165 gallons, (three drums), had been placed in the chemical reservoir or tank on the Halliburton truck, the solution employed being in proportions of approximately 82 percent linear alkyl sulfonate, 15 percent lauric superamide, 3 and percent sodium phosphate.

With the first 1,000 barrels of water in the well, the water suction line valve was closed and the suction connection valve to the chemical tank was opened, and the contents of the chemical tank (three drums) was pumped into the well casing almost instantaneously. Then the chemical tank suction connection valve was promptly closed, and the water suction line valve opened, and the pumping of water into the well was resumed, 2,000 additional barrels being pumped. The gauge on the Halliburton truck continued to hold a reading of approximately 800 p.s.i. for about 5 minutes after water pumping had been resumed, and then the gauge almost instantaneously increased indication to approximately 900 p.s.i. This indicated that the solution had reached the bottom of the well, or therebelow.

The phenomenon of the increase in the gauge pressure indication would best be supported by physical and geophysical explanation, as follows: The 500 barrels of water first pumped to insure a substantially neutral pH factor had first occupied a formation area A, FIG. 1, below, and around the bottom of the cased well, the area having to be broken into under some pressure, so that the pressure gauge reading stood around 1,200 p.s.i. As the second 500 barrels of water outwardly into an ever increasing peripheral area B with consequence that the indicated gauge pressure reading dropped to approximately 800 p.s.i. Then when the three barrels of solution at least in part reached the bottom of the well, as urged in part by the 2,000 barrels of water pumped behind it, had in some substantial part penetrated through the areas A and B and had begun emulsification of oil in an Area C, peripheral around the area B.

As the penetrating solution had come into contact with oil peripheral to the water that was acting in manner to shove or displace the oil further back from the periphery of the outermost ring of water, emulsification of the peripheral oil encountered had set in, with the consequent increase of the peripheral contact ring viscosity, while the oil/water outwardly of this peripheral ring of oil under emulsification has

opposed greater resistance to being pushed further outwardly. For this reason the opposition to the last 2,000 barrels of water introduced into the well had been opposed by greater resistance in being pushed outwardly behind the equivalent of a slowly expanding emulsifying seal, causing the indicated pressure to rise from 800 p.s.i. to 900 p.s.i., as aforesaid.

After the last 2,000 barrels of water had been pumped the valve in the discharge line to casing was closed, thus isolating the casing space from the Halliburton pump on the truck. The pressure gauges in the discharge line, downstream from the discharge line valve, now recorded well pressure, which over a period of approximately 1 hour, dropped to indicate a pressure of about 650 p.s.i. This drop could be attributed to the solution having been expended as an emulsification agent that had been causing the equivalent of a seal of emulsifying oil, and also due to the fact that a pressure relief resulted due to the expansion of the outer ring defining an ever increasing area C through which the total of approximately 3,000 barrels of water by this time had been distributed.

Thus, the introduction of the viscous penetrating solution slowed the flow to existing channels; and, consequently pressure to "back up" and to force the penetrating solution into clogged or previously nonexistent or nonavailable channels. This "back up" of pressure is in essence hydraulic pressure which is exerted, by definition, in equal force in all directions from the fluid; and, this increase in pressure is due to the physical properties of the solution. Then physical properties, together with the chemically active properties of the penetrating solution create a pronounced and swift opening of clogged and sealed chambers.

At the time the well pressure had dropped to 650 p.s.i., the Halliburton pump truck had been disconnected, and the gauge and discharge line or conduit had been taken away with the truck. After 2½ hours had passed, the valve at the casing head was opened slightly and instead of any fluid being ejected, it was felt that the aforesaid POM 2 well was "pulling vacuum." This indication could be accounted for by the fact that the water bearing the speedily penetrating and fast travelling solution, had spread from the area C to even greater areas, with probability of having reached voids, space reservoirs, crevices, cavities, fissures, and the like, so that the water and products carried thereby encountered decreasing resistance while the outward travel of the water drew vacuum, in degree, in its wake. The valve was then closed after discovering this vacuum and after about 16 hours this "pulling" of vacuum still continued, indicating that the total introduced 3,000 barrels of water was still, at least in part, moving outwardly. Then, the casing head valve was opened to permit air from the atmosphere to be pulled into the well bore. The well pump was then connected again to the pumping apparatus in the tubing string, the producing of the well by pumping was resumed, and the water began to be raised in about 2 hours. In this case the casing head valve to which the Halliburton pump discharge conduit had been connected was closed, and the valve above the casing in the line to the oil-water separator had been opened, the producing first of water being indicated visually by observation through a transparent section of the casing-to-separator conduit, or by sampling through the sample valve at the head of the casing opposite the outlet to separator.

Samples of the water were now taken which first measured approximately 35° C., (95° F.), with successively higher temperatures being indicated by successively taken samples. This indicated to a resident geologist (reservoir engineer) that the water came from an area D, obviously penetrated by the water bearing the solution as its pioneer or pathfinding penetrant. Samples also indicated that petroleum gas was being produced with the water; the gas, upon being lit, would flash and burn above the water sample. By history, this aforesaid well POM 2 had never before produced warm or hot water, and had never before produced gas. On the other hand, by history, the said well had produced water that had been quite cold, with heavy deposits of paraffin in its lines having caused difficulties, including low and losing oil production.

Although the introduction of 3,000 barrels of water into the well POM 2 had the natural tendency of displacing oil from areas beneath this cased well bore, samples indicated that the test well showed oil traces within one week after being put back on pump. Now, after the well has been back on pump for about three weeks, (as of Oct. 15, 1969), samples indicate that the aforesaid test well is approaching at least the 2½ barrels of oil per day that it was producing before tests, with projection that its production may level off at say about eight barrels per day, or over three times its production at outset of treatment. Support for this projection is based upon the estimates of geologists, reservoir engineers, and drillers familiar with the locality known as the Luling field, and is further based upon the performance of a well POM 1, which is located 1,000 feet from the test well POM 2, as will be set forth immediately hereinbelow.

A well, designated POM 1, was located approximately 1,000 feet from the above-described well POM 2. This well also had been drilled to a depth of 2,500 feet, and the casing had been perforated opposite the same eight levels or strata as well POM 2. The production of this well, also approximately 3 years old, had fallen in production and had been producing at a very low rate on pump for at least 2 years, flow being as low at 1½ barrels per day. Approximately 3 hours after the last 2,000 barrels had been pumped into well POM 2, as hereinabove described, samples taken from POM 1, taken by infrared spectrophotometer, indicated that traces of the three barrels of flow-stimulating solution included by this invention, had arrived at this adjacent (1,000 ft. apart) well. Also, it was noticed that well POM 1 had increased in production to approximately 9½ barrels per day within 24 hours after termination of the tests on POM 2. Within about six days after the aforesaid POM 2 tests, the POM 1 well production had increased to approximately 15 barrels per day.

Noticeably in FIG. 1, the production from well POM 1 passes from its casing head valve to the separator, as well as does the production from well POM 2. Thus it was obvious during the period of days right after the tests, before the well POM 2 had again been pumping long enough to produce oil, (after 3,000 barrels had so recently been pumped downwardly therethrough to displace oil outwardly, as into the areas A, B, C, D in FIG. 1), that all oil separated from water in the separator or "gun barrel" that could be measured in the oil storage tank, came at that time from well POM 1.

As the oil production redistributes to normal production, both wells on pump, and the channels opened up by the water-flooding treatment through well POM 2 flow oil to respective nearest wells, it is fairly projected that the production of well POM 2, estimated by sight gauge to be about 4½ barrels per day or some bit over 2½ barrels per day, the rate of oil production prior to treatment, should rise to approximately 8 barrels per day. On the other hand the projection is fairly estimated that the production of well POM 1, which did not receive the water with solution thereinto, will continue to fall slightly in production, day by day, until the respective wells level off with well POM 2 producing approximately 8½ barrels of oil per day, and with well POM 1 finally stabilizing at a production of say 7½ barrels per day.

Thus, by the employment of the solution in this type of flooding or water injection system the consensus of experts, as geologists, reservoir engineers, drillers and producers acquainted with the Luling field generally, and having knowledge of these two wells, and of the tests or treatment hereinabove described in particular, is to the effect that the treatment or tests indicate that the combined production of these two wells, after stabilization, will be approximately 16 barrels per day, or four times the combined production of approximately four barrels per day (2½ barrels, well POM 2, and 1½ barrels well POM 1) that these two wells had been producing prior to the aforesaid tests or treatment.

Notice is taken that the projection appeared mostly based upon surmise that the treatment was primarily effective at the eighth perforation level, or in the area or space about the bot-

tom of well POM 2. However, it may be pointed out that in the time of approximately five minutes required for the solution to reach the bottom of the cased well, some small proportions of solution could have gone out through the perforations at the strata levels above the lowermost strata level, and conjecture is opened as to the effects of treatment when the solution may be pumped down at a substantially reduced rate, so that at least part of the solution may have time assuredly to penetrate to some effective extent through the higher perforations.

Also query is raised as to any increased effectiveness of treatment in case the solution had been mixed with the water prior to injection, either with the first 1,000 barrels or the second 1,000 barrels, or in any other combinations of the total 3,000 barrels of water employed?

In the description set forth hereinabove the emulsified oil has most obviously cleared in the settling tank or separator without requiring the assistance of any special settling or separating agent. However, it is well known that when the overall time of treatment and production or recovery may need shortening or quickening, the use of such a separating or settling agency may become very important. Hence it is pointed out that a medium, as sodium hydroxide, NaOH may be very well chosen for this purpose. Notice should also be taken of the suitability of other hydroxides, as potassium hydroxide, or of other bases.

The apparatus, equipment, elements, and features hereinabove described with relation to FIG. 1 may be designated by reference numerals as the practice may dictate, although in the specification hereinabove these matters have been only designated by description.

Thus the well POM 2 may be designated by reference numeral 10a and the well POM 1 by reference numeral 10b; with respective casings designated by reference numerals 11a, 11b; the Halliburton truck 12 having truck pump 13 thereon, with discharge line 14 having pressure gauge 15 therein and connected by casing head valve 16 to the casing 11a. The casing 11a has tubing 17a therein and the casing 11b has tubing 17b therein. The tubing 17a has sample valve 18a therefrom; and the tubing 17b has a sample valve 18b therefrom. A production line 20a is connected to the tubing 17a by valve 21a, such line 20 delivering into a settling tank or separator 22.

The Halliburton pump 13 is shown taking suction through a flexible conduit 23a (having valve 24a therein) from the San Marcos river 25. Also the tubing 17b of well POM 1 is shown having a delivery or production line 20b connected thereto by a valve 21b, such line 20b also being connected to deliver into the separator 22. The Halliburton truck pump 13 is shown having an alternate suction line 23b connected by a valve 24b to take suction from a chemical tank or solvent reservoir 26 on the Halliburton truck 12. The well pump 27a for the well POM 2 is shown with pumping string 28a having been interrupted, and the pumping string 28b of the well pump 27b, which stayed consistently pumping, is shown continuous into the top of the casing 11b. A conventional water trap 29 is shown provided upon the separator 22 and a discharge line 31 is shown from the upper part of the separator 22 to a storage tank 30.

As a second specific example, various tests were run on various types of soiled, contaminated, or overly viscous products, three tests each being made on crude oil emulsified by relatively low amounts (1 cc.) of solution with relatively high (16-49 percent) ratios of oil to other liquids; on refined oil emulsified by slightly greater amounts (1-10 cc. s.) of solution, with relatively lower (14-28 percent) ratios of oil to other liquids; on crankcase oil emulsified by still slightly greater amounts (7-20 cc. s.) of solution, with relatively higher (12½ to 40 percent) ratios of oil to other liquids; on crude oil emulsified by relatively lower amounts (7-10 cc. s.) of solution, with comparably lower ratios (3-24 percent) of oil to other liquids. The amount of other liquids included sodium hydroxide as the emulsion breaker in all but one of the tests (no. 11), and in one test (No. 12) it included a mixture of sodium hydroxide with another emulsion breaker, not very

satisfactory. In all of the tests but tests No. 11 and No. 12, the emulsions were broken in as short a time as 1 minute, and no longer than (10) minutes. On the other hand, test No. 11 which employed $\text{Ca}(\text{OH})_2$ alone as emulsion breaker, it required substantially 30 minutes to clear the emulsion, while in test No. 12, which employed $\text{Ca}(\text{OH})_2$ (lime) mixed with NaOH , it also required almost 30 minutes to clear the emulsion. Consequently, it can be determined that sodium hydroxide is much the better emulsion breaker.

Noticeably clarification or complete breaking of the emulsion took place in from 1 to 10 minutes and this exceptionally short time may be attributed to the character of the solution comprising this invention, or the emulsifying agent. All tests cumulatively supported the conclusion that the respective penetrant and detergent, fatty acid emulsifier (to attract oil into emulsion), and emulsifier of action comparable to hydroscopic action (to attract water into emulsion) did not appreciably harm the oil, but only emulsified it quickly and could almost as quickly release the oil when it became desirable to separate it from the other liquid components.

The tests, as set forth by the chart, stand by themselves for the information contained therein, while the graphs of FIGS. 3A, 3B, 3C and 3D show plots of three tests each, time as ordinate against degree of coloration (in reverse) as ordinate. Thus Color Grade 10, at the top of the graphs implies that the lower layer of other liquids is substantially plaque or darkly opaque when the emulsion has been broken, while Color Grade 0 at the bottom of the graphs implies that the lower layer of other liquids is substantially clear and transparent when the emulsion has been broken.

The ingredients or liquid members are exemplary and not by way of limitations. Other related compounds, additives, ingredients or components may serve conceivably as well. For instance, it may be necessary or advantageous to add a base, as NH_4OH , NaOH , or $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ to the water that may be first required to condition the well as to pH factor. On the other hand, an acid such as HCl or HF may be added with the water to bring an excessively base testing well into proper pH factor range. Also, water softener or water conditioners may be added with preliminary conditioning water, prior to use of the solution and further water. Also any chain hydrocarbon having an amide on the end of the chain may serve though doubly presently as inexpensive as a lauric amide. Also, as to the agent for drawing water into solution, Na_2SO_4 could be used, although not nearly as effective and in cases likely to cause damage.

As shown in FIG. 4 an open top agitation tank 35 is provided for receiving contaminated oil, usually quite viscous, such as slag or "bottoms" from refineries, crude oil, used refined oil as crankcase oil, or any other type of difficulty usable petroleum product. A drive 36 is indicated diagrammatically for rotating an agitator 37. A storage tank 38 containing blender solution is shown connected to discharge into the agitation tank 35, in case the oil or petroleum product in the agitation tank 35 were too viscous to be handled by the pump 39 without first being diluted.

The pump 39 is shown discharging into the top of an emulsion tower 40 to fall through a series of perforate or mesh trays 41 and through nozzle ejected sprays 42 which discharge into the tower the solution of this invention as carried by water. The solution, per se, is indicated as being stored in a chemical reservoir or tank 43, which discharges the solution through a valve 44 into a mixing line 45 to which is also connected the discharge, via a valve 46 from a water supply tank 47. A pump 48 takes suction from the mixing line 49 and delivers the mixture of solution and water to a header 50 for the sprays 42. A discharge line 51 from the bottom of the emulsion tower 40, having a valve 54 therein, delivers the emulsified oil and other liquids into a settling tank 52. A tank 55 for use for a settling agent or emulsion breaker, such as sodium hydroxide is con-

nected via a valve 53 into the discharge line 51 from the emulsion tower.

The solution is inherently selected to support synergism between its three active ingredients. That is, a linear alkylsulfonate with a lauric amide is designed to produce greater emulsification of oil than either ingredient acting alone in the same quantity as the combination. This is true because of the great penetration and carrying action of the linear alkylsulfonate which so greatly translates or distributes the lauric amide afar, and through a much wider range of travel than the lauric amide, in equal quantity, could traverse. Correspondingly, the great penetration and carrying action of the linear alkylsulfonate so greatly can distribute the emulsifier of hydroscopic action afar and into a much wider range of contact with a much greater volume of water, than the much slower traveling emulsifier of hydroscopic action in the same quantity as the combination, but acting alone.

Obviously synergism must be inherent between the lauric amide emulsifier of oil and the emulsifier of hydroscopic action which acts to bring water into emulsion, since the object of the combination is to bring both oil and water into emulsion. Thus any set quantity of the lauric amine emulsifier taken alone, would not have any ingredient in association with propensity to draw the water into emulsion. And conversely, any same quantity of the emulsifier of hydroscopic action taken alone would not have any ingredient in association with propensity to draw the oil into emulsion.

The apparatus hereinabove described forms a background for the employment of the solution of this invention in manner that the oil bearing emulsion with substantial fluidity, may be discharged to the settling tank, with the settling agent already introduced therein so that the emulsion is breaking up and on its way to settling as soon as it enters the settling tank.

The apparatus, equipment and various devices and mechanisms hereinabove described are also shown by way of example and not by way of limitation. Thus any means for delivering water, solution, and water mixed with solution into the well may serve, and also any means of drawing water bearing oil to the surface for separation, analysis and distribution are considered. Additionally, the invention considers a fair equivalent range of solution, ingredients and proportions, and method steps in equivalency and various operative sequences. Thus the application is illustrative and is completed by the claims.

We claim:

1. The process of recovering oil from a formation penetrated by a well comprising the steps of introducing, into the well, water in volume under pressure to pass through a first portion of said formation adjacent the lower portion of the well, introducing into the well a three-component solution comprised of a linear alkyl sulfonate in substantial proportion as penetrant and carrying an emulsifier, and an agent of hydroscopic action, in still lesser proportion to draw water into emulsion, the solution penetrating through the water to emulsify encountered oil and to the periphery of said first portion to emulsify peripheral oil, introducing additional water into the well casing to urge, at least in part, the water first introduced and carrying the solution, into a second portion of said formation peripheral about the first portion to emulsify encountered oil including further peripheral oil, drawing back into said well from said formation the aforesaid water, at least in part, with oil therein, and separating the oil from the water thus drawn back.

2. The process of recovering oil from a well, as claimed in claim 1, in which the water first introduced into said well and solution are introduced as mixed together.

3. The process of recovering oil from a well, as claimed in claim 1, in which the water first introduced into said well is introduced into the first space and followed by the solution.