FLUOROCHEMICAL SURFACTANTS: THEIR CURRENT AND FUTURE APPLICATIONS IN OIL AND GAS WELL STIMULATION

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INTRODUCTION

Surfactants have performed well in a variety of applications with regard to stimulation. The role of surfactants, or surface active agents, in both acidizing and fracturing has been somewhat taken for granted; but these agents nonetheless play an extremely important and ever-increasing part in almost all successful stimulation treatments. Surfactants have been discussed thoroughly in the literature with respect to use in oil well treating fluids.^{1,2,3} Until recently, most surfactants used in stimulation have come from one of two families. The most commonly used are hydrocarbon-based, and the others consist of silicone-based materials. Numerous blends of these types are used to deal with a number of situations. In varying concentrations, the above-mentioned "conventional" surfactants have been used in a variety of applications which are as follows.

- 1. To lower the surface tension or interfacial tension of a fluid.
- 2. To provide non-emulsion characteristics to a fluid.
- 3. To provide emulsion-breaking characteristics to a fluid.
- 4. To provide emulsion-forming characteristics to a fluid.
- 5. To provide foaming characteristics to a fluid.
- 6. To suspend fines or particles in fluids.
- 7. To retard or extend the reaction time of various acids.
- 8. To allow more effective penetration by aqueous or acid systems.
- 9. To facilitate a desired wetting function on a particular surface (i.e., metal, rock, etc.).

- 10. To assist or prevent various types of material in adsorbing to particular surfaces under certain conditions or to allow low adsorption.
- 11. To provide protection from various harmful reactions (i.e., corrosion, precipitation, etc.).⁴
- 12. To allow interaction with other physical problems in the oil or gas reservoir such as fluid imbibition, capillarity, saturation or permeability.^{5,6}
- 13. To allow water block removal or more effective treatment load recovery.
- 14. To improve wetting and thereby hydration of polymers used in stimulation.

There are probably other uses which could be mentioned, but those above are generally considered most essential. Correct use requires careful selection of a particular surfactant type. The criteria for surfactant selection for use in a treatment is given below to emphasize the importance of appropriate materials.

CRITERIA FOR SURFACTANT SELECTION

Four important criteria for choosing a surfactant - hydrocarbon or fluorocarbon - are, in order of priority, as follows.⁷

- 1. COMPATIBILITY WITH OTHER CHEMI-CALS - In selecting a surfactant for use in combination with other chemicals which are anionic, many cationic surfactants would be incompatible and the best candidates may be anionic, nonionic or amphoteric. If the medium in which the surfactant is to be used (for example, chromic acid) is highly reactive, a fluorosurfactant may be needed.
- 2. REQUIRED SURFACE-ACTIVE PRO-PERTIES - The second criterion for surfact-

ant selection limits the candidates further to those which can provide the particular surfaceactive properties required: wetting, emulsification, dispersing action, foaming action, or detergency. In many cases, this selection process must be empirical, based upon trial and error, but some knowledge of the correlation between surfactant performance and chemical composition can greatly simplify the selection process. Fluorosurfactants provide effects not attainable with hydrocarbon surfactants.

- 3. REQUIRED PHYSICAL PROPERTIES -The number of potential surfactant candidates can then be reduced further by matching physical properties against those required. A particular use may require a surfactant which is a solid or a liquid. The use may require a surfactant with a certain minimum solubility in a particular solvent or, in the case of nonionic products, a cloud point not lower than a particular operating temperature.
- 4. VALUE-IN-USE: PRICE VS. PERFOR-MANCE - After the first three criteria reduce the available surfactants to a manageable number, it is time to consider value-in-use, or price vs. performance. The price of a surfactant per pound may be low or high but the amount of surfactant required, multiplied by the price determines the value. If a nonfluorinated surfactant is useful at a low to moderate concentration, it may have good value. Even though fluorosurfactants are much higher priced than the hydrocarbon types, their value can be even better than that of hydrocarbon surfactants because extremely low concentrations are effective.

A third family of surfactants which has been used in many industries but only in limited areas of oilfield chemical applications are the fluorocarbonbased surfactants, or fluorochemical surfactants. The fluorochemical surfactants possess characteristics which can stand alone or improve either of the other two families of surfactants with regard to all of the previously-mentioned applications. Fluorochémical surfactants can be used at significantly lower concentrations, in most cases, to provide the required surface active property than either hydrocarbon or silicone-based surfactants.

It has been demonstrated that fluorocarbons can often surpass the cost-effective performance of many common hydrocarbon surfactants. Similarly, low levels of fluorochemical surfactants in conjunction with common hydrocarbon surfactants have been shown to allow a substantial reduction in the total amount of hydrocarbon surfactant required. This can be of crucial importance where materials must be added to and mixed properly with large volumes of aqueous-based stimulation fluid. (See Table 1).

FLUOROCARBON CHEMISTRY

The chemical nature of fluorocarbon materials is unique. Organic fluorine compounds, specifically fluorine-containing surfactants, have provided a whole new realm of actual and potential improvements in conventional oilfield-related surfactants. As shown in Figure 1, surfactants possess a typical structure containing a hydrophilic ("water loving") head, and a hydrophobic ("water hating") tail.



FIG. 3-A FLUOROCARBON SURFACTANT

 TABLE 1 -COREFLOW TESTS IN CARBONATE ROCK & DOLOMITES (FOLDS OF FLOW RATE CHANGE AT 100 PSIG, @ 25°C. WITH 100 CC. THROUGHPUT)

I.	Formation - S	an Andres, West Texas (4250') Permeabili	ty 8.8 md
	A. Fluid; Fre	esh Water with: No Surfactant 3 gal. Hydrocarbon Surfactant/1000 gals. (Nonionic) 3 gal. Fluorocarbon Surfactant/1000 gals. (Cationic)	Folds of Flow Rate Change -1.07 -1.85 +1.04
	B. Fluid; 9	lb. Brine with: No Surfactant 3 gal. Hydrocarbon Surfactant/1000 gals. (Nonionic) 3 gal. Fluorocarbon Surfactant/1000 gals. (Cationic)	+1.01 0 +1.3
	C. Fluid; 1%	KCl Water with: No Surfactant 3 gal, Hydrocarbon Surfactant/1000 gals. (Nonionic) 3 gal, Fluorocarbon Surfactant/1000 gals. (Cationic)	+1.14 +1.20 +2.0
II.	Formation - H	unton, Central Oklahoma (8700') Permeability	
	A. Fluid; 1%	KCl Water plus: No Surfactant 2 gal. Cationic Fluorocarbon Surfactant/1000 gals. 2 gal. Nonionic Hydrocarbon Surfactant/1000 gals.	Folds of Flow Rate Change -1.16 +1.34 -1.1
	B. Fluid; 15	<pre>% HCl plus: 2 gal. Fluorocarbon Surfactant/1000 gals. 5 gal. Hydrocarbon Surfactant plus 2 gal. Fluorosurfac 1000 c</pre>	+1.16 ctant/ +1.16
		No Surfactant	+1.01
III	. Formation -	Lower Albany Dolomite (3000') Hutchinson Co., Texas	
	A. Fluid; Fr	esh Water with: No Surfactant 3 gal. Hydrocarbon Surfactant/1000 gals. 3 gal. Fluorocarbon Surfactant/1000 gals.	Folds of Flow Rate Change -1.4 -0.8 +1.3
	B. Fluid; 1%	6 KCl Water plus; No Surfactant 3 gal./1000 Hydrocarbon Surfactnat/1000 gals. 3 gal./1000 Fluorocarbon Surfactant/1000 gals.	-1,1 +0.5 +1.5
	C. Fluid; 7	% HCl plus: 5 gals. Nonionic Hydrocarbon Surfactant/1000 + 3 gals Fluorocarbon Surfactant/1000 gals.	. +8.2
		3 gals, Hydrocarbon Surfactant/1000 + 2 gal. Fluoroca 1000 gals.	rbon/ +2.1
		3 gals./1000 Fluorocarbon Surfactant/1000 gals. 5 gals Nonionic Hydrocarbon Surfactant/1000 gals.	+1.6 +1.7
	D. Fluid; 15	% HCl 2 gals. Fluorocarbon Surfactant/1000 gals. 2 gals. Nonionic Hydrocarbon Surfactant + 2 gals. Fluorocarbon Surfactant/1000 gals.	+1.93 +12.8
		5 gals. Nonionic Hydrocarbon Surfactant/1000 gals.	+2.2

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A conventional hydrocarbon surfactant can be represented as in Figure 2, with the $R_{H.}$... symbolizing the hydrocarbon tail and ... x representing a solubilizing group. In Figure 3, fluorochemical surfactants can be represented by an $R_{F.}$.. or fluorocarbon tail, and ... x again as a solubilizing group. It is the unique fluorocarbon "tail," modified in length and structure, which provides exceptional resistance to thermal and chemical degradation — the weaknesses of most other surfactant types.

This fluorocarbon portion of each fluorochemical surfactant is responsible for its ability to dramatically reduce surface tension. The solubilizing "head" group, . . . x, is commonly water-soluble, but can be designed for oil solubility when associated with non-aqueous systems. The anionic, cationic, nonionic, or amphoteric nature is also provided by the solubilizing "head." By the alteration of the "head" group of a fluorochemical surfactant (hereafter referred to as "F.S."), surfactants have been prepared which possess high surface activity in a number of environments, including many systems (strong acids, alkalines, H_2S , high salinity, and high alkalinity) which would degrade or render less efficient many hydrocarbon or silicone surfactants.⁴

The presence of fluorine in the hydrophobic portion of a surfactant molecule is of major significance. This occurs when most of the hydrogen atoms have been replaced by fluorine atoms (3M-Simons Electrofluorination) so that the hydrophobic group is a fluorocarbon. The work of many investigators has shown that the fluorocarbon groups - CF₂, CF₃ and polymerized tetrafluoroethylene $(C_2F_4)_N$ —form surfaces of very low free energy, considerably lower in fact than the free energy of hydrocarbon surfactants. Molecules of these compounds can become oriented along interfacial boundaries to achieve unusual surface effects at low concentrations.

Just as a variety of conventional hydrocarbon surfactants are used for a variety of applications, so are a variety used in the fluorochemical family. In most systems F.S. are far more efficient in reducing surface tension to levels that are lower than conventional surfactants. In many aqueous systems, air-liquid surface tensions as low as 15-16 dynes/cm. can be obtained. Fluorochemical surfactants are used which can produce these extremely low values at concentrations as low as 20 parts per million.⁸

Wettability of a variety of surfaces (i.e., metals, carbonate rocks, sandstones, dolomites, etc.) in the oilfield is an important function for a surfactant solution. Wettability using F.S. or a blend of F.S. and hydrocarbon surfactants is usually excellent, as it is a function of low surface tension in many cases. The blend often provides a wetting action not achieved by either portion alone. This superior blend activity is referred to as synergism. Normally in a blend, the F.S. reduces the surface tension (airliquid) while the hydrocarbon portion reduces the interfacial tension (liquid-liquid).⁸ The net result can produce a system which wets and spreads on an otherwise hard-to-wet surface. Improvements in corrosion inhibitors, scale inhibitors, polymer adsorption, particle suspenders, and clay-stabilizing agents can be realized by this increased activity. Outside the realm of stimulation, the fields of secondary- and tertiary-recovery efficiency can be enhanced by this blend synergism in many instances, providing either improved injectivity or oil recovery.

CURRENT F.S. APPLICATIONS IN A VARIETY OF FLUIDS

Acid-fracturing, particularly in low permeability sandstone reservoirs, has been a proving ground for F.S.^{5, ϕ} A cationic F.S. has been used most successfully both as an individual additive prepared with a special blend of co-solvents, or as a synergist in combination with other hydrocarbon surfactants (i.e., an improved agent with increased acid and oil tolerance).

The cationic material most often used belongs to the F.S. family of fluorinated alkyl quaternary ammonium iodides. In aqueous media, this material provides superior surface-tension-lowering qualities compared to other additives. The concentration level required to produce this low surface tension is only a 0.0042 percent solution or 42 ppm F.S. This concentration is made in a co-solvent blend to improve solubility and elminate adsorption loss. This requires the 42 ppm to be added in a solution strength of 1.5 to 3 gallons per 1,000 gallons of acid or treatment fluid.

Table 2 shows this cationic F.S. blend in a variety of fluids and the resultant surface tension reduction. All measurements were made on a DuNouy

		<u>Blend A</u>				<u>Blend B</u>						
		<u>Cationic Fl</u>	uorochemi	ical Bler	nd gal./1	1000	Noni	onic Eth	oxylated	Nonylph	enol gal./	1000
Fluids:			1	3	5	<u>10</u>	0	1	3	5	10	
a.	Fresh Water	72	24	18	16.5	14	72	38.8	37.8	37	31.5	
b.	1-3% Hydrochloric Acid	74	25	17	17	17	74	38.4	36.9	36	30	
c.	5-7.5% Hydrochloric Acid	75	28	18	17	17	75	38.6	37.0	34	32	
d.	15-20% Hydrochloric Acid	75	26.5	18	17	17	75	39	38.5	36.5	33.5	
e.	28-35% Hydrochloric Acid	76	29	20	17	17	76	40	39	38	35	
f.	3-15% Spent HC1 Acid	76	47	45	25	21	76	41	39	38.2	36	
g.	15-28% Spent HC1 Acid	76	49	47	27	21	76	43	40	39	37	
h.	1-2% KCl Water	74	25	19	18	17	74	37.5	37	36	29	
i.	9-10 lb Brine	75	25,5	24.5	18	17	75	38.5	38	36	33	
j.	3% HC1 + 0.6% HF	73	22	18	17	17	73	38.2	37.7	37.5	32	
k.	Spent 3% HC1 + 0.6% HF	76	59	34	25	21	76	60	54	49	40	

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tensiometer at room temperature. Increased temperature and pressure often result in even lower values. It should be noted that there is excellent reduction of surface tension in a *variety* of fluids. As a comparison, a good nonionic ethoxylated nonylphenol type surfactant is shown with the cationic F.S.

1. Water plus 1 gal./1000 Surfactant B 38.8

ADSORPTION

Although adsorption principles are the same for F.S. as for any other type of surfactant, both field and laboratory data have shown that the usual adsorptive losses with cationic materials in surfactants are not realized with F.S. as with hydrocarbon or silicone cationics. The exact nature of this lack of adsorption loss is not fully understood, but has been demonstrated by flow tests through laboratory sand packs as shown in Table 3. In these tests, 200 cc of fluid containing four (4) gallons of surfactant per 1,000 gallons total were flowed through a 15 inch high, 3.5 inch diameter sand pack 100 mesh sand. Surface tensions were measured to show the change in the surface activity of the solution before and after flow. Field measurements taken after using treating fluids in large fluid volumes designed for formation penetration have shown that with F.S., relatively

low surface tensions are present after flowing back high volume percentages of load fluid, as compared to hydrocarbon surfactants. Data comparable to that in Table 2 was obtained after flowback of 50,000 gallons of load water in less than 4 days out of a total treatment volume of 62,000 gallons in the troublesome Canyon Sand formation of Sutton County, Texas. Tests with hydrocarbon surfactants have usually shown a small, but ill-afforded loss in surface activity of returned load fluids. Although many nonionic hydrocarbon surfactants show low percentage losses in activity, their starting surface tensions were often too high (over 35 dynes/cm) to be effective in low permeability situations. (See Table 2, blend "B").

COREFLOW TESTS

Adsorption losses can be considered most significant with respect to the location at which they occur in the reservoir. If surfactant adsorption or plate-out is significant, it will occur gradually as fluid either penetrates the reservoir matrix, leaks off away from a fracture face of travels back through a sand pack. The further the travel, the greater loss of imbibition or saturation-fighting surface activity by the fluid. Thus a fluid with planned effectiveness in surfactant design loses that effectiveness when it is

TABLE 3—ADSORPTION TESTS IN A 15-INCH LONG, 3.5-INCH WIDE, 100 MESH SANDPACK AT 100°F AND 500 PSIG., CHANGE IN SURFACE TENSION

Blend A: Fluorochemical	Surfactant (Cationic)	Surface Tension Before	Surface Tension After	Change
Conc. gal./1000	Fluid	dynes/cm.	dynes/cm.	dynes/cm.
3	Fresh Water	18.0	30.0	15.0
5	Fresh Water	16.5	24.0	7.5
3	15% HC1	18.0	29.0	11.0
5	15% HC1	17.0	26.5	9.5
3	9 lb. Brine	24.5	38.0	13.5
5	9 lb. Brine	18.0	31.0	13.0
3	2% KCl Water	19.0	37.5	18.5
5	2% KCl Water	18.0	29.5	11.5
3	Spent 15% HC1	45.0	47.0	2.0
5	Spent 15% HCl	25.0	29.0	4.0
3	Spent 3% HCl + 0.6% HF	34.0	38.0	4.0
5	Spent 3% HCl + 0.6% HF	25,0	28.0	3.0
Blend B: Ethoxylated M Conc. gal./1000	lonylphenol (Nonionic) Fluid	Surface Tension Before dynes/cm.	Surface Tension After dynes/cm.	<u>Change</u> dynes/cm.
3	Fresh Water	37.8	41.0	3.2
5	Fresh Water	37.0	40.2	3.2
3	15% HCl	38.5	58.0	19.5
5	15% HC1	36.5	56.5	20.0
3	9 lb. Brine	38.0	48.0	10.0
5	9 lb. Brine	36.0	46.0	10.0
3	2% KC1	37.0	43.0	5.0
5	2% KC1	36.0	41.8	5.8
3	Spent 15% HCl	39.0	48.0	9.0
5	Spent 15% HCl	38.2	45.6	7.4
3	Spent 3% HCL + 0.6% HF	54.0	60.0	6.0
5	Spent 3% HCl + 0.6% HF	49.0	57.5	8.5

most needed. It is lost at the farthest point of penetration or in the smallest pores of the reservoir where capillary holding action is greatest. Lost effectiveness in this vicinity can mean lost permeability and subsequent poor load recovery after stimulation, and even poor return of production if not, in fact, a lower-than-expected return of production.

F.S. have shown superior activity in allowing particular fluids to be more compatible with certain types of reservoirs. Formation damage from fluids via some form of saturation or capillary imbibition mechanism has probably caused innumerable cases where, in spite of excellent treating fluid design, the compatibility of that fluid with respect to surface activity was not considered, and the excellent fluid design was offset by improper or interior surfactant design.

Tables 1 and 4 show coreflow tests which document comparisons of using various types of surfactants and the resultant damage, improvement or even lack of damage in these particular formations.

Coreflow tests are run according to procedures

used in previous investigation.⁶ A brief summary is included below:

PROCEDURE

Coreflow tests are run by subjecting 1-inch x 1-inch cylindrical core-plugs to the flow of a reference fluid (white oil or kerosene in an oilbearing core, and hexane or nitrogen in a gas section core) and a test fluid. Tests are run at approximate bottom hole temperatures with 1000 psi pressure applied to an "ampcoloy" flow chamber.

The sequence of reference fluid and test fluid flow is as follows:

- 1. Reference fluid in a production direction (†)
- 2. Test fluid in an injection direction (1)
- 3. Test fluid in a backflow or load recovery direction (†)
- 4. Reference fluid in a production direction (†)

In each case, the time to flow 100 cc of fluid is recorded (if possible), and a comparison is made between the initial and final reference fluid flow to determine the multiple changes of rate increase or decrease.

b

Most of these cores are from areas where fluid damage in the formation has been well documented. Damage, which in many cases has been attributed to fines or particulate matter, may have been in only a small percentage of the total formation. More often than not, damage from improper surfactant design may have been the case in which materials were used that either failed to provide enough surface active power, or surface activity was severely impaired by contamination or loss due to excessive adsorption onto reservoir rocks. As previous reports have stated, many conventional hydrocarbon surfactants can provide surface tension reduction of only 28-38 dynes/cm. This has proven to be virtually ineffective in fighting possible damage from imbibition or saturation in low permeability (0.1-10.0 md) situations. Even the often-used and highly recommended alcohols can produce surface tension reductions of only 23 dynes/cm at uneconomical concentrations of 100 volume percent. Economical blends of alcohols and aqueous systems can provide surface tension reduction to only about 35-45 dynes/cm at 25-50 percent by volume. Figure 4 illustrates the various surface tensions acquired by



FIGURE 4

using varying concentrations of alcohol vs. a commercially used anionic quaternary amine, and the cationic F.S.

Surface tension reduction simply for the sake of reduction is not the goal with these F.S. materials, The fluorochemical activity is emphasized as a means of designing a surfactant or surfactant system which will improve or enhance the 14 applications reviewed earlier in this paper. It is not the purpose of this discussion to delve into the surface chemistry intricacies of these materials, but rather to point out the usefulness of F.S. and blends incorporating F.S. as being an economical method of providing excellent surface activity. Oilwell technology has more challenging and complex questions than ever before. Materials such as these fluorochemical surfactants have and should continue to provide a more efficient product to remedy many problems with the applications mentioned at the beginning of this paper. Fluorochemical blends are economically competitive with hydrocarbon blends, and, in fact cheaper, if activity and stability are considered. Their successful use has been documented in all the formations listed in Table 4.

SUMMARY

Fluorochemical surfactants have long been useful in providing superior products and superior applications in various non-oilfield related industries.

Wherever chemical resistance in instances such as high salinity, hardness, high or low pH, and oxidizing or reducing systems is required, fluorochemical surfactants can outperform almost any commercial hydrocarbon surfactant. Wherever thermal resistance (up to 600° F in many cases) is required, fluorochemical-based surfactants are again without peer in their effectiveness.

Acidizing systems, particularly low-pH systems designed for low-permeability sandstone reservoirs, have been the proving ground for increased treatment successes allowed when fluorochemical surfactants are used. They provide low surface tension for load recovery, enhanced corrosioninhibitor wetting, foaming power, and possible claystabilizing characteristics from the commonly used cationic, polyfluoro material. This combination of applications is seldom realized in many hydrocarbon surfactants.

TABLE 4---COREFLOW TESTS IN CARBONATE ROCK (FOLDS OF FLOW RATE CHANGE AT 1000 PSIG.@ 25°C. WITH 100 CC.

т	For	mation - Delaware West Texas (5800')					
1.	A.	Fluid; P_2 % HCl plus:	Folds of Flow Rate Change				
		 3 gals. Hydrocarbon Surfactant/1000 gals. 	-6.54				
		2. 3 gals. Fluorocarbon Surfactant/1000 gals.	-2.10				
		3. NO SUFFACTANT	Plugged				
	В.	Fluid; 3% HCl + 1.2% HF plus:					
		 3 gals, Hydrocarbon Surfactant/1000 gals, 	+2.14				
		2. 3 gals. Fluorocarbon Surfactant/1000 gals.	+5.63				
		3. No Surfactant	+2,26				
	ſ	Fluid: 3% HCl nlus.					
	•••	1. No Surfactant	Plugged				
		3 gals. Hydrocarbon Surfactant/1000 gals.	-4 .85				
		3 gals. Fluorocarbon Surfactant/1000 gals.	-1.88				
T T	For	mation Canvon Host Toxas (57001)					
11.	Δ.	Fluid: 1% KCl Water nlus.					
		1. 5 gals. Nonionic Hydrocarbon Surfactant/1000 gals.	-1.14				
		2. 3 gals. Cationic Fluorocarbon Surfactant/1000 gals.	+1.52				
		3. No Surfactant	Plugged				
	n						
,	в.	1 No Surfactant	-2.74				
		2. 3 gals, Cationic Fluorocarbon Surfactant/1000 gals.	+6.00				
		3. 5 gals. Nonionic Hydrocarbon Surfactant/1000 gals.	-1.33				
	_						
111	. +0	rmation - Morrow, Eddy Co., New Mexico (11,000')	Folds of Flow Pate Change				
	А.	I No Surfactant	-3 02				
		2. 3 gals. Fluorocarbon Surfactant/1000 gals. (Cationic)	+1.75				
		3, 5 gals. Anionic Surfactant/1000 gals.	-1.06				
	_						
	Β.	Fluid; /% HCI plus:	-3.05				
		2 3 gals Eluorocarbon Surfactant (Cationic)/1000 gals.	+13.0				
		3. 5 gals. Anionic Surfactant/1000 gals.	+10.0				
	C.	Fluid; 3% HCl + 0.6% HF plus:	- 04 - 70				
		1. 3 gals. Fluorocarbon Surfactant/1000 gals, (Lationic)	+24.72				
		3. 5 gals. Anionic Surfactant/1000 gals.	+7.04				
IV.	IV. Formation - Morrow, Texas Co., Oklahoma (6135')						
	А.	1 No Surfactant	-1.05				
		2. 3 gals. Fluorocarbon Surfactant/1000 gals. (Cationic)	+1.42				
		3. 5 gals, Nonionic Hydrocarbon Surfactant/1000 gals.	-1.46				
	~						
	в.	riula; /½% HUI plus:	+1 02				
		2. 3 gals, Eluorocarbon Surfactant (Cationic)/1000 gals	+8,54				
		3. 5 gals. Hydrocarbon Surfactant (Nonionic)/1000 gals.	+2,26				
	с.	Fluid; 3% HCl + 0.6% HF plus:	T1 01				
		1. NO SURTACIANI 2 3 gale Elyonocarbon Surfactant (Cationic)/1000 gale	+2 56				
		3. 5 gals. Nonionic Hydrocarbon Surfactant/1000 gals.	+1.98				

TABLE 4 (cont.)

V. Formation - Cleveland Sand - Ochiltree Co., Texas (6850')

	Α.	Fluid; 3% HCl plus:	Folds of Flow Rate Change
		 No Surfactant 3 gals. Cationic Fluorocarbon Surfactant/1000 gals. 3 gals. Nonionic Hydrocarbon Surfactant/1000 gals. 	-1.02 +1.75 -1.42
	B.	Fluid; 7½% HCl plus: l. No Surfactant 2. 3 gals. Fluorocarbon Surfactant (Cationic)/1000 gals. 3. 5 gals. Nonionic Hydrocarbon Surfactant/1000 gals.	-3.01 +10.43 +2.46
	C.	Fluid; 3% HCl + 0.6% HF plus: l. 3 gals. Fluorocarbon Surfactant Cationic/1000 gals.	+2.95
	D.	Fluid; 12% HCl + 3% HF plus: l. 3 gals. Fluorocarbon Surfactant Cationic/1000 gals.	-3.20
VI.	For	mation - Redfork, Central Oklahoma (4500!)	
	Α.	Fluid; 3% HCl plus: l. No Surfactant 2. 3 gals. Fluorocarbon Surfactant Cationic/1000 gals. 3. 3 gals. Hydrocarbon Surfactant Nonionic/1000 gals.	-2.55 -1.86 -1.55
	Β.	Fluid; 3% HCl + 0.6% HF plus: l. No Surfactant 2. 3 gals Fluorocarbon Surfactant (Cationic)/1000 gals. 3. 3 gals. Hydrocarbon Surfactant/1000 gals.	+2.45 +5.42 -2.10
	C.	Fluid; 1% KCl plus: 1. 3 gals. Hydrocarbon Surfactant Nonionic/1000 gals. 2. 3 gals. Fluorocarbon Surfactant/1000 gals. 3. No Surfactant	+1.14 +1.85 -1.40

Coreflow tests have proven valuable as aids in showing the application of these surfactants in relation to those conventionally used. Compatibility with hydrocarbons, either oil or gas, as well as produced waters has been shown as adequate and no problems have arisen which might show that fluorochemical surfactants are detrimental in any way to refinery processes. In fact, the particular fluorochemical group discussed here, the cationic fluorinated quaternary ammonium iodide, is extremely oleophobic ("oil hating") and is not carried even in small quantities by the hydrocarbons produced. Α partial listing of numerous fluorochemical species with comments on their application is summarized in Table 5. Investigation is continuing into unlocking the numerous potential uses of these and other fluorochemical species either as individual agents or in blends with many of our

already-proven hydrocarbon materials. Toxicity is within safe limits with most of these materials.

The ever-increasing problems of oil recovery and associated expenses are ample justification to carefully investigate and use these highly efficient Fluorocarbon stability compounds. under conditions of harshness, not unlikely to be found in the oilfield (i.e., pH changes, salinity changes, pressure, temperature, bacteria, etc.) is perhaps the secret to the successful potential of F.S. Many of our present-day hydrocarbon systems are often limited by sensitivity to various oilwell environments. The real fact that stimulation fluids are in every way associated with a variety of changing surfaces, and surface conditions make the unique and highly active fluorocarbon species useful in improving the previously-mentioned applications in oil and gas well stimulation.

TABLE 5—FLUOROCHEMICAL SURFACTANTS: A BASIC GUIDE

TYPE	DESCRIPTION OF CHEMISTRY	COMMENTS AND USES
Anionic	Ammonium perfluoroalkyl sulfonates	Excellent chemical and thermal stability. Active in acidic and alkaline systems.
Anionic	Potassium perfluoroalkyl sulfonates	Outstanding chemical and thermal stability, especially in acidic and oxidizing systems.
Anionic	Potassium perfluoroalkyl sulfonates	Outstanding chemical and thermal stability, especially in acidic and oxidizing systems.
Anionic	Potassium fluorinated alkyl carboxylates	Excellent levelling agent in alkaline systems. Good foamer.
Cationic	Fluorinated alkyl quaternary ammonium iodides	Outstanding activity in acid solutions. Excellent in basic and neutral solutions.
Anionic	Ammonium perfluoroalkyl carboxylates	Effective emulsifier for fluorocarbon systems. Excellent chemical stability.
Nonionic	Fluorinated alkyl polyoxyethylene ethanols	Excellent activity in neutral and acid solutions.
Nonionic	Fluorinated alkyl esters	Active in organic polymer coatings. Effective in some aqueous systems.
Nonionic	Fluorinated alkyl esters	Active in organic polymer coatings. Effective in some aqueous systems.
Nonionic	Fluorinated alkyl esters	Active in low polarity organic solvents. Foams hydrocarbon liquids.

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