FOAMING AGENTS FOR REMOVING PROBLEM LIQUIDS FROM GAS WELLS

By J. L. Eakin

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UNITED STATES DEPARTMENT OF THE INTERIOR
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J. L. Eokin¹

ABSTRACT

The Bureau of Mines determined agents that are effective in foaming heavy brines and oil from gas wells in severe concentrations of sodium chloride, in severe concentrations of calcium chloride, or in moderate oil-brine mixtures. Dynamic foam tests were designed to select the more effective foaming agents.

Numerous foaming agents were tested in concentrated simulated brines, in oilfield brines having varied concentrations of ions, in heavy natural brines, and in a commercial brine generally used as a reservoir pressure-balancing fluid. Several agents were detected that could perform efficiently in the field under the most severe saline conditions. Agents that promote foaming in oil-brine mixtures were also determined.

INTRODUCTION

The work described in this report was part of the Bureau of Mines overall program on the use of detergents to improve productivity of natural gas wells by removing liquids and solids from the wellbores. It supplements earlier research (2)² to establish guidelines for determining the applicability of foam treatments in the field. A specific objective was to evaluate by previously standardized laboratory and field methods new foaming agents developed for use in wells to remove heavy brine (brine with higher than average total solids), oil, and oil-brine mixtures. This research was performed both to assist in removing brine from problem wells and to assist in reviving gas production from new and reconditioned wells that showed decreased production. Wells considered here are those with decreased productivity as a result of formation damage from mud filtrate and water or those damaged wells that had the gas flow "balanced" with heavy commercial brines during completion or servicing.

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² Underscored numbers in parentheses refer to items in the list of references at the end of this report.

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THEORY

The accumulation of concentrated brine and liquid hydrocarbons makes it difficult for gas well operators to clean wellbores by the foam method patented by Dunning and Walker (4). The foaming and liquid-carrying ability of most commercial detergents is severely dampened in mixtures of brines and liquid hydrocarbons and in oilfield and gasfield brines that have high concentrations of sodium and/or calcium chloride.

When properly mixed with liquids in the wellbore and agitated by a small amount of gas from the producing formation, foaming agents normally form a light foam column. This lightened column can be lifted from the well by gas pressure insufficient to lift an equal column of water. However, in the present investigation many detergents failed to foam efficiently in brines as the sodium chloride content approached the saturation point and in brines having high concentrations of calcium; no detergent was applicable to a broad range of crude oil-brine mixtures.

Recently, the use of foaming agents in various phases of oil and gas operations has been emphasized considerably. Detergents of all types have been used extensively during cleanout operations in oil- and gas-production wells, in water-input wells, in connection with acidizing wells, and in other stimulative treatments (6, 8). A choice of detergents is available commercially to perform practically any assignment.

The detergents and foaming agents available for testing in commercial applications represent a wide variety of chemical compositions and properties. Johansen, Dunning, and Beaty (7) divided detergents into three types (cationic, anionic, and nonionic) according to their ionization products. If the oil-soluble part of the molecule forms a positive ion, the detergent is classed as cationic; however, if the oil-soluble ions are negatively charged the detergent is anionic. Amphoteric detergents contain cationic and anionic groups and are either cationic or anionic under acidic or basic conditions, respectively. True amphoterism occurs in a system when the right amount of acid is added to balance the cationic and anionic properties. At this point a balanced ion, often called a zwitterion, is formed; such ions are both positive and negative at the same time. Detergents that do not ionize but owe their solubility in water to the polar group in the hydrophilic (water-loving) side chain are classed as nonionic. Built or commercially formulated detergents commonly contain inorganic substances such as carbonates, borax, and polyphosphates, which enhance the effectiveness of the detergent.

A modern adaptation of the foaming action of detergents is used to assist in lifting water, brine, and drill-cuttings from wells being drilled with

either air or gas. Detergents are used as additives in drilling mud to reduce friction and in cleanout operations on gas wells "drowned" by brine, oil, or mud. Detergents are also effective for removing water blocks from the formation around gas wells (5), as shown by the Bureau of Mines in a recently developed alcohol-surfactant treatment.

FOAMING HEAVY BRINES

Because balancing the reservoir pressure of individual gas wells with fresh water causes clay swelling and other detrimental effects, more operators are using weighted commercial brines as balancing fluids during these operations. Concentrated commercial brines vary in their mineral content, depending upon the source bed; however, they are principally sodium chloride. Usually less than 1 percent of the total dissolved solids is represented by the combined calcium chloride and bicarbonates.

Numerous reports have been published on brine analyses (9-11). Differences in mineral content, even in trace quantities, aid in identifying the sources of particular brines. These reports also show that gasfield brines generally contain higher concentrations of dissolved salts than oilfield brines. High mineral concentrations in the reservoir and wellbore are probably caused by the evaporative action of the gas removing the formation water. It is not uncommon for gas wells to produce only periodically and at relatively high rates. In wells from which only small amounts of formation water are produced, water tends to evaporate at the sand face, probably leaving either concentrated brine or an accumulation of recrystallized salt in the wellbore. Greater depths of gas wells, with accompanying increased reservoir temperatures and pressures, also probably enhance the concentration in brines of gas-productive formations and wellbores.

Fortunately the problem of lifting heavy natural brine from gas wells is not widespread. Isolated wells produce heavy brine in areas of the Texas Panhandle, west Texas, Michigan, and Ohio.

Because many gasfield brines and balancing fluids are highly concentrated with salts, removing them from drowned gas wells by the foam method is difficult. Selecting effective foaming agents for the current study was simplified to some extent through the cooperation of various detergent or foaming-agent manufacturers. Several suppliers of detergents suggested better foaming agents that appeared to be least affected by increased salinity. Other manufacturers compounded agents specially designed to foam in heavy brines. Unfortunately, many detergents with good static foam characteristics are not particularly efficient liquid carriers. In this application the critical measure of effectiveness is the amount of liquid held in the foam and carried out of the well.

Apparatus

Evaluation tests were made using the Bureau of Mines standard dynamic foam test apparatus (2). To 500 ml of the test solution, foaming agents are added in concentrations of 0.05 weight-percent active ingredient. Briefly,

the apparatus consists of a Pyrex³ glass tube column with standard tapered joints sealed to the top and bottom. A plastic hose attached to a cap on the top joint directs the effluent to a graduated cylinder. A Pyrex funnel with a sealed-in, medium-fritted-glass disk attached to the bottom standard tapered joint of the column serves as an aerator. The system air supply is regulated with a Fisher float-type, laboratory flowmeter and is maintained manually at a flow rate of one-half liter per minute. The volume of water measured in the graduated cylinder is recorded after 20 minutes. Except for duplicate runs made with natural brines, the results of all tests are given as the average of at least four runs. Maximum variation between results from identical tests is plus or minus about 5 percent.

Results of Laboratory Tests

Numerous detergents that are effective for foaming either fresh water or light brines rapidly lose their ability to foam brines that have a higher mineral content. Normally, to be effective in field operations, a detergent should have a liquid removal capacity or "carryover" of approximately 300 ml from the foam column to the graduated cylinder after 20 minutes.

Table 1 presents the results of mineral analyses of the concentrated natural and commercial brines used during this series of tests. The brines were selected from wells in which the concentration of dissolved salts in the water had prohibited the successful field application of the foam method. Natural brines were supplied by companies operating wells in Michigan and the Texas Panhandle. A sample of commercial brine was furnished by a supplier in the Odessa, Tex., area. A sample of Bartlesville sandstone brine was used as a standard test brine in which to concentrate various ions. Morton's medium salt, a water softener, was used to prepare solutions of simulated brines at various concentrations. The mineral content of Morton's medium salt was measured in parts per million as follows: Calcium chloride (CaCl_2), 4,000; sodium chloride (NaCl), 995,020; and bicarbonate (HCO_3^-), 980.

TABLE 1. - Analyses of concentrated natural and commercial brines

	Michigan brines			Texas brines		Oklahoma Bartlesville brine
	Salina 1	Salina 2	Stray	Kryder- Winfield	West Texas commercial	
Specific gravity.....	1.220	1.218	1.218	1.215	1.208	1.087
Analysis, mg/liter:						
Barium (Ba^{++}).....	280	900	0	0	0	0
Calcium (Ca^{++}).....	41,800	38,000	29,200	12,260	1,840	8,620
Magnesium (Mg^{++})...	5,700	5,400	6,800	12,700	1,070	940
Sodium (Na^+).....	68,200	71,900	81,800	86,900	118,600	39,000
Bicarbonate (HCO_3^-)..	70	70	70	40	160	90
Sulfate ($\text{SO}_4^{=}$).....	1,120	1,450	1,130	760	4,160	290
Chloride (Cl^-).....	195,000	193,200	196,800	195,000	186,150	77,800
Total solids....	312,170	310,920	315,800	308,660	311,980	126,740

³Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

Selected detergents were tested in distilled water at a concentration of 0.05 weight-percent active ingredient, but only those that performed most satisfactorily during the series of tests were listed in table 2. Generally, the efficiency of foaming or water-carrying capacity of most detergents decreases with increased salinity. Many detergents failed and were eliminated as the sodium chloride content approached 20 percent. Data listed in this table indicate the most successful foaming agents tested and the comparative volumes of liquid carryover with sodium chloride concentrations ranging from 0 to 25 weight-percent near the saturation points of the liquids.

The results of the second series of tests, listed in the middle portion of table 2, show the effect of altering Bartlesville brine on the foaming tendency of some detergents. A series of tests were run on numerous detergents at concentrations of 0.05 weight-percent active ingredient in oilfield brine in which the content of calcium, magnesium, bicarbonate, carbonate, and sulfate were increased to the maximum values usually found in natural brines. Calcium appears to have the most significant effect on foaming. From the results of auxiliary tests, not presented in table 2, it was found that in general brines containing calcium adversely affect the foaming ability of Triton X-102, Triton X-165, Deriphath 170-C and Howco suds.

Results reported in the lower part of table 2 indicate that only a few of the dozen detergents are efficient foamers of these concentrated brines. All agents listed in the table perform efficiently under the severe conditions of changed mineral content. However, the proof of all testing comes only

when the foaming agents perform efficiently under field conditions.

FIGURE 1. - Relative Effectiveness of Foaming Ability of Detergents at 0.05 Weight-Percent in Concentrated NaCl Solutions.

Figure 1 shows the relative foaming ability the detergents tested at 0.05 weight-percent active ingredient. The top curve shows that Deriphath 170-C foams exceptionally well in highly concentrated sodium chloride solutions. However, succeeding tests showed this agent was unsuccessful in foaming brines containing calcium ions. Tergitol TMN, Dowell G5 stick,

FIGURE 2. - Effect of Temperature on the Foaming Ability of 0.05 Weight-Percent Triton X-100 in Brine Solutions.

and Howco stick were relatively unaffected by increased salinity. These tests indicated that the foaming efficiency of many proven detergents is depressed in concentrated brines. However, these results do not reflect upon the detergents' ability to foam in normal brines, in air and gas drilling, and in other applications for which they were originally developed.

The foaming tendency of both Aliquat 4 and Howco suds was noticeably increased by the

addition of as little as 0.5 weight-percent sodium chloride. This feature results from the agents being formulated especially for foaming in electrolytes.

The foaming characteristics of three nonionic agents listed in table 2 did not follow the general pattern because of an anomaly that occurred when approaching and passing the cloud point. The cloud point is the temperature at which sufficient detergent precipitates to cloud the test solution. Examples of the effects of the cloud point may be noted from data tabulated for Dowell G2, Tergitol TMN, and Triton X-100. All solutions made up with Tergitol TMN that were more saline than the initial solution with distilled water were beyond the cloud point, and efficient foaming resulted. The cloud point for an aqueous solution of Triton X-100 was reached at room temperature at about 15 percent NaCl; at concentrations above 23 percent NaCl, the agent foamed remarkably well. Dowell G2 and Triton X-100 follow similar patterns with respect to the effect on foaming brought about by clouding of the test solutions. Special tests were performed with these two agents.

Figure 2 shows an example of the effect of a moderate change in temperature on the foaming ability of 0.05 weight-percent Triton X-100 in sodium chloride solutions. This phenomenon is of particular interest to manufacturers and research chemists. The tiny particles of detergent coming out of solution apparently have a relatively high surface viscosity, affording more efficient foaming action than that obtained from the original detergent. Nonionic detergents normally drop out of solution and produce low foaming when exposed to higher temperatures and increased NaCl concentrations. These unexpected results indicate nonionic detergents may perform satisfactorily beyond their cloud points in wells having high bottom-hole temperatures.

TABLE 2. - Effects of mineral additives on the foaming ability of detergent-brine solutions¹

	Cationic detergents			Anionic detergents		Nonionic detergetns						
	General Mills		Armour Armomist	American Cyanamid RC-250	Antara Gafac RE 610	Dowell		Antara Gafen FA-5	Howco stick	Union Carbide Tergitol TMN	Rohm & Haas	
	Alifoam 4	Aliquat 4				G2	G5				Triton X-100	Triton X-114
Foaming of NaCl Solutions in Distilled Water, ml												
NaCl, percent:												
0.....	403	168	262	379	384	404	325	368	374	395	399	400
5.....	458	313	256	362	414	306	375	393	376	351	356	385
10.....	464	317	254	313	374	165	358	374	354	357	279	320
15.....	366	319	276	275	378	205	332	344	328	397	152	310
20.....	238	300	243	268	370	378	300	310	316	379	93	255
25.....	244	195	222	253	281	305	300	276	285	365	381	132
Foaming of Bartlesville Brine Solutions with Selected Additives, ml												
Additives, percent:												
0.....	366	370	393	350	353	225	352	390	354	384	264	378
2 Ca ⁺⁺	276	361	357	351	291	176	337	388	324	368	222	415
3 Ca ⁺⁺	256	326	351	260	293	294	335	354	331	376	193	428
4 Ca ⁺⁺	245	331	320	255	200	336	353	320	294	389	180	422
0.1 HCO ₃ ⁻	388	408	392	274	318	233	356	420	417	368	265	393
0.003 CO ₃ ⁼	392	407	390	312	324	260	365	418	412	370	284	424
0.255 SO ₄ ⁼	372	383	326	319	327	204	367	414	400	344	277	400
1.315 Mg ⁺⁺	295	392	314	344	397	183	351	385	303	377	175	416
Foaming of Concentrated Natural Brines, ² ml												
Salina 1.....	275	244	255	125	168	328	305	243	262	351	228	189
Salina 2.....	274	237	241	151	202	390	305	211	289	305	225	184
Stray.....	82	160	166	235	114	345	331	218	228	324	345	283
Kryder-Winfield.....	251	240	249	-	-	367	113	260	244	349	346	205
West Texas Commercial.....	250	123	125	182	249	187	277	233	135	274	354	161

¹ Detergent concentration, 0.05 weight-percent active ingredient; figures in milliliters represent liquid removed from foam column in 20 minutes.

² Average of duplicate tests.

The available information on chemical compositions of all agents studied is summarized in table 3.

FOAMING OIL AND OIL-BRINE MIXTURES

Gas wells often suffer loss in production rate because of the gradual accumulation of crude oil, brine, or a combination of these liquids. Existing reservoir energy is sometimes incapable of lifting these liquids to the surface. After numerous requests from industry for information, means were sought to apply the foam method to this problem.

Considering the complexities and number of well conditions encountered in foaming crude oil and oil-brine mixtures, only minor success could be expected in developing effective methods and agents for use over a broad range of field conditions. A few of the variable conditions are pressure, volume and type of well fluid, completion with respect to wellbore diameter and size of tubular goods, and changing surface phenomena. The surface forces are further complicated by adding detergents to the systems. The large number of books and papers on surface chemistry testifies to a considerable understanding of surface forces and behavior. However, the problem of foaming oil and oil-brine mixtures from wells is not urgent enough to support either basic studies involving the general categories of surface chemistry and physics or a prolonged applied research effort.

Although the extensive field test program on removing brine by the foam method revealed that most oils and oil-brine mixtures resisted foaming by ordinary detergents, some foaming agents were moderately effective. Concurrently, several manufacturers of detergents developed and tested improved foaming agents. Results from earlier Bureau of Mines research (1-2) and industry research (3) indicated that, although the foaming properties of some cationic fatty quaternaries differed widely, they were effective at very low concentrations. The low-molecular-weight fatty quaternaries were most effective for foaming strong acids, heavy brines, and mixtures of oil and brine. The higher-molecular-weight quaternaries were effective in brines and straight oil. Foaming is dependent upon an increase in surface activity and its relationship to the film foaming properties of the solution being tested. Some crude oils foam readily owing to the presence of natural surface-active materials; one such class of compounds is naphthenic acids. As reported earlier, some of the quaternary ammonium compounds have been effective in foaming a variety of crude oils. However, no universal oil-foaming agent has been made available.

Reduction of Surface Tension

It appeared logical to investigate the problem of foaming mixtures of crude oil and brine by reducing the surface tension of the brine phase with an agent that would produce relatively stable foam and tolerate the presence of oil. Foam formed by most nonionic detergents is usually broken by the oil phase of the system. The surface tension of the oil phase, being low, was found most difficult to reduce significantly. Foaming agents that were moderately effective in crude oil failed in tests with oil-brine mixtures. In the more successful tests the oil phase was lifted as a film interspersed through the foam.

TABLE 3. - Composition of foaming agents tested

Manufacturer and trade name	Type	General description	Percent active ¹	Composition
American Cyanamid Co., Round Brook, N.J.: RC-250.....	Anionic...	Experimental material....	65	
Armour Industrial Chemical Co., Chicago, Ill.: Armomist.....	Cationic..	Polar organic nitrogen derivative.	40	Quaternary nitrite.
Arquad C-12.....	...do.....	Quaternary ammonium salt	75	Polyoxyethylated coco fat methyl ammonium chloride.
Arquad C-50.....	...do.....	...do.....	50	Coco fat trimethyl ammonium chloride.
Arquad 12-50.....	...do.....	...do.....	50	Lauryl trimethyl ammonium chloride.
Arquad T-2C-50.....	...do.....	...do.....	50	Mixed tallow and dicoco fat ammonium chlorides.
Duomeen CD50.....	...do.....	Aliphatic diamine.....	50	N-alkyl trimethylene diamine.
Atlas Powder Co., Houston, Tex.: Aquaness APD 2564.....	...do.....	Tertiary amine.....	74	Derived tertiary amine.
Dow Chemical Co., Tulsa, Okla.: Dowell G2.....	Nonionic..	Foaming agent.....	70	
Dowell G5 stick.....	...do.....	Foaming agent, solid form	100	
General Aniline & Film Corp., Antara Chem. Div., New York, N.Y.: Gafac RE610.....	Anionic...	Salt water foaming agent.	100	
Gafen FA-1.....	...do.....	Fresh water foaming agent	58	
Gafen FA-5.....	Nonionic..	Salt water foaming agent.	100	
Igepal CO-430.....	...do.....	Foaming agent.....	99	
General Mills, Inc., Minneapolis, Minn.: Alifoam 4.....	Cationic..	Fatty quaternary ammonium chloride.	35	Lower molecular weight fatty quaternary ammonium chloride.
Aliquat 4.....	...do.....	...do.....	50	Lauryl trimethyl ammonium chloride.
Aliquat 21 F.....	...do.....	...do.....	35	Coco fat trimethyl ammonium chloride (foaming-grade).

See footnotes at end of table.

TABLE 3. - Composition of foaming agents tested--Continued

Manufacturer and trade name	Type	General description	Percent active ¹	Composition
General Mills, Inc., Minneapolis, Minn.:--continued				
Aliquat 400.....	Cationic..	Fatty quaternary ammonium chloride.	50	Mixed mono tallow-dicoco fat quaternary ammonium chlorides.
Deriphath 170-C.....	Amphoteric ²	Fatty amphoteric.....	50	N-lauryl β -aminopropionic acid.
Halliburton Co., Duncan, Okla.:				
Howco stick.....	Nonionic..	Foaming agent, solid form	84	
Howco suds.....	...do.....	Foaming agent.....	65	
Jefferson Chemical Co., Inc., Houston, Tex.: Sulfonic N-150....	...do.....	Polyoxyethylated alkyl phenol.	100	Polyoxyethylated nonylphenol (150 oxyethylene units).
Minnesota Mining & Manufacturing Co., St. Paul, Minn.: 3M L-1083..	Amphoteric ²	Flurochemical surfactant.	100	
Procter & Gamble Co., Cincinnati, Ohio:				
O.K. liquid.....	Anionic...	Lauryl sulfate.....	70	Ammonium lauryl sulfate plus amide builder.
P&G BHO.....	Nonionic..	Experimental material....	23	Foaming agent No. 29.
P&G T-3.....	Nonanionic	...do.....	32	
P&G T-5.....	Nonionic..	...do.....	27	
Rohm & Haas Co., Philadelphia, Pa.:				
Hyamine 1622.....	Cationic..	Quaternary ammonium chloride.	100	Diosbutyl phenoxyethoxy ethyl dimethyl benzyl ammonium chloride.
Triton QS-15.....	Amphoteric ²	Amphoteric oxyethylated sodium salt.	100	Polyoxyethylated sodium salt or sulfated ethoxy product.
Triton X-15.....	Nonionic..	Polyoxyethylated phenol..	100	Polyoxyethylated octylphenol.
Triton X-100.....	...do.....	...do.....	100	Do.
Triton X-102.....	...do.....	...do.....	100	Do.
Triton X-114.....	...do.....	...do.....	100	Do.
Triton X-165.....	...do.....	...do.....	70	Do.
Union Carbide Corp., New York, N.Y.: Tergitol TMN.....	...do.....	Polyoxyethylated nonanol.	90	Trimethyl nonanol.

¹ Percent active ingredient listed usually diluted with isopropyl alcohol but sometimes with water.

² Cationic or anionic under acidic or basic conditions, respectively.

Mixtures of brine and crude oil present difficult problems in foaming; however, the substantial research has resulted in agents that foam a few selected samples of crude oil and mixtures of some crude oils and brine. Although completely satisfactory materials and methods that can be applied to a wide range of field conditions have not been developed, this fact emphasizes the importance of testing specific well liquids.

Results of Laboratory Tests

Hundreds of commercial and experimental detergents and other chemicals were tested by a simple test tube shake test from which the better foaming agents were selected for further testing. Although these foaming agents did not equal the performance of the common foaming agents for water, the results of some of the more successful tests performed in the standard dynamic foam apparatus are shown in table 4. Satisfactory foaming was induced under specific test conditions by those agents listed in the table. Satisfactory in this application represents a liquid carryover of more than 250 ml from a possible volume of 500 ml of test solution in 20 minutes.

TABLE 4. - Detergents for satisfactory foaming at specific test conditions

Trade names of individual detergents tested separately	Detergent, weight- percent active ingredient	Conditions	
		Mixture	
		Components ¹	Volume- percent ²
Arquad T-2C-50, Gafen FA-1, Igepal CO-430...	1	Kerosene.....	100
Howco suds, Hyamine 1622, P&G BHO.....	1	H ₂ O-kerosine	50-50
Alifoam 4, Aliquat 4, Arquad C-50, Arquad 12-50, APD 2564, Howco suds, Triton QS-15..	1	10 pct brine-kerosine....	50-50
Alifoam 4, Triton QS-15.....	1	do.....	25-75
Alifoam 4, Aliquat 4, Aliquat 21 F, Aliquat 400, Arquad C-12, Arquad C-50, P&G BHO, P&G T-3, P&G T-5, Surfonic N-150.	1	20 pct brine kerosine....	50-50
Alifoam 4, Triton QS-15; P&G BHO.....	1	do.....	25-75
Armomist, Arquad 12-50, APD-2564.....	1	10 pct brine-condensate 61.2° API.	50-50
Arquad T-2C-50 (2).....	1	Numerous crude oils.....	100
Howco suds.....	1	10 pct brine-Bartlesville crude.	50-50
None.....	1	Bartlesville brine- Bartlesville crude.	50-50
Alifoam 4, Howco suds, P&G BHO.....	0.5	10 pct brine-kerosine....	50-50
Alifoam 4, 3M L-1083, P&G BHO.....	.5	do.....	25-75
Alifoam 4, 3M L-1083.....	.5	20 pct brine-kerosine....	50-50
Triton QS-15.....	.05	10 pct brine-kerosine....	50-50
Alifoam 4, Aliquat 4, Aliquat 21 F, Triton QS-15, P&G T-5, Surfonic N-150.	.05	20 pct brine-kerosine....	50-50
Alifoam 4.....	.05	do.....	25-75

¹Artificial brine used in mixtures unless otherwise identified.

²Figures key to components column; for example for 10 percent brine-kerosine, and 25-75 volume-percent, the mixture would contain 25 volume-percent brine and 75 volume-percent kerosine.

Table 4 records 10 foaming agents that may be expected to induce satisfactory foaming at 1 weight-percent active ingredient in 50-50 mixtures of 20 percent brine and kerosine. However, only 6 agents were effective at 0.05 weight-percent active ingredient in similar mixtures. The manufacturers and chemical compositions of the additional foaming agents studied are summarized in table 3.

Other chemicals and materials tested for their foam-producing characteristics included emulsifying agents and viscosity building materials such as guar gums, finely divided silica, and other powdery substances. These were tested in the foam column at 1 weight-percent in oil and in oil-brine mixtures and by adding 1 weight-percent active ingredient of selected detergents. Similarly, some of the fatty oils, including some spreading oils, were tested with few promising results. The vegetable and animal oils tested were cottonseed, corn, coconut, banana, turpentine, olive, castor, codliver and neat's-foot oils. In addition, the testing of a variety of acids, solvents, industrial soaps, cleaning compounds, patented oil foamers, and other chemicals at 1 weight-percent in the foam column provided few encouraging results.

For example, four good water-foaming agents failed to foam in kerosine at 1 weight-percent active ingredient. Further tests with these agents failed at 0.5 weight-percent active ingredient and 0.5 weight-percent naphthenic acid in 50-50 mixtures of kerosine and 10 percent brine. A 1-percent concentration of naphthenic acid in a sample of 42.1° API gravity crude oil induced moderate foaming from which liquid carryover of 160 ml was produced after 20 minutes. Numerous foaming agents were tested at 1 weight-percent active ingredient in 34° API gravity Bartlesville sand crude oil. All agents failed; however, Triton X-15 and Duomeen CD50 each induced moderate foaming at about 130-ml carryover. In another series of tests involving 10 of the better foaming agents at 1 weight-percent active ingredient in 50-50 mixtures of Bartlesville sand crude oil and 10 percent brine, each agent induced some foaming. The best results were with Howco suds, which produced a carryover of 275 ml.

Some increased foaming was induced in a crude oil-brine-detergent system by adding finely divided silica. The height of foam extended only to the top of the foam column when testing a 1 percent active ingredient of Aliquat 4 in a 50-50 mixture of Bartlesville sand brine and crude oil. When 400 ml of Cab-O-Sil (silica powder) was included in identical subsequent tests, the average carryover of liquid was improved slightly to 197 ml. However, this was too low to expect efficient foaming in the field.

The agent BHO at 1 weight-percent active ingredient in 50-50 mixtures of Bartlesville brine and crude oil produced an average carryover of 221 ml. This volume of carryover was depressed during eight tests where 1 weight-percent of various vegetable and animal oil was added and minor increases resulted from the addition of banana oil and olive oil. The volume of carryover from the various crude oil-brine-detergent fatty oil mixtures were depressed by including neat's-foot oil, linseed oil, castor oil, Mazola corn oil, turpentine, peanut oil, coconut oil, and codliver oil. The average carryover of 221 ml was increased only slightly to 229 and 234 ml by adding banana oil and olive oil, respectively. These minor increases are not significant because they are within the experimental error of the test results.

CONCLUSIONS

The laboratory test results indicate that some detergents can foam brines under severe saline conditions. Detergents in the cationic and anionic groups performed reasonably well through the first two series of tests, as shown by results recorded in table 2. A few of the nonionic agents performed reasonably well throughout the entire series, and only these agents might be expected to perform well under field conditions. In selecting a detergent to foam heavy brine from a gas well, a few simple preliminary tests should be made. Selection can be simplified by vigorously shaking bottles containing samples of brine from the well with carefully selected detergents and observing their relative foaming tendency.

Although only a few foaming agents effectively foamed crude oil and oil-brine mixtures, the resulting data indicate the conditions under which the better foamers produce satisfactorily. Light liquid hydrocarbons and brine in approximately equal amounts may be removed from wells by the foam method using one of the agents listed. Wells that have impaired gas production from the accumulation of crude oil only would be difficult to revive by using any of the surfactants now available. However, attempts by commercial companies to develop improved foaming agents are continuing.

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