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**TOPICAL REPORT: Screening Methods for
Selection of Surfactant Formulations for IOR
from Fractured Carbonate Reservoirs**

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ABSTRACT

This topical report presents details of the laboratory work performed to complete Task 1 of this project; developing rapid screening methods to assess surfactant performance for IOR (Improved Oil Recovery) from fractured carbonate reservoirs. The desired outcome is to identify surfactant formulations that increase the rate and amount of aqueous phase imbibition into oil-rich, oil-wet carbonate reservoir rock. Changing the wettability from oil-wet to water-wet is one key to enhancing this water-phase imbibition process that in turn recovers additional oil from the matrix portion of a carbonate reservoir.

The common laboratory test to evaluate candidate surfactant formulations is to measure directly the aqueous imbibition rate and oil recovery from small outcrop or reservoir cores, but this procedure typically requires several weeks. Two methods are presented here for the rapid screening of candidate surfactant formulations for their potential IOR performance in carbonate reservoirs. One promising surfactant screening protocol is based on the ability of a surfactant solution to remove aged crude oil that coats a clear calcite crystal (Iceland Spar). Good surfactant candidate solutions remove the most oil the quickest from the chips, plus change the apparent contact angle of the remaining oil droplets on the surface that thereby indicate increased water-wetting. The other fast surfactant screening method is based on the flotation behavior of powdered calcite in water. In this test protocol, first the calcite powder is pre-treated to make the surface oil-wet. The next step is to add the pre-treated powder to a test tube and add a candidate aqueous surfactant formulation; the greater the percentage of the calcite that now sinks to the bottom rather than floats, the more effective the surfactant is in changing the solids to become now preferentially water-wet. Results from the screening test generally are consistent with surfactant performance reported in the literature.

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DOE Project: DE-FC26-04NT15521

Topical Report June 2005

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1.0 EXECUTIVE SUMMARY

This topical report presents details of the laboratory work performed to complete Task 1 of this project; namely developing rapid screening methods to assess surfactant performance for IOR (Improved Oil Recovery) from fractured carbonate reservoirs. The desired action is to have the chemical (surfactant) additive increase the rate and amount of aqueous phase imbibition into oil-rich, oil-wet carbonate reservoir rock, and thereby displace some of the oil normally still trapped in place after a conventional waterflood. A key to improve the rate of water imbibition is to have the surfactant change the mineral surfaces from an oil-wet to a water-wet condition. The normal laboratory test to mimic the field process measures the aqueous imbibition rate and oil recovery from small outcrop or reservoir cores, but this is a very time consuming procedure.

Two methods are presented here for the rapid screening of candidate surfactant formulations for their potential IOR performance. One promising surfactant screening protocol is based on the ability of a surfactant solution to remove aged crude oil that coats a clear calcite crystal (Iceland Spar). Good surfactant candidate solutions exhibit the greatest and fastest removal of oil from the calcite chip, plus change the apparent contact angle of the remaining oil droplets on the surface so as to indicate a more water-wet condition. Screening tests were performed both with a heavy crude oil from the San Joaquin Valley and a light oil from McElroy Field, a major carbonate field in the Permian Basin. This technique was used successfully to screen almost 250 different surfactants. The observations from this surfactant screening test are largely consistent with the oil recovery performance results reported in the literature.

The other fast surfactant screening method is based on the flotation behavior of powdered calcite in water. In this test protocol, first the calcite powder is pre-treated to make the surface oil-wet. The next step is to add the pre-treated powder to a test tube and add a candidate aqueous formulation and shake the suspension. The calcite powder that is still oil-wet stays at the top of the water column. The greater the percentage of the calcite that now sinks to the bottom rather than floats, the more effective the surfactant is in changing the solids to become now preferentially water-wet. Those surfactant solutions that are efficient in altering the wettability to a water-wet condition are then better candidates for further testing as agents to promote rapid imbibition of an aqueous phase into oil-saturated carbonate porous media.

2.0 INTRODUCTION

The goal of this ongoing project is to develop cost-effective chemical formulations that will recover incremental oil beyond a waterflood operation from carbonate reservoirs. About 80% of carbonate reservoirs are classified as neutral to oil-wet (Standnes and Austad, 2002), and an oil-wetting condition is even more likely to be the case in cooler, more shallow reservoirs (Austad and Standnes, 2000). The particular target for this improved technology is large, domestic carbonate reservoirs that are at a mature point in their waterflood operations, most especially those that are fractured reservoirs and with the matrix blocks in an oil-wet state. For such reservoirs, the waterflood is usually very inefficient, in part, because the injection water can not imbibe into the porous, matrix blocks due to their oil-wet condition.

Adding the right surfactants to the injection water will change the wettability of the carbonate reservoir surfaces to a water-wet condition and decrease the interfacial tension (IFT) so as to increase the penetration of the injected aqueous phase into the rock matrix holding trapped oil. The oil forced out of the oil-rich matrix blocks due to the imbibition of the aqueous (chemical) solution then is forced into the fracture/high permeability network. These flow networks act as a “highway” to convey the newly mobilized oil to a production well. If properly designed, this process will increase significantly the recovery of this oil otherwise not recovered by a conventional waterflood.

The conventional procedure to evaluate candidate surfactant solutions is to immerse an outcrop or reservoir core sample high in oil saturation into a container (Amott cell) containing a surfactant solution held at reservoir temperature (Austad and Standes, 2002, Chen, 2000, Hirasaki, and Zhang, 2004, Seethpalli, 2004). The amount of oil produced moves into a graduated burette attached to the top of the container. The oil recovered is monitored versus time; of course the greater the volume and the faster the oil produced, the better the surfactant performance. This test has the advantage of being a fair physical analog to the actual field conditions, but a major disadvantage is that the time required to perform this test (requires several days or even weeks).

The objective of Task 1 of this project is to develop rapid screening methods to evaluate quickly and conveniently candidate surfactant formulations for their potential performance as IOR agent for fractured carbonate reservoirs. This report summarizes the procedures and results of two such rapid screening test methods.

3.0 FAST METHODS FOR CHEMICAL FORMULATION SCREENING

3.1 Calcite Chip Screening Method to Evaluate Surfactant Performance for Changing Carbonate Mineral to Become Water-Wet

3.1.1 Procedure for Calcite Chip Screening Method

The developed test procedure and the rationale for these procedures are:

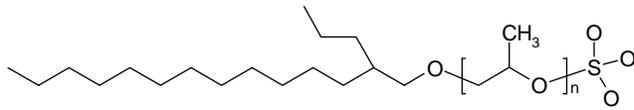
1. Select clear calcite crystals (Iceland Spar), roughly ½” on each edge. These calcium carbonate crystals come from Ward’s Natural Science (Catalog 46-1437), and are attractive for this screening test program because they are inexpensive and are clear with flat smooth sides. This means it is easy to see where the oil is removed from the surface, and to observe and estimate the contact angle of the oil drops that remain on the surface.
2. Soak the crystals in warm (80 °C) crude oil. This will render the surface oil-wet and provide a target for removal by candidate chemical formulations. The heavy crude selected comes from Midway-Sunset Field (identified as Fee oil) located in the San Joaquin Valley (SJV), and was supplied by Chevron. This heavy oil is typical of that located in shallow sandstone formations and that are produced by steam flood projects in SJV. It has a relatively high viscosity and significant asphaltene and naphthenic acid content (has a high acid number of approximately 4). In this test the oil covers the calcite crystal completely and forms a layer of “sticky” oil that wets the surface well and adheres to the crystal. The concept is that this heavy, high acid number oil provides a more difficult screening test than with a chip coated with lighter oil. For the heavy oil the chips were aged for one day. Fewer, similar tests were performed with the McElroy crude oil; some of these calcite chips were aged with McElroy crude oil for only one day and some for one week.
3. Pick out a single crystal with a pair of tweezers and let the excess hot oil drain off. Place the crystal into a small bottle containing 20 grams of surfactant solution. Our default conditions are 0.1 wt% (active) of surfactant in a synthetic brine (2 wt% NaCl, with 20 ppm of calcium). Some tests involving McElroy oil used a synthetic McElroy brine as the make-up water for surfactant solutions (see table below).

Table 1. Recipe for McElroy Field synthetic field brine:

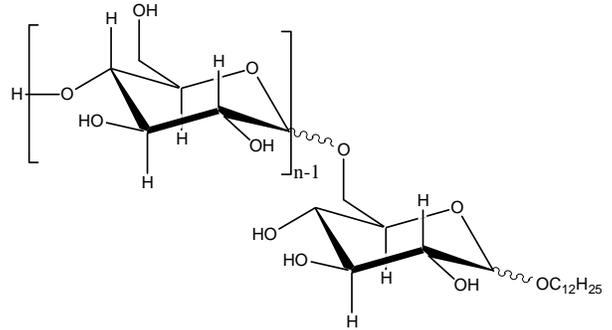
<u>Salt</u>	<u>mg/l</u>	<u>Ion</u>	<u>mg/l</u>
NaCl	20000	Na	8838
Na2SO4	2950	Ca	1197
CaCl2.2H2O	4400	Mg	400
MgCl2.6H2O	3350	SO4	1000
NaHCO3	70	Cl	18835
TDS	30770	HCO3	51

4. Monitor at room temperature the appearance of the crystal versus elapsed time (e.g. 8 hours, 1 day, 3 days, 1 week, 1 month and 2 months). In particular, note the percent of the crystal surface that is cleared of oil and visible, and also estimate the contact angle of the remaining oil drops on the crystal surfaces. Note by our convention 0° refers to the oil drop spreading on the surface (completely oil-wet) and 180° refers to the oil not wetting the calcite crystal. Also observe if the bulk aqueous solution remains clear or discolored, thereby indicating some of the oil is solubilized into the surfactant solution, and if there is floating crude oil visible on top of the aqueous phase (indicates removal of some crude as free oil from the calcite chip).

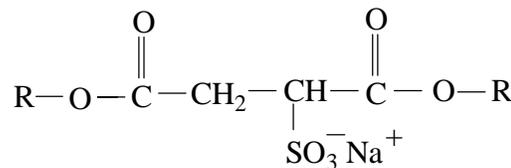
The figure below provides chemical structure information for many of the products tested with the screening tests.



Branched alkyl propoxylated sulfates (Alfoterra)

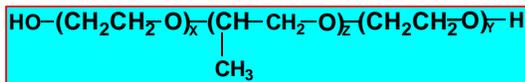


alkyl polyglycoside (APG)



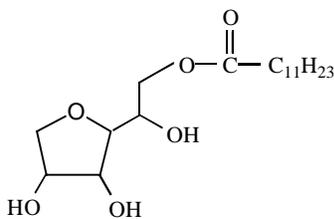
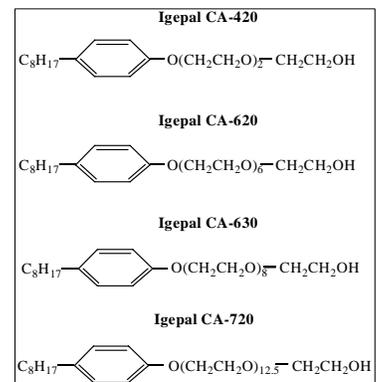
Sulfosuccinate Surfactant (Aerosol Series)

Aerosol MA-80 R = branched C6 Aerosol OT-B R = branched C8
 Aerosol TR-70 R=linear C13

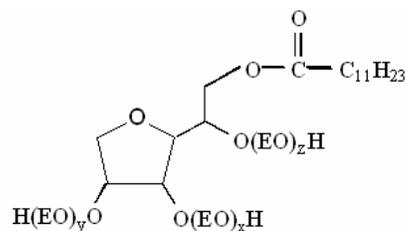


Pluronic block co-polymers of EO – PO – EO

Examples of Igepal series of surfactants (octyl- and nonyl-phenol ethoxylates)



Example of SPAN surfactant (SPAN 20)

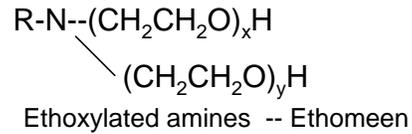


Example Structure of Tween Surfactants



Ethoxylated alcohols -- NEODOL series R straight alkyl chain

$R-NH-CH_2-CH_2-CH_2-NH_2$
Tertiary amines – Doumeen series



$R-N^+(CH_3)_3 Cl^-$
Quaternary ammonium chloride– Arquad series

Figure 1. Chemical Structure of Selected Surfactants

3.1.2. Results/Discussion - Calcite Chip Screening Method – Heavy Oil

The photographs below illustrate the test procedure and observations used to evaluate the surfactant solution performance.



Figure 2. (Left) -- calcite crystal initially coated with a heavy oil and immersed in a surfactant solution
(Right) - calcite crystal after several weeks exposure to an efficient surfactant. Almost all of the surface of the crystal is visible.



Figure 3. Photograph of calcite crystal after being submerged in an efficient surfactant solution for one month. Note the blob of oil leaving the surface and oil on top.

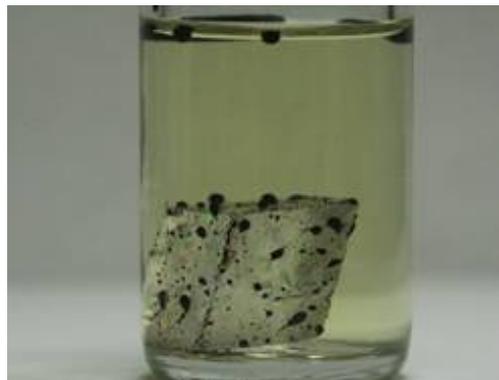


Figure 4. Photograph showing a calcite crystal with only a few drops of heavy crude oil still on the surface. The contact angle of the oil droplets are estimated by eye.

The graph immediately below shows an example of the data collected for each of the surfactant solutions versus time. As expected, the percent of the area cleaned and the increase in contact angle of the oil droplets remaining on the surface both increase with length of exposure.

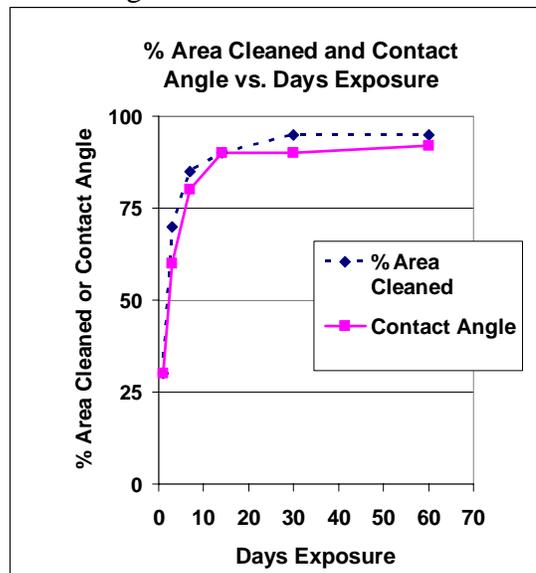


Figure 5. Example of raw data collected -- response for a Neodol 25-3 (nonionic ethoxylated alcohol) surfactant solution.

Appendix A has a complete list of the surfactant-cleaning results for calcite chip results with the heavy oil pre-treatment.

Data trends observations:

1. There is a rough correlation between the percent of the area cleared of heavy oil and the estimated contact angle of the oil remaining on the crystal. See the figure below. It would be expected that surfactant solutions that clean the crystal surface also are acting to increase the

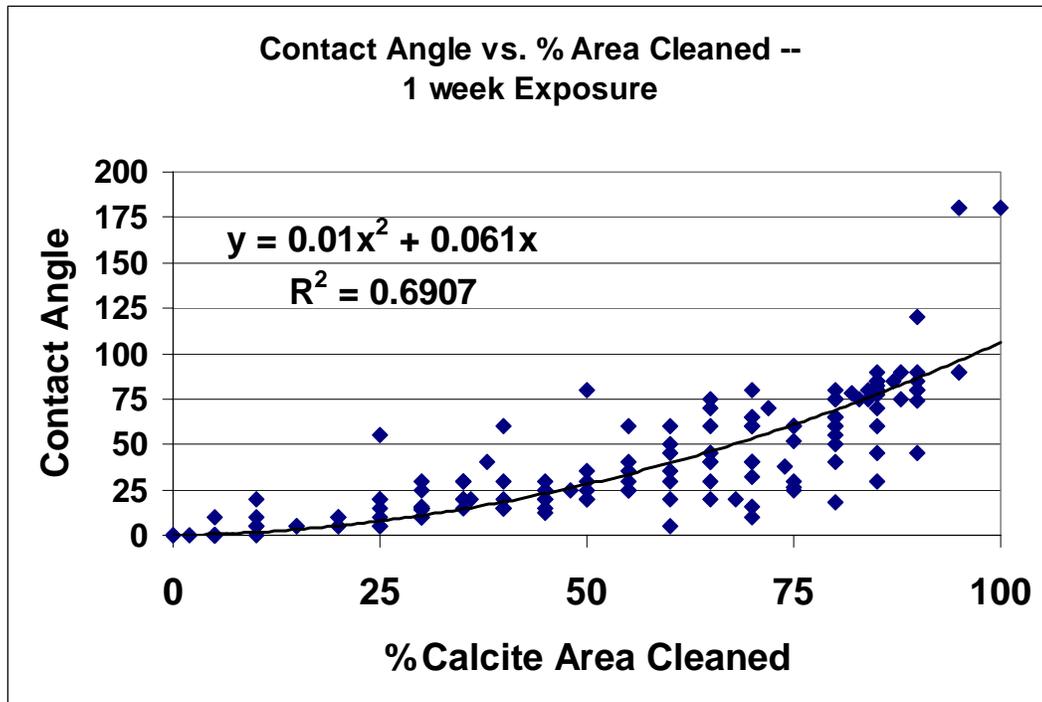


Figure 6. Correlation between contact angle of oil remaining and the percent of the calcite crystal area cleaned.

oil contact angle (decrease the oil-wetting). Those chemical systems that both clean the surface and change the contact angle the fastest are judged to be have the best performance. Some (nonionic) surfactant solutions had the effect of cleaning the surface quickly, but created only a modest increase in oil contact angle. A lesser change in the contact angle is thought to be less desirable as this means that larger large blobs of oil can still be attached strongly to the calcite surface, and so this solution would not be expected to be as efficient in displacing oil.

2. The early time results are a good predictor of the relative performance at longer exposure times. That is, the best performing surfactants early on are also among the best much later.

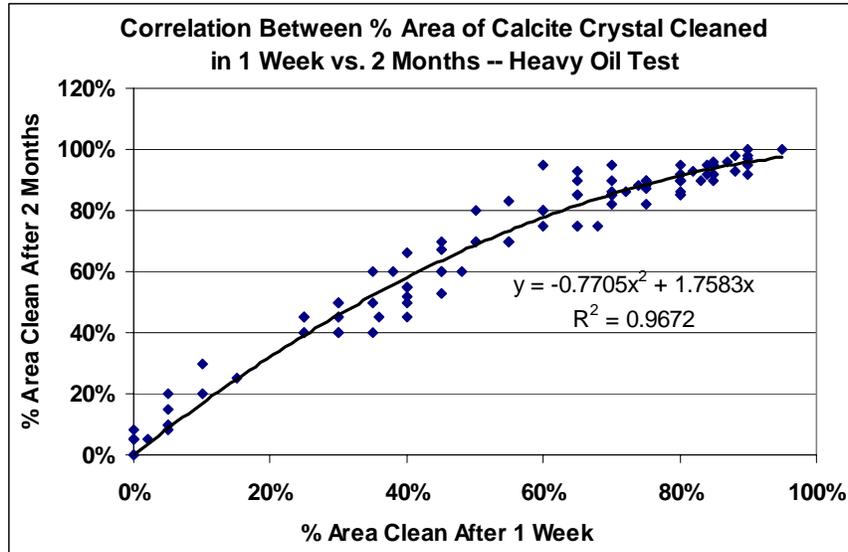


Figure 7. Strong correlation between the percent of cleaning at 1 week and 2 months. The r^2 is 0.967 if using a quadratic fit, and still over 0.9 if restricted to a simple linear fit.

The practical implication of this observation is that one could do this screening test procedure for just one week and arrive at almost the same conclusions regarding the relative performance among the surfactant solutions tested.

2. The trends of surfactant type/structure and their performance found with this screening test are consistent generally with that reported in the literature.

Several authors describe imbibition oil recovery tests where a carbonate core containing crude oil is immersed in a candidate surfactant solution (e.g. Chen, 2000, Seethepalli, 2004, and Standnes, and Austad, 2000). Their results generally match our observations, such as:

- Cationic surfactants can be efficient, but create a strong emulsion effect as evidenced by the aqueous solution becoming dark.
- Nonionic and anionic surfactants generally maintain clear aqueous solutions and the recovered oil floats to the top as a separate phase.
- With the better surfactant systems, the oil is seen to “stream” off the crystal.

More specifically, we find in common with these other studies:

- The “blank” case (no surfactant) shows virtually no oil recovery.
- Cationic surfactants such as the CTAB series (trimethyl, alkyl ammonium salts) with a long alkyl chain length have very good performance.
- The hyamine type of cationic surfactants have poor performance.
- A small number of the branched alkyl propoxylated sulfate anionic surfactants (Sasol manufactures) show good performance.
- SDS (sodium dodecyl sulfate) anionic surfactant has poor performance.
- Several nonionic surfactants (such as from the Neodol series of ethoxylated alcohols) which have been used in successful field experiments) have good performance in our

screening test. We found for our test system that better performance is favored with nonionic surfactants having a HLB ranging 10 – 12.

These common observations provide support for the validity of the simple screening test that we developed here; good and not so good IOR surfactants identified with our simple and fast screening test appear to be consistent with literature data about the same relative performance in the more complicated, but more realistic imbibition oil displacement tests.

3. Other observations about results with heavy oil/calcite chip tests.

Many of the samples used in these screening tests had nonionic surfactants. One general observation was that in these tests samples with a nonionic surfactant having a HLB in the range of 10 – 15 have a better probability of good performance (larger percent of calcite chip surface being cleaned). See the figure below.

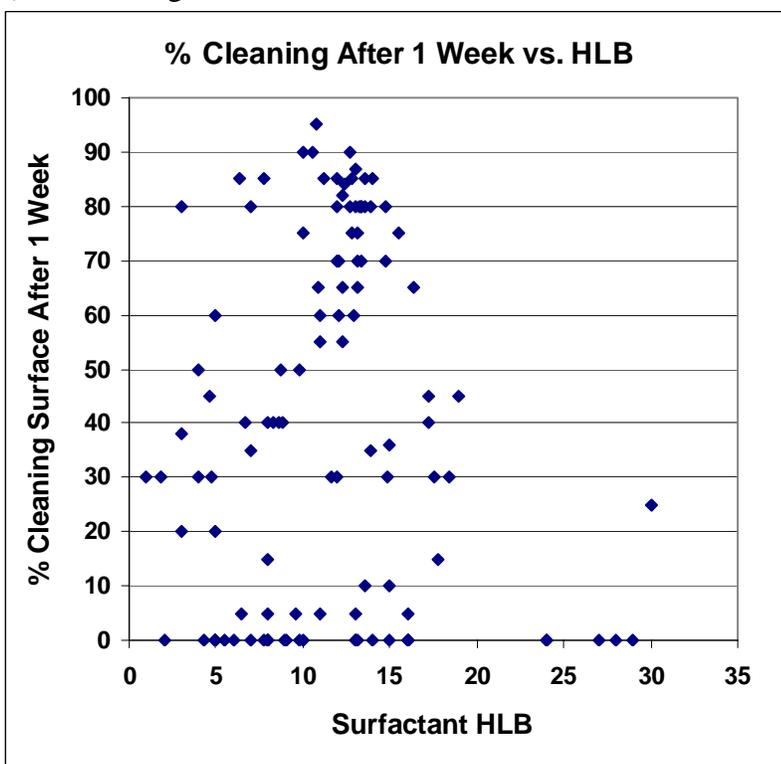


Figure 8. Cleaning efficiency of calcite chip coated with heavy oil versus the HLB of nonionic surfactants tested. Best performance seen with HLB 10 – 15.

These results encompass different types of nonionic surfactants such as alkyl ethoxylated octyl and nonyl-phenols, linear ethoxylated alcohols, secondary alcohol ethoxylated alcohols, alkyl polyglycosides, sorbitan, polyethoxylated thioethers, and block copolymers of polyethylene and ethylene oxides. Results are given below for selected groups of surfactants. Each group of surfactants is sorted from best to worst by the percent cleaning of the calcite chip after 1 week: Most of the tables below include observed chip area cleaned and the estimated contact angle also after 1 month of exposure time.

Table 2. Results for calcite chip cleaning and oil contact angle for Neodol series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	No. Carbons	No. EO	Area% of crystal cleaned		Contact Angle (Degrees)	
							1 wk.	1 mth	1 wk.	1 mth
199	Neodol 1-5	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	11.2	11	5	85%		60	
200	Neodol 1-7	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	12.8	11	7	85%		70	
133	Neodol 25-3	C12-15 linear primary alcohol ethoxylate	Shell Chemicals	7.8	13.5	3	85%	95%	80	90
201	Neodol 1-9	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	13.9	11	9	80%		65	
134	Neodol 1-7	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	12.8	11	7	75%	81%	60	70
132	Neodol 23-6.5	C12-13 linear primary alcohol ethoxylate	Norman, Fox & Co	12.1	12.5	6.5	70%	92%	80	90
136	Neodol 25-7	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	12.3	13.5	7	65%	87%	40	70
204	Neodol 25-9	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	13.1	13.5	9	65%		70	
202	Neodol 23-6.5	C12-13 linear primary alcohol ethoxylate	Norman, Fox & Co	12.1	12.5	6.5	60%		45	
203	Neodol 25-7	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	12.3	13.5	7	55%		25	
198	Neodol 1-3	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	8.7	11	3	50%		80	

No. Carbons – length alkyl chain EO – number ethoxy groups Contact angle - oil on chip

One of these nonionic surfactants has been used in a field test of this process (Chen, 2000).

Table 3. Results for calcite chip cleaning and oil contact angle for Tergitol series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	No. Carbons	No. EO	Area% of crystal cleaned		Contact Angle (Degrees)	
							1 wk.	1 mth	1 wk.	1 mth
107	Tergitol® 15-S-5	C12-C14 secondary alcohol ethoxylate	Union Carbide	10.6	12-14.	5	90%	98%	90	150
108	Tergitol® 15-S-7	C12-C14 secondary alcohol ethoxylate	Union Carbide	12.4	12-14.	7	84%	93%	80	90
110	Tergitol® 15-S-12	C12-C14 secondary alcohol ethoxylate	Union Carbide	14.7	12-14.	12	80%	88%	65	70
109	Tergitol® 15-S-9	C12-C14 secondary alcohol ethoxylate	Union Carbide	13.3	12-14.	9	80%	84%	75	83
111	Tergitol® 15-S-20	C12-C14 secondary alcohol ethoxylate	Union Carbide	14.7	12-14.	20	70%	84%	40	50
112	Tergitol® 15-S-40	C12-C14 secondary alcohol ethoxylate	Union Carbide	16.4	12-14.	40	65%	82%	30	35
106	Tergitol® 15-S-3	C12-C14 secondary alcohol ethoxylate	Union Carbide	8.3	12-14.	3	40%	50%	20	30

The results with these secondary ethoxylated alcohols reinforce the notion that there is an optimum HLB. Note that it is the samples with either the low (EO = 3) or high end of ethoxylate groups (EO = 20, 40) and HLB that perform much worse than the other surfactants.

Table 4. Results for calcite chip cleaning and oil contact angle for ethoxylated octylphenol surfactants

No.	Name	Chemical	Num EO	HLB	Area% of crystal cleaned		Contact Angle (Degrees)	
					1 wk.	1 mth	1 wk.	1 mth
127	Triton X-114	Ethoxylated octylphenol, octoxynol-8	8	12.3	82%	91%	78	89
51	Igepal® CA-630	Octoxynol-9	9	13.0	80%	90%	65	90
50	Igepal® CA-620	Octoxynol-7	7	12.0	80%	90%	60	80
126	Triton X-100	Ethoxylated octylphenol, octoxynol-9	9	13.4	80%	90%	75	90
128	Triton X-165	Ethoxylated octylphenol, octoxynol-16	16	15.5	75%	90%	60	80
123	Triton™ X-15	Ethoxylated octylphenol, octoxynol-1	1	4.9	60%	75%	20	30
125	Triton X-45	Ethoxylated octylphenol, octoxynol-5	5	9.8	50%	66%	35	50
129	Triton X-405	Ethoxylated octylphenol, octoxynol-40	40	17.6	30%	43%	15	16
130	Triton X-705	Ethoxylated octylphenol, octoxynol-70	70	18.4	30%	38%	15	20
49	Igepal® CA-420	Octoxynol-3	3	8.0	5%	15%	0	15
124	Triton™ X-35	Ethoxylated octylphenol, octoxynol-3	3	7.8	0	0	0	0

Table 5. Results for calcite chip cleaning and oil contact angle for ethoxylated nonylphenol surfactants

No.	Name	Chemical	Num EO	HLB	Area% of crystal cleaned		Contact Angle (Degrees)	
					1 wk.	1 mth	1 wk.	1 mth
12	Igepal® CO-530	Nonoxynol-6	6	10.8	95%	95%	90	150
13	Igepal® CO-630	Nonoxynol-9	9	13.0	87%	94%	85	100
14	Igepal® CO-710	Nonoxynol-11	11	13.6	85%	86%	80	90
116	Tergitol® NP-10	Ethoxylated nonylphenol, nonoxynol-10	10	13.2	80%	88%	60	80
11	Igepal® CO-520	Nonoxynol-5	5	10.0	75%	85%	60	80
115	Tergitol® NP-9.5	Ethoxylated nonylphenol, nonoxynol-9.5	9.5	13.1	70%	82%	65	80
114	Tergitol® NP-6	Ethoxylated nonylphenol, nonoxynol-6	6	10.9	65%	75%	20	25
143	Tergitol® NP-9	Ethoxylated nonylphenol, nonoxynol-9	9	12.9	60%	90%	60	90
9	Igepal® CO-210	Nonoxynol-2 (1.5 EO)	1.5	4.6	45%	55%	20	27
16	Igepal® CO-880	Nonoxynol-30	30	17.2	45%	55%	25	43
10	Igepal® CO-430	Nonoxynol-4	4	8.8	40%	50%	15	46
17	Igepal® CO-887	Nonoxynol-30	30	17.2	40%	45%	15	27
15	Igepal® CO-730	Nonoxynol-15	15	15.0	36%	42%	20	40
117	Tergitol® NP-13	Ethoxylated nonylphenol, nonoxynol-13	13	13.9	35%	40%	20	25
18	Igepal® CO-897	Nonoxynol-40	40	17.8	15%	24%	5	20
113	Tergitol® NP-4	Ethoxylated nonylphenol, nonoxynol-4	4	8.9	0	5%	0	0

The results with these ethoxylated octyl- and nonyl-phenols also show this same trend; a HLB range of approximately 10 – 13 produces the best cleaning and a larger oil drop contact angle, whereas HLB values outside of this range are not as effective either in cleaning the chip or increasing the contact angle of the oil drops remaining on the chip.

The Alcodet series of thioether surfactants also showed promising results. Perhaps the sulfur linkages are beneficial to performance by interacting with some of the sulfur containing components in the crude oil. Also the range of HLB (11 - 13) for these particular Alcodet surfactants should be favorable, given the results of other nonionic surfactants tested under these conditions.

Table 6. Results for calcite chip cleaning and oil contact angle for Alcodet series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of crystal cleaned		Contact Angle (Degrees)	
					1 wk.	1 mth	1 wk.	1 mth
2	ALCODET SK	PEG 8 isolauryl, thioether	Rhodia, Inc.	12.7	90%	90%	75	80
6	ALCODET MC-2000	POE thioether	Rhone-Poulenc	12.0	85%	92%	85	95
3	ALCODET 218	PEG 10 isolauryl, thioether	Rhone-Poulenc	13.6	80%	83%	75	80
5	ALCODET HSC-1000	POE thioether	Rhone-Poulenc	12.0	70%	85%	60	90
4	ALCODET 260	PEG 6 isolauryl, thioether	Rhone-Poulenc	11.0	60%	75%	50	65

Sorbitan type of surfactants (SPAN and Tween series) generally was not very good performers, with the exception of Tween 21 and 81.

Table 7. Results for calcite chip cleaning and oil contact angle for the Sorbitan and the Tween series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of crystal cleaned		Contact Angle (Degrees)	
					1 wk.	1 mth	1 wk.	1 mth
92	SPAN [®] 20	Sorbitan monolaurate	ICI Chemicals	8.6	40%	60%	60	75
93	SPAN [®] 40	Sorbitan monopalmitate	SIGMA	6.7	40%	50%	30	45
94	SPAN [®] 60	Sorbitan monostearate	ICI Chemicals	4.7	30%	45%	15	18
97	SPAN [®] 85	Sorbitan trioleate	ICI Chemicals	1.8	30%	47%	15	20
95	SPAN [®] 80	Sorbitan monooleate	ATLAS Chemicals	4.3	0	0	0	0
96	SPAN [®] 83	Not Available	Aldrich	n/a	0	5%	0	5
101	Tween [®] 81	POE (5) Sorbitan monooleate	ICI Chemicals	10.0	90%	94%	80	92
98	Tween [®] 21	POE (4) Sorbitan monolaurate	ICI Chemicals	13.3	70%	85%	60	70
102	Tween [®] 85	POE (20) Sorbitan trioleate	Aldrich	11.0	55%	68%	40	45
99	Tween [®] 60	POE (20) Sorbitan monostearate	Unknown	14.9	30%	38%	10	15
100	Tween [®] 61	POE (4) Sorbitan monostearate	ATLAS Chemicals	9.6	5%	9%	0	5

The Pluoronic series of block polyethylene and ethylene co-polymers were not effective in these tests. The relatively high molecular weight of these products may play a role in decreasing their performance. Another feature of these surfactants is that it does not follow the rule of thumb of best performance when the HLB ranges from 8 – 15. The few Pluoronic products with a positive result have HLB values as low as 1 and as high as 30.

Table 8. Results for calcite chip cleaning and oil contact angle for Pluoronic series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of crystal cleaned		Oil Contact Angle	
					1 wk.	1 mth	1 wk.	1 mth
173	Pluronic L 122	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	4.0	30%	85%	30	30
167	Pluronic L 43	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	12.0	30%	75%	10	20
170	Pluronic L 101	Block copolymers of propylene, ethylene oxides	BASF	1.0	30%	70%	16	18
163	Pluronic F 38	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	30.0	25%	50%	5	10
172	Pluronic L 121	Block copolymers of propylene, ethylene oxides	BASF	5.0	20%	40%	10	18
166	Pluronic L 42	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	8.0	15%	40%	5	10
168	Pluronic L 44	Block copolymers of propylene, ethylene oxides	BASF	16.0	5%	20%	0	10
169	Pluronic L 63	Block copolymers of propylene, ethylene oxides	BASF	11.0	5%	15%	0	10
189	Pluronic L-72	Block copolymers of propylene, ethylene oxides	BASF	6.5	5%	15%	10	10
190	Pluronic L-81	Block copolymers of propylene, ethylene oxides	BASF	2	0	10%	5	5
191	Pluronic L-92	Block copolymers of propylene, ethylene oxides	BASF	5.5	0	5%	5	5
175	Pluronic 17R2	Block copolymers of propylene, ethylene oxides	BASF	n/a	0	0	0	0
164	Pluronic F 77	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	24.0	0	0	0	0
179	Pluronic F-108	Block copolymers of propylene, ethylene oxides	BASF	27.0	0	0	0	0
176	Pluronic F-68	Block copolymers of propylene, ethylene oxides	BASF	29.0	0	0	0	0
177	Pluronic F-87	Block copolymers of propylene, ethylene oxides	BASF	24.0	0	0	0	0
178	Pluronic F-88	Block copolymers of propylene, ethylene oxides	BASF	28.0	0	0	0	0
171	Pluronic L 103	Block copolymers of propylene, ethylene oxides	BASF	n/a	0	0	0	0
184	Pluronic L-31	Block copolymers of propylene, ethylene oxides	BASF	5	0	0	0	0
185	Pluronic L-44	Block copolymers of propylene, ethylene oxides	BASF	16	0	0	0	0
186	Pluronic L-61	Block copolymers of propylene, ethylene oxides	BASF	16	0	0	0	0
187	Pluronic L-62	Block copolymers of propylene, ethylene oxides	BASF	7	0	0	0	0
188	Pluronic L-64	Block copolymers of propylene, ethylene oxides	BASF	15	0	0	0	0
165	Pluronic P 104	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	13.0	0	0	0	0
182	Pluronic P-103	Block copolymers of propylene, ethylene oxides	BASF	9	0	0	0	0
183	Pluronic P-123	Block copolymers of propylene, ethylene oxides	BASF	8	0	0	0	0

Three series of anionic surfactants evaluated included the NEODOX (alkyl ethoxy carboxylate) series made by Shell, Alfoterra (alkyl propoxylated sulfate) made by Sasol, and the Aerosol surfactant series (sodium sulfosuccinates) from Cyanamid. The first two had no outstanding candidates, and the third series did have a couple of surfactants with encouraging results. See the Tables below.

Table 9. Results for calcite chip cleaning and oil contact angle for the NEODOX surfactant series

Surfactant			Area% of crystal		Oil	
			cleaned		Contact Angle	
Ref. No	(Trade Name)	Manufacturer	1 wk.	1 mth	1 wk.	1 mth
210	NEODOX 23-6	Westhollow Tech.	95%	96%	90	90
212	NEODOX 25-11	Westhollow Tech.	65%	65%	40	40
211	NEODOX 25-6	Westhollow Tech.	90%	90%	45	45
213	NEODOX 91-5	Westhollow Tech.	85%	85%	30	40
214	NEODOX 91-7	Westhollow Tech.	75%	75%	25	40

Table 10. Results for calcite chip cleaning and oil contact angle for the Alfoterra branched alkyl propoxy sulfate surfactant series

Surfactant			Area% of crystal		Oil	
			cleaned		Contact Angle	
Ref. No	(Trade Name)	Manufacturer	1 wk.	1 mth	1 wk.	1 mth
55	Alfoterra [®] 13	Sasol, Inc.	0	0	0	0
56	Alfoterra [®] 15	Sasol, Inc.	0	0	0	0
57	Alfoterra [®] 18	Sasol, Inc.	0	0	0	0
58	Alfoterra [®] 23	Sasol, Inc.	0	0	0	0
59	Alfoterra [®] 25	Sasol, Inc.	0	0	0	0
60	Alfoterra [®] 28	Sasol, Inc.	0	0	0	0
61	Alfoterra [®] 33	Sasol, Inc.	25%	35%	20	20
62	Alfoterra [®] 35	Sasol, Inc.	25%	35%	20	25
63	Alfoterra [®] 38	Sasol, Inc.	0	0	0	0
64	Alfoterra [®] 43	Sasol, Inc.	0	0	0	0
65	Alfoterra [®] 45	Sasol, Inc.	0	0	0	0
66	Alfoterra [®] 48	Sasol, Inc.	0	0	0	0
67	Alfoterra [®] 53	Sasol, Inc.	35%	45%	20	27
68	Alfoterra [®] 55	Sasol, Inc.	5%	10%	0	5
69	Alfoterra [®] 58	Sasol, Inc.	0	0	0	0
70	Alfoterra [®] 63	Sasol, Inc.	45%	50%	25	27
71	Alfoterra [®] 65	Sasol, Inc.	2%	5%	0	5
72	Alfoterra [®] 68	Sasol, Inc.	0	0	0	0

Table 11. Results for calcite chip cleaning and oil contact angle for Aerosol series of surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	Area% of crystal cleaned		Contact Angle (Degrees)	
				1 wk.	1 mth	1 wk.	1 mth
81	AEROSOL® OT 75%	Dioctyl ester of sodium sulfosuccinic acid	Cyanamid	80%	84%	50	54
79	AEROSOL® OT-S	Dioctyl sodium sulfosuccinate	Cyanamid	70%	88%	65	80
76	AEROSOL® OT-B	Dioctyl ester of sodium sulfosuccinic acid	Cyanamid	65%	92%	75	90
78	AEROSOL® TR-70	Bis(tridecyl) ester of sodium sulfosuccinic acid	Cyanamid	45%	60%	20	30
80	AEROSOL® MA-80	Dihexyl sodium sulfosuccinate	Cyanamid	25%	35%	15	22

It might be with more formulation effort that the other anionic surfactant series, such as the Alforterra surfactants then would be effective. Note that the literature reports this series of anionic surfactants have good oil recovery performance characteristics for carbonate formations when formulated at high pH. In that way they can create a very low interfacial tension and not suffer from excessive solid adsorption (Hirasaki, 2004 and Seethepalli , 2004).

The best "chip cleaning" and largest contact angle effect occurred with tests using several of the cationic surfactants, especially the alkyl-trimethyl ammonium chlorides. . See below.

Table 12. Results for calcite chip cleaning and oil contact angle for cationic surfactants

Ref. No	Surfactant (Trade Name)	Chemical Description	Manufacturer	Area% of crystal cleaned		Contact Angle (Degrees)
				1 wk.	1 mth	1 wk.
225	ARQUAD T-50	Tallowalkyl - trimethyl ammonium chloride	Akzo Nobel	100%		180
222	ARQUAD 18-50	Octadecyl - trimethyl ammonium chloride	Akzo Nobel	95%		180
223	ARQUAD C-50	Cocoalkyl - trimethyl ammonium chloride	Akzo Nobel	95%		180
224	ARQUAD S-50	Soyalkyl - trimethyl ammonium chloride	Akzo Nobel	90%		120
74	C10-triphenyl bromide	Decyl triphenylphosphonium bromide	AVOCADO	85%	90%	80
73	C12-triphenyl bromide	Dodecyl triphenylphosphonium bromide	AVOCADO	85%	95%	77
75	Trimethyl amm bromide	Trimethyl(tetradecyl) ammonium bromide	SIGMA	88%	98%	90

This is consistent with some literature reports that have discussed some quaternary amines having good performance characteristics in recovering crude oil from carbonate (chalk) cores via imbibition (Austad, 2002, Standnes, 2000, and Standes, 2002).

For comparison, consider the performance of two other amine surfactants. The Doumeen series of surfactants is a diamine and the Ethomeen series is a tertiary amine (see Figure 1).

Table 13. Results for calcite chip cleaning and oil contact angle for amine surfactants

Surfactant		Area% cleaned	Oil Contact Angle			
			1 wk.	1 wk.		
Ref. No	(Trade Name)	HLB	1 wk.	1 wk.		
226	DUOMEEN O	N-oley-1,3-propane diamine	Akzo Nobel	15.2	75%	30
227	DUOMEEN T	Tallow-1,3-diamino propane	Akzo Nobel	15.6	50%	20
215	ETHOMEEN C/12	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	12.2	85%	45
216	ETHOMEEN C/15	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	13.5	85%	85
218	ETHOMEEN S/12	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	10.0	50%	25
219	ETHOMEEN S/15	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	11.1	45%	15
220	ETHOMEEN S/25	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	14.7	0	0
217	ETHOMEEN C/25	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	16.8	0	0

The performance of these surfactants ranges from nil to very good (Ethomeen C/12 and C/15). The better chemical performance occurs for members with nominal HLB of 12.2 and 13.5, inside the optimum HLB range reported above in this document.

3.1.3 Results/Discussion - Calcite Chip Screening – McElroy Oil

Other experiments used the calcite chip (Iceland Spar) coated and aged with McElroy crude oil testing some of the same surfactants as before. There is a 2-by-2 matrix of 4 different run conditions:

Chip Aging Time at 80 °C	1 Day	7 Days
Water Chemistry	2 wt% NaCl	Synthetic McElroy Brine

The complete listing of results for the cleaning experiments with these chips is given in Appendix B.

Results for the faster test protocol (where calcite chips pre-aged for only 24 hours with McElroy oil) are shown in the table below. For this situation the calcite chips are cleaned relatively quickly. The calcite chips aged for 7 days with McElroy oil however, showed hardly any response (see Appendix B), even after a week or more with exposure to a surfactant solution

Table 14. Performance in cleaning calcite chips coated with aged McElroy oil. Results sorted by best to worst for both samples with 2 wt% NaCl brine and synthetic McElroy brine. Calcite chips pre-treated with McElroy oil for 24 hours at 80 °C . Percent of chip cleaned after 1 day in surfactant solutions at RT in 2 wt% NaCl and synthetic McElroy brine shown below.

McElroy Oil Age 24 hours at 80 C on Calcite Chips

Brine 2.0 wt%			Synthetic McElroy Brine		
Surfactant Name	HLB	24 hours	Surfactant Name	HLB	24 hours
Igepal® CO-530	10.8	95%	Triton X-114	12.3	93%
Tergitol® 15-S-7	12.4	95%	Neodol® 1-7	12.8	90%
Neodol® 1-7	12.8	92%	Tergitol® 15-S-7	12.4	90%
Tergitol® 15-S-9	13.3	92%	Tergitol® 15-S-9	13.3	85%
Neodol® 25-7	12.3	90%	SIL WET® L-77	n/a	85%
Tergitol® 15-S-5	10.6	90%	ALCODET SK	12.7	85%
Neodol® 25-9	13.1	85%	Igepal® CO-630	13	80%
Tergitol® 15-S-12	14.7	85%	Neodol® 1-9	13.9	80%
Triton X-114	12.3	85%	Neodol® 25-9	13.1	80%
ALCODET SK	12.7	85%	Tergitol® 15-S-5	10.6	80%
ALCODET 218	13.6	85%	Triton X-100	13.4	80%
Igepal® CO-630	13	80%	Neodol® 25-7	12.3	75%
Igepal® CO-710	13.6	80%	NEODOX® 25-6	n/a	75%
Neodol® 1-9	13.9	80%	ARQUAD T-50	n/a	75%
NEODOX® 25-11	n/a	80%	Igepal® CO-530	10.8	70%
SIL WET® L-77	n/a	80%	Tergitol® 15-S-12	14.7	70%
Triton X-165	15.5	75%	ALCODET 218	13.6	70%
NEODOX® 25-6	n/a	70%	Triton X-405	17.6	65%
Tergitol® 15-S-20	14.7	70%	NEODOX® 25-11	n/a	60%
Triton X-100	13.4	70%	Triton X-165	15.5	60%
Triton X-405	17.6	70%	Tergitol® 15-S-20	14.7	55%
ARQUAD T-50	n/a	65%	Igepal® CO-710	13.6	50%
SIMULSOL SL 4	n/a	20%	Triton™ BG-10	n/a	10%
Triton™ BG-10	n/a	10%	Agrimul® PG 2067	13.6	5%
Agrimul® PG 2067	13.6	10%	SIMULSOL SL 4	n/a	5%
SIMULSOL SL 55	n/a	10%	C ₁₀ -triphenyl-bromide	n/a	0%
C ₁₀ -triphenyl-bromide	n/a	0%	SIMULSOL AS 48	n/a	0%
SIMULSOL AS 48	n/a	0%	SIMULSOL SL 55	n/a	0%
AVERAGE		68%			60%

Similar to the results shown earlier for the heavy oil-coated calcite chips, nonionic surfactants with a HLB in the range of 10 – 15 are relatively effective. The average HLB is 12.7 for the nonionic surfactants that remove 80% or more of the McElroy oil from these chips after a 1 day, whether the surfactant is dissolved in 2 wt% brine or a synthetic McElroy brine. On average, the chip cleaning is more efficient if the brine is 2 wt% NaCl (average of 68% cleaning) rather than

synthetic McElroy brine (average of 60% cleaning). Somewhat contrary to the heavy oil results, the cationic surfactants are inferior rather than superior to the nonionic surfactants. For example, the Arquad T-50 has decent efficiency when tested versus the chips coated with McElroy oil, but it is not as good as the best Tergitol and Neodol surfactants. Recall that the Arquad T-50 was one of the particularly good products for cleaning the chips coated with the heavy oil.

3.3 Screening Method Based on Calcite Powder Flotation

3.2.1 Introductory Remarks

Task 2 of this project is pointed towards gaining a better fundamental understanding about the wetting behavior of carbonate minerals, and how that changes with exposure to oil and aqueous surfactant solutions. That is, how is it that certain components in the oil (e.g. naphthenic acids (NAs) and asphaltenes) promote the mineral surface to be oil-wet? What are the chemical processes that can alter that oil-wet condition to the desired outcome of becoming strongly water-wet via exposure to an aqueous surfactant solution? Standes and Austad (2000, 2002) for example, have addressed the surfactant wetting mechanisms with a carbonate surface covered by a naphthenic acid.

One outcome from conducting the experimental portion of this Task 2 has been the development of another rapid, efficient method to screen surfactant formulations for IOR performance in carbonates (i.e. screen surfactants for their ability to alter the surface from an oil-wet to a water-wet condition). The general concept is to pre-treat a powdered calcite material with a NA compound to render it oil-wet. This powder then will float on top when agitated in water because it is oil-wet. If, however, the aqueous phase contains an efficient water-wetting surfactant, then some of the calcite powder now will sink to the bottom. More details about all of the work associated with this Task 2 are given in the first semi-annual and the third quarter report for Year 1. The literature (Skvarla and Kmet, 1991, and Ozkan and Yekeler, 2003) describes the flotation action that can occur with a carbonate mineral that has been contacted with a naphthenic acid (such as sodium oleate).

3.2.2 Experimental Procedure – Calcite Flotation Test

The first step in this procedure is to select the hydrocarbon and the treatment details that will make the calcite powder initially oil-wet. To test this concept, we first selected a series of specific naphthenic (carboxylic) acids as model compounds, and that may be present in a crude oil and contribute to oil-wetting behavior in actual reservoirs. Powdered calcite (calcium carbonate) was selected as the mineral surface and formulations with single surfactant products as agents to induce water-wetting behavior. Per details below, based on the results of the first test, cyclohexanepentanonic acid was selected as the oil-wetting agent for part two of the test.

The second step in the procedure is to then use the cyclohexanepentanonic acid oil-wet treated calcite powder as the starting material. This powder almost all floats when dispersed in water. However, when this powder is exposed to effective aqueous surfactant solutions, all or a

significant fraction of the powder sinks, thereby indicating conversion of the solid to a water-wet state.

These flotation tests (as was the calcite chip cleaning tests) all were performed at room temperature. These same procedures could be adapted easily to elevated temperatures.

Experimental Procedure to Select Oil-Wetting Agent NA

A selected suite of naphthenic acid (NA) compounds included in the study are shown below:

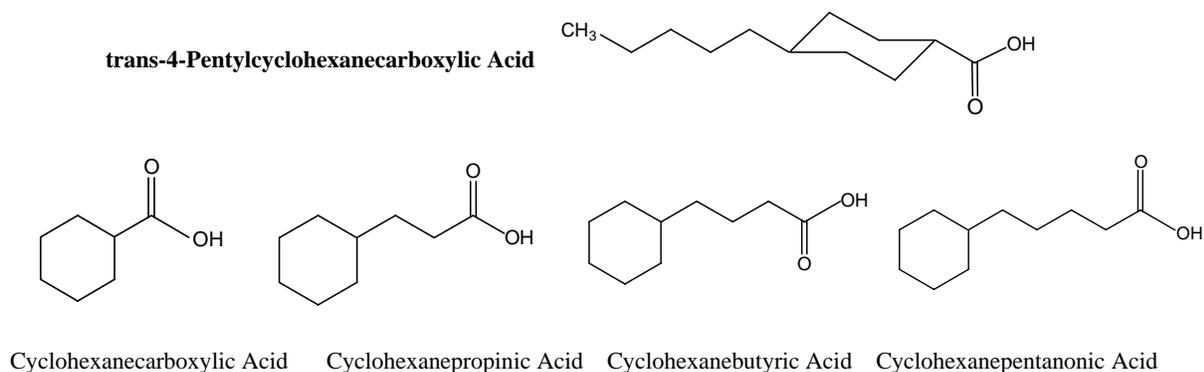


Figure 9. Structures of model naphthenic acids (NA)

The literature suggests that NAs can create an oil-wet condition via their carboxylate group binding to the carbonate mineral surface. Then the hydrophobic (e.g. alkyl chain) group protruding from the surface creates effectively an oil-like coating (Standes and Austad, 2000).

The first portion of this test development program is to measure the wetting behavior induced by the different chemical structures of the selected NA compounds. The general procedure to do this via flotation behavior is:

1. Prepare naphthenic acid solution in decane. Solutions were made from 0.005 - 0.067 M, which is equivalent to acid numbers of 0.45 - 5.1 for the selected naphthenic acids.
2. Mix 10.0 ml naphthenic acid-decane solution with 0.5 g calcite powder (first pre-heated at 120 °C for 2 hours) in a test tube. The average size of the powder is 5 microns, with a surface area of 1.6 sq. m/gram. Then shake the test tube at room temperature for 12 hours in order to establish adsorption to its equilibrium.
3. Put the test tube containing calcite powder with adsorbed naphthenic acid in an oven at 85 °C to remove extra solvent until a constant weight is obtained. Cool it to room temperature for the flotation test.
4. Add 10 g distilled water to a test tube with calcite powder and shake it vigorously for 2 minutes. Then leave the test tube stand vertically for several hours. The volume of calcite powder in bottom (water-wet portion) and top (oil-wet portion) are measured.

Per the procedure above (Steps 3 and 4), several tests were performed to compare the tendency of the calcite powder treated with different NA compounds to float. See the photos below.

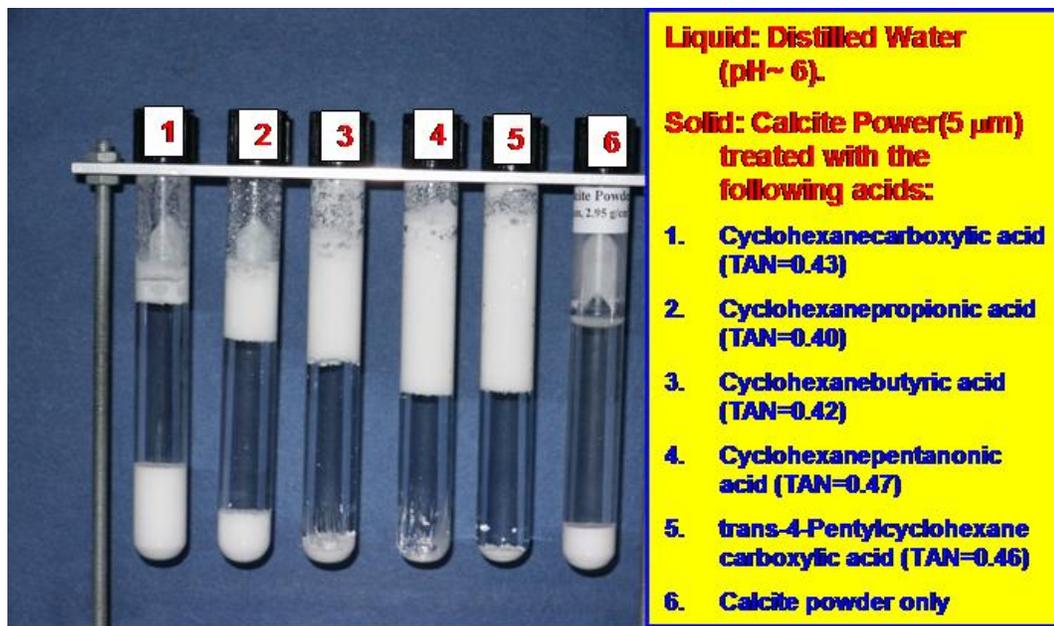


Figure 10. Flotation of calcite powder treated by different NAs at TAN of about 0.45

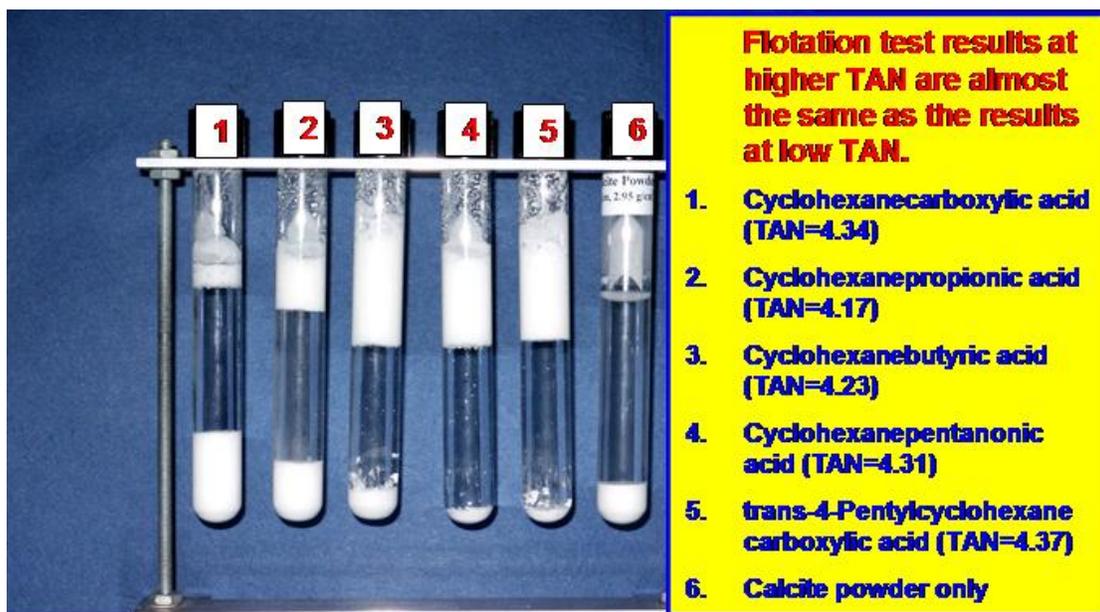


Figure 11. Flotation of calcite powder treated by different NAs at TAN of about 4.5

The volume percent of the powdered calcite observed to be floating at the top (called “oil-wet percentage”) for all of the acid numbers examined are shown in the plots below, both in terms of the NA molar concentration and expressed as total acid number, TAN.

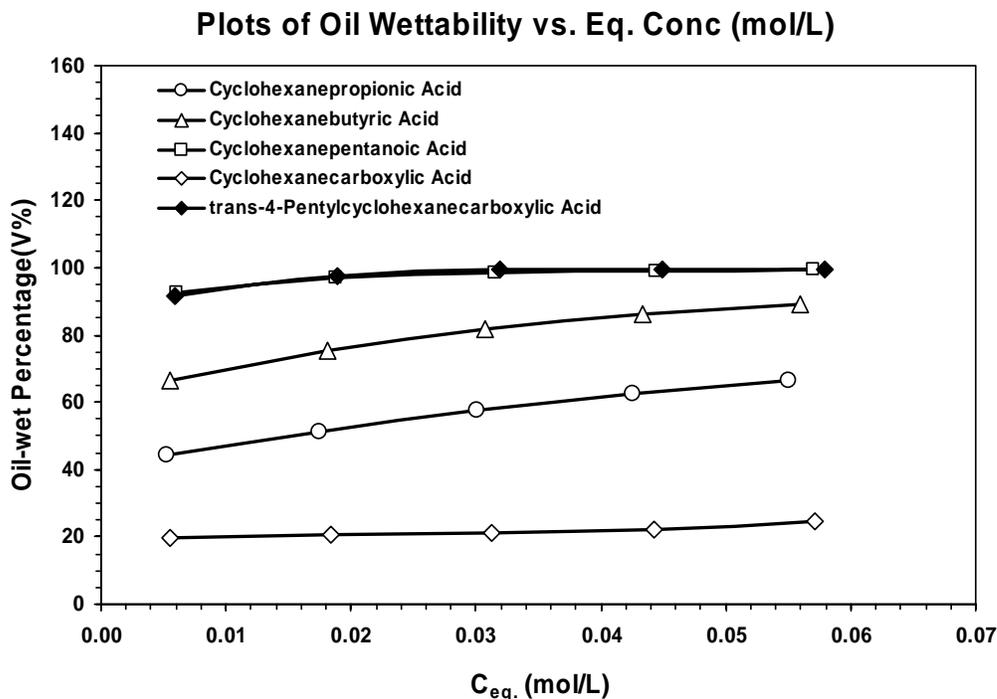


Figure 12. Flotation of calcite powder treated by different NAs versus molar concentration.

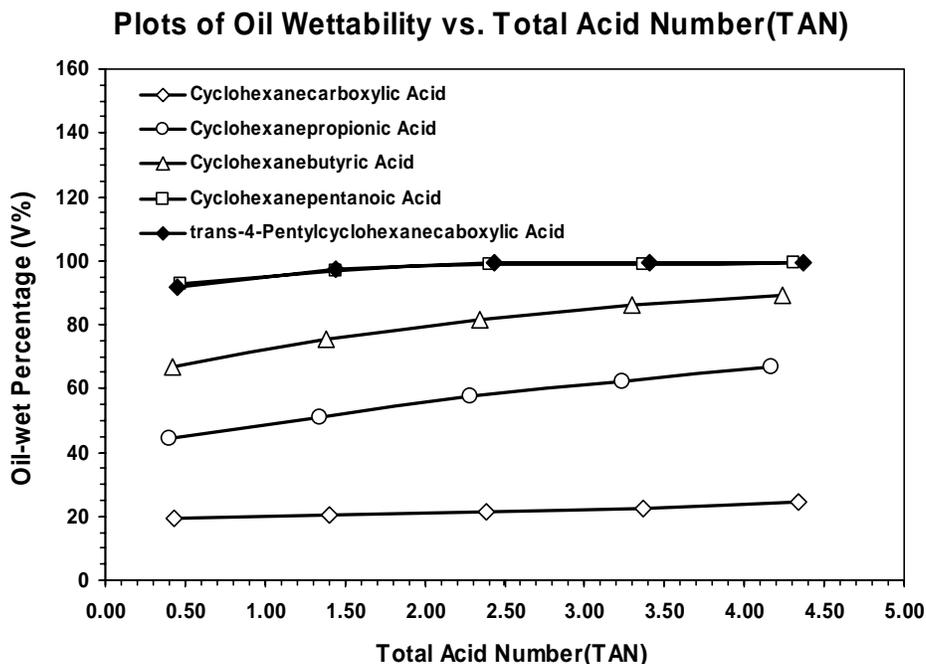


Figure 13. Flotation of calcite powder treated by different NAs versus their TAN.

The greater the hydrophobic character of the NA, the greater the percentage of the treated calcite powder that floats in distilled water. Based on these above results, we selected powdered calcite pre-treated with cyclohexanepentanonic acid as the “standard” initially oil-wet material for the second part of the overall test procedure which tests the performance of surfactants. Thus, the “blank” result when testing surfactants and additives to the aqueous phase is nearly 100% of the powder remains at the top.

Experimental Procedure to Screen Surfactant Performance

In the surfactant screening test, one prepares a quantity of treated calcite powder, and then observes how that powder behaves when dispersed into different surfactant candidate solutions.

1. Clean new calcite crystals. Wash the crystals with heptane and toluene separately, and then dry the samples in an oven at 85 °C for an hour.
2. Prepare a 0.066 M cyclohexanepentanonic acid solutions in decane (equivalent to total acid number, TAN, of about 5).
3. Immerse the clean calcite crystal in the naphthenic acid solution in decane for 24 hours at room temperature. Take the crystals out of the solutions carefully. Dry the treated crystals in an oven at 85 °C for an hour to remove all extra solvent.
4. Add 1 gram of this pre-treated calcite powder (now oil-wet) to a test tube.
5. Add 10 grams of surfactant solution and shake vigorously.
6. Allow to settle over night. Note the volume fraction of calcite powder that has sunk or is floating. If there is foam at the top (often there is), then proceed to Step 7. The foam should be broken because it may induce a false reading. Any foam could hold some of the water-wet calcite powder to remain floating at the top and not allow it to sink.
7. For the case when there is some foam at the top, gently tilt and rotate the test tube to gradually break the bubbles. Carefully replace the test tube and allow it sit for 2 hours or more. Take a final reading of the percent of solids floating or now at the bottom. Those aqueous chemical solutions that cause more of the solids to sink are judged to be Superior candidates that merit further testing.

3.2.3 Results and Discussion – Calcite Flotation Test

The results of the flotation test response are shown in the table below.

Table 15. Results of surfactant flotation test. Calcite powder pre-treated with cyclohexanepentanoic acid is exposed to different aqueous surfactant solutions. The percent of the powder that then sinks to the bottom of the test tube indicate the success in converting the solid to a water-wet condition.

Wettability Alteration Test (Flotation) for Selected Surfactants				
Percent of Calcite Powder that Sinks				
Surfactant Concentration				
No.	Surfactants	100 ppm	50 ppm	20 ppm
1	Alcodet ^(R) SK	0	0	
2	Alcodet ^(R) MC-2000	95%	55%	
3	Alkamide ^(R) WRS-166	0	0	
4	Igepal ^(R) CO-530	100%	95%	2%
5	Arquard ^(R) C-50	100%	50%	
6	Arquard ^(R) T-50	100%	100%	60%
7	Neodol ^(R) 1-5	95%	45%	
8	Neodol ^(R) 1-7	95%	40%	
9	Neodol ^(R) 25-7	100%	80%	
10	Neodol ^(R) 25-9	100%	80%	
11	Neodox ^(R) 23-6	0%	0%	
12	Sil wet ^(R) L-77	100%	80%	
13	Sil wet ^(R) L-7614	100%	30%	
14	Tergitol ^(R) 15-S-3	100%	70%	
15	Tergitol ^(R) 15-S-5	100%	65%	
16	Tergitol ^(R) 15-S-7	100%	45%	
17	Tergitol ^(R) 15-S-20	75%	50%	
18	Tergitol ^(R) 15-S-40	50%	40%	
19	Triton ^(R) BG-10	0%	0%	
20	C ₁₂ TAB	60%	45%	
21	Sodium Dodecyl Sulfate	0%	0%	

The results are shown for surfactant concentrations of 100 ppm and less. At 100 ppm surfactant concentration we see a spread of results, but several surfactants still show 100% effectiveness. There is more spread of results at the 50 and 25 ppm level. These results then are internally consistent, with respect to a decrease of performance as the surfactant dosage rate decreases. Note that at higher dosages this procedure does not discriminate performance and hence is not a useful test; for example, we found at 1000 ppm active surfactant concentration that all of these products tested were 100% effective.

Some of the trends with respect to changes of performance with the surfactant chemical structure are expected. For example, within the Tergitol series we see that the performance is poorer for the two products (Tergitol 15-S-20 and Tergitol 15-S-40) with a large number of EO (ethoxy) groups (20 and 40, respectively) and relatively high HLB (14.7 and 16.4, respectively). Per earlier findings with the calcite chip cleaning test, these appear to be too water soluble. One inconsistency, however, is that the Tergitol 15-S-3 with only 3 EO groups and a low HLB of 8.3

performs the best among this series of surfactants. The calcite chip results would suggest this surfactant is not water soluble enough for good performance.

The Arquad T-50 (a cationic quaternary amine) was the best performing surfactant in this flotation test. Having a quaternary amine as a good surfactant is consistent with the calcite chip heavy oil test results (and other literature). For the calcite chip results with heavy oil the Arquad C-50 was almost as good as the Arquad T-50, but not so for the flotation test. Note that the difference is in the alkyl chain, with the C-50 based on coconut oil (circa C12) and the T-50 based on a tallow oil (circa C15). One other common result is that the pure cationic compound, C₁₂TAB (dodecyl trimethyl ammonium bromide), has moderate performance for both the flotation and calcite cleaning screening tests.

4.0 CONCLUSIONS

1. One screening test was developed for surfactant recovery performance based on the relative ability of different chemical formulations to remove oil that is coating a clear calcite chip. These tests can be designed to be relatively simple and quick to perform (only a few days exposure time) and provide a measure of relative performance of removing oil coating a carbonate mineral surface, and thereby an indication of the surfactant's ability to recover incremental oil via enhancing aqueous phase imbibition into carbonate porous media.
2. A second surfactant screening test was developed based on the ability of an aqueous chemical solution to make an oil-wet calcite powder water-wet. This method also is a relatively quick and easy procedure to screen surfactant for their potential performance as EOR agent for carbonate reservoirs. The general procedure is to render a powdered carbonate material oil-wet, and then add it to a surfactant solution. After agitating and aging this suspension, the success in converting the powder to a water-wet condition is indicated by the fraction of the powder that is made to sink. This is compared to the blank case with no surfactant in which almost all of the powder (still oil-wet) will float.

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APPENDIX A.

**LIST OF CALCITE CHIP – HEAVY OIL
CLEANING RESULTS WITH SURFACTANTS**

WETTABILITY ALTERATION

No.	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Crude oil contact angle on calcite surface (deg. 0 = spreading, 180 = non-wet to oil)											
					Area% of oil-wet to			water-wet								
					24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
240	ABIL B 88183	Polysiloxane polyether copolymer	Goldschmidt	n/a	0	0	0	0				0	0	0	0	
241	ABIL B 88184	Polysiloxane polyether copolymer	Goldschmidt	n/a	0	0	0	0				0	0	0	0	
239	ABIL B 8851	Polysiloxane polyether copolymer	Goldschmidt	n/a	0	0	0	0				0	0	0	0	
242	ABIL EM 90	Cetyl dimethicone copolyol	Goldschmidt	5.0	0	0	0	0				0	0	0	0	
77	AEROSOL® GPG	Dioctyl ester of sodium sulfosuccinic acid	Cyanamid	anionic	25%	45%	55%	70%	80%	83%		30	40	60	70	75
80	AEROSOL® MA-80	Dihexyl sodium sulfosuccinate	Cyanamid	anionic	10%	20%	25%	30%	35%	40%		5	10	15	20	22
81	AEROSOL® OT 75%	Dioctyl ester of sodium sulfosuccinic acid	Cyanamid	anionic	20%	70%	80%	82%	84%	86%		18	48	50	52	54
76	AEROSOL® OT-B	Dioctyl ester of sodium sulfosuccinic acid	Cyanamid	anionic	25%	50%	65%	85%	92%	93%		20	50	75	88	90
79	AEROSOL® OT-S	Dioctyl sodium sulfosuccinate	Cyanamid	anionic	30%	60%	70%	85%	88%	90%		30	50	65	70	80
78	AEROSOL® TR-70	Bis(tridecyl) ester of sodium sulfosuccinic acid	Cyanamid	anionic	25%	35%	45%	50%	60%	70%		15	20	20	25	30
245	Agniquil® PG 9116	Alkyl polyglycosides	Cognis	13.1	0	0	0	0				0	0	0	0	
243	Agrimul® PG 2062	Alkyl polyglycosides	Cognis	11.6	0	0	30%	30%				0	0	10	cloudy	
244	Agrimul® PG 2067	Alkyl polyglycosides	Cognis	13.6	0	0	10%	20%				0	0	20	20	
3	ALCODET 218	PEG 10 isolauryl, thioether	Rhone-Poulenc	13.6	75%	80%	80%	80%	83%	85%		60	75	75	78	78
4	ALCODET 260	PEG 6 isolauryl, thioether	Rhone-Poulenc	11.0	50%	55%	60%	70%	75%	80%		35	40	50	60	65
5	ALCODET HSC-1000	POE thioether	Rhone-Poulenc	12.0	40%	50%	70%	80%	85%	85%		28	35	60	80	90
6	ALCODET MC-2000	POE thioether	Rhone-Poulenc	12.0	75%	80%	85%	90%	92%	92%		70	80	85	92	95
2	ALCODET SK	PEG 8 isolauryl,thioether	Rhodia, Inc.	12.7	76%	85%	90%	90%	90%	92%		62	68	74	78	80
55	Alfoterra® 13	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
56	Alfoterra® 15	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
57	Alfoterra® 18	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
58	Alfoterra® 23	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
59	Alfoterra® 25	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
60	Alfoterra® 28	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
61	Alfoterra® 33	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	15%	20%	25%	30%	35%	45%		10	15	20	20	20
62	Alfoterra® 35	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	10%	20%	25%	30%	35%	45%		10	15	20	25	25
63	Alfoterra® 38	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
64	Alfoterra® 43	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
65	Alfoterra® 45	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
66	Alfoterra® 48	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
67	Alfoterra® 53	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	15%	35%	35%	40%	45%	50%		10	15	20	25	27
68	Alfoterra® 55	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	0%	0%	5%	10%	10%	15%		0	0	0	5	5
69	Alfoterra® 58	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
70	Alfoterra® 63	Branched alcohol propoxylate sulfate(3 PO)	Sasol, Inc.	anionic	10%	35%	45%	50%	50%	53%		15	20	25	27	27
71	Alfoterra® 65	Branched alcohol propoxylate sulfate(5 PO)	Sasol, Inc.	anionic	0	0	2%	2%	5%	5%		0	0	0	0	5
72	Alfoterra® 68	Branched alcohol propoxylate sulfate(8 PO)	Sasol, Inc.	anionic	0	0	0	0	0	0		0	0	0	0	0
1	ALKAMIDE WRS-166	Oleamide DEA(Anionic/Nonionic)	Rhone-Poulenc	n/a	80%	85%	90%	95%	95%	98%		70	75	80	83	87
23	Antarox 17-R-2	Alkoxylated glycols,Merxipol 172	Rhodia, Inc.	8.0	10%	30%	40%	45%	47%	50%		5	10	15	20	25
22	Antarox 31-R-1	Alkoxylated glycols,Merxipol 131	Rhodia, Inc.	4.0	10%	35%	50%	60%	68%	70%		5	20	30	35	40
25	Antarox L-61	Alkoxylated glycols,poloxymr 181	Rhone-Poulenc	3.0	10%	28%	38%	55%	58%	60%		10	15	40	48	50
26	Antarox L-62	Alkoxylated glycols,poloxymr 182	Rhone-Poulenc	7.0	10%	25%	35%	45%	55%	60%		8	20	30	40	48

WETTABILITY ALTERATION

No.	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of oil-wet to water-wet						Crude oil contact angle on calcite surface (deg. 0 = spreading, 180 = non-wet to oil)					
					24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
27	Antarox L-64	Alkoxylyated glycols, Polyoximer 184	Rhone-Poulenc	15.0	0%	5%	10%	15%	20%	20%	0	0	10	15	20	
29	Antarox LA-EP-15	Modified oxyethylated straight chain alcohol	Rhodia, Inc.	7.0	15%	75%	80%	85%	90%	92%	10	45	55	65	75	
30	Antarox LA-EP-16	Modified oxyethylated straight chain alcohol	Rhodia, Inc.	13.1	15%	70%	75%	80%	85%	88%	10	40	52	63	75	
24	Antarox LF-222	Ethoxylated alkylphenols	Rhodia, Inc.	n/a	45%	80%	85%	90%	93%	95%	20	75	80	85	90	
28	Antarox P-104	Alkoxylyated glycols, Polyoximer 334	Rhone-Poulenc	13.0	0	0	0	0	0	0	0	0	0	0	0	
221	ARQUAD 12-50	N-alkyl trimethyl ammonium chloride	Akzo Nobel	cationic	Very Cloudy	Very Cloudy	Very Cloudy				N/A	N/A	180	180		
222	ARQUAD 18-50	N-alkyl trimethyl ammonium chloride	Akzo Nobel	cationic	N/A	90%	95%	95%			N/A	120	180	180		
223	ARQUAD C-50	N-alkyl trimethyl ammonium chloride	Akzo Nobel	cationic	cloudy	90%	95%	95%			N/A	95	180	180		
224	ARQUAD S-50	N-alkyl trimethyl ammonium chloride	Akzo Nobel	cationic	cloudy	80%	90%	90%			N/A	90	120	120		
225	ARQUAD T-50	N-alkyl trimethyl ammonium chloride	Akzo Nobel	cationic	cloudy	90%	100%	100%			N/A	100	180	180		
228	Bio Soft N-411	Isopropylamine salt of linear alkylbenzenesulfonicacid	STEPAN	anionic	0	0	0	0			0	0	0	0	0	
233	BLO	(Not available)	ISP Corp.	n/a	25%	30%	45%	60%			5	10	12	30		
74	C10-triphenyl bromide	Decyl triphenylphosphonium bromide	AVOCADO	cationic	33%	80%	85%	85%	90%	95%	30	75	80	85	90	
73	C12-triphenyl bromide	Dodecyl triphenylphosphonium bromide	AVOCADO	cationic	30%	77%	85%	92%	95%	96%	25	45	77	88	90	
155	Calamide C	Coconut diethanolamide	PILOT	Nonionic	0	0	0	0	0		0	0	0	0	0	
156	Calamide CW-100	Modified coconut dialkanolamide	PILOT	Nonionic	0	0	0	0	0		0	0	0	0	0	
157	Calamide CWT	Modified coco amide soap superamide	PILOT	Nonionic	0	10%	15%	30%	40%		cloudy	cloudy	cloudy	cloudy	cloudy	
158	Calamide F	Vegetable oil diethanolamide	PILOT	Nonionic	15%	35%	65%	85%	92%		15	30	60	70	80	
159	Calamide O	Coco/oleic diethanolamide	PILOT	Nonionic	0	0	0	0	0		0	0	0	0	0	
160	Calfax 10L-45	Sodium n-decyl diphenyl oxide disulfonate	PILOT	anionic	0	10%	20%	30%	40%		0	0	5	10	20	
161	Calfax 16L-35	Sodium n-hexa-decyl diphenyl disulfonate	PILOT	anionic	0	5%	10%	20%	30%		0	0	5	10	15	
162	Calfax DB-45	Sodium dodecyl diphenyl oxide disulfonate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
148	Calfoam EA-603	Ammonium alcohol ether sulfate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
149	Calfoam ES-603	Sodium alcohol ether sulfate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
147	Calimulse EM-22	Sodium branched alkylbenzenesulfonate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
146	Calimulse PRS	Isopropylamine sulfonate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
145	Caloxylate N-9	Nonylphenol ethoxylate, 9 moles	PILOT	anionic	10%	20%	35%	55%	75%		0	15	30	45	55	
150	Calsoft AOS-40	Sodium C14-C16 olefin sulfonate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
151	Calsoft L-40 Slurry	Sodium dodecyl-Benzene sulfonate	PILOT	anionic	0	0	0				0	0	0			
152	Calsoft LAS-99	Dodecylbenzene sulfonic acid, linear	PILOT	anionic	10%	20%	30%	40%	50%		5	15	25	35	40	
153	Calsoft T-60	Triethanolamine alkylaryl sulfonate	PILOT	anionic	0	0	0	0	0		0	0	0	0	0	
154	Calsoft TSA-99	Linear tridecyl benzene sulfonic acid	PILOT	anionic	15%	45%	55%	70%	85%		5	20	30	35	45	
193	DERMOL 2022	(Not available)	ALZO International	n/a	0	15%	25%	45%			0	5	5	15		
195	DERMOL DGDIS	Polyglycerol-2 diisostearate	ALZO International	n/a	0	0	0	0			0	0	0	10		
196	DERMOL DGMIS	Diglycerol-2 monoisostearate	ALZO International	n/a	0	0	0	0			0	0	0	0		
192	DERMOL DO	(Not available)	ALZO International	n/a	20%	50%	60%	70%			5	5	5	20		
194	DERMOL NGDI	Neopentyl diisostearate	ALZO International	n/a	0	0	0	20%			0	0	0	20		
208	DOWFAX 2A0	Dodecyl diphenyl oxide disulfonic acid	DOW Chemicals	anionic	0	10%	35%	35%			0	10	15	20		
207	DOWFAX 2A1	Sodium dodecyl diphenyloxide disulfonate	DOW Chemicals	anionic	0	0	0	0			0	0	0	0		
206	DOWFAX 8390	Sodium n-hexadecyldiphenyloxide disulfonate	DOW Chemicals	anionic	0	0	0	0			0	0	0	0		

WETTABILITY ALTERATION

Crude oil contact angle on calcite surface
(deg. 0 = spreading, 180 = non-wet to oil)

No.	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of oil-wet to water-wet						Crude oil contact angle on calcite surface (deg. 0 = spreading, 180 = non-wet to oil)					
					24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
209	DOWFAX C6L	Sodium hexyl diphenyloxydisulfonate	DOW Chemicals	anionic	0	0	0	0			0	0	0	0		
226	DUOMEEN O	N-oleyl-1,3-propane diamine	Akzo Nobel	15.2	65%	75%	75%	75%			25	30	30	30		
227	DUOMEEN T	Tallow-1,3-diamino propane	Akzo Nobel	15.6	30%	50%	50%	70%			15	20	20	20		
137	Dynol® 604	(Not available)	Air Products	n/a	0	0	0	0	0	0	0	0	0	0	0	0
246	Elmsorb® 2500	(Not available)	Cognis	n/a	0	0	0	0			0	0	0	0		
247	Elmsorb® 2503	(Not available)	Cognis	n/a	10%	15%	20%	30%			5	5	5	20		
248	Elmsorb® 2515	(Not available)	Cognis	n/a	0	0	25%	45%			0	0	55	0		
138	ENVIROGE MAD01	(Not available)	Air Products	n/a	0	0	0	0	0	0	0	0	0	0	0	0
215	ETHOMEEN C/12	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	12.2	50%	80%	85%	85%			30	40	45	45		
216	ETHOMEEN C/15	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	13.5	25%	80%	85%	85%			30	75	85	85		
217	ETHOMEEN C/25	Tertiary amines ethylene oxide, cocoalkyl	Akzo Nobel	16.8	0	0	0	0			0	0	0	0		
218	ETHOMEEN S/12	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	10.0	35%	40%	50%	50%			15	20	25	20		
219	ETHOMEEN S/15	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	11.1	0	10%	45%	90%			0	5	15	30		
220	ETHOMEEN S/25	Tertiary amines ethylene oxide, soyalkyl	Akzo Nobel	14.7	0	0	0	5%			0	0	0	15		
19	Ethoxylated Oleic Acid	Ethoxylated Oleic Acid	Rhone-Poulenc	n/a	45%	55%	65%	75%	80%	85%	20	28	45	70	75	
232	Fluid Q4-3667	(Not available)	Dow Corning	n/a	0	0	0	0			0	0	0	0		
236	GANEX V-216	PVP/hexadecane copolymer	ISP Corp.	10.0	0	0	0	0			0	0	0	0		
238	GANEX V-220	PVP/eicosene copolymer	ISP Corp.	8.0	0	0	0	0			0	0	0	0		
237	GANEX WP-660	(Not available)	ISP Corp.	n/a	0	0	0	0			0	0	0	0		
250	Hyamine® 1622	Di(isobutylphenoxythyl)dimethylbenzylammonium chloride	EM Science	cationic	0	5%	10%	20%			0	0	5	30		
49	Igepal® CA-420	Octoxynol-3	Rhone-Poulenc	8.0	0%	0%	5%	10%	15%	20%	0	0	0	5	15	
50	Igepal® CA-620	Octoxynol-7	Rhone-Poulenc	12.0	25%	55%	80%	85%	90%	90%	30	55	60	70	80	
51	Igepal® CA-630	Octoxynol-9	Rhone-Poulenc	13.0	27%	60%	80%	85%	90%	95%	30	55	65	75	90	
52	Igepal® CA-720	Octoxynol-12	Rhone-Poulenc	14.6	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	
9	Igepal® CO-210	Nonoxynol-2 (1.5 EO)	Rhone-Poulenc	4.6	25%	35%	45%	50%	55%	60%	10	14	20	24	27	
10	Igepal® CO-430	Nonoxynol-4	Rhone-Poulenc	8.8	20%	30%	40%	45%	50%	55%	5	10	15	30	46	
11	Igepal® CO-520	Nonoxynol-5	Rhone-Poulenc	10.0	60%	70%	75%	80%	85%	90%	45	50	60	70	80	
12	Igepal® CO-530	Nonoxynol-6	Rhone-Poulenc	10.8	80%	88%	95%	95%	95%	100%	75	85	90	120	150	
13	Igepal® CO-630	Nonoxynol-9	Rhone-Poulenc	13.0	80%	83%	87%	92%	94%	96%	70	78	85	90	100	
14	Igepal® CO-710	Nonoxynol-11	Rhone-Poulenc	13.6	76%	82%	85%	86%	86%	90%	60	75	80	88	90	
15	Igepal® CO-730	Nonoxynol-15	Rhone-Poulenc	15.0	22%	30%	36%	40%	42%	45%	10	15	20	30	40	
16	Igepal® CO-880	Nonoxynol-30	Rhone-Poulenc	17.2	30%	40%	45%	50%	55%	60%	12	18	25	36	43	
17	Igepal® CO-887	Nonoxynol-30	Rhone-Poulenc	17.2	20%	33%	40%	45%	45%	45%	6	11	15	24	27	
18	Igepal® CO-897	Nonoxynol-40	Rhone-Poulenc	17.8	0%	10%	15%	20%	24%	25%	0	0	5	15	20	
38	Lubrhophos LL-550	Free acid of complex org. phosphate alcohol	Rhone-Poulenc	anionic	23%	55%	60%	70%	75%	80%	20	30	30	35	40	
36	Lubrhophos LP-700	Complex org phospho ester of ethoxylated phenol, acid free	Rhone-Poulenc	n/a	10%	50%	55%	60%	65%	70%	5	20	25	30	35	
35	Lubrhophos LB-400	Org phosphate ester of ethoxylated oleyl alcohol, acid free	Rhone-Poulenc	n/a	20%	60%	72%	80%	84%	86%	20	60	70	80	85	
37	Lubrhophos LK-500	Org phosphate ester of ethoxylated hexanol, acid free	Rhone-Poulenc	n/a	10%	45%	48%	50%	56%	60%	5	20	25	25	28	
249	Mednique 2062	(Not available)	Cognis	n/a	0	0	5%	5%			0	0	0	5		
20	Miranol DM Conc 45%	Sodium stearoamphoacetate(Amephoteric)	Rhone-Poulenc	amepho	20%	70%	83%	85%	87%	90%	8	60	75	80	80	

WETTABILITY ALTERATION

No.	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of oil-wet to						Crude oil contact angle on calcite surface (deg. 0 = spreading, 180 = non-wet to oil)											
					water-wet			water-wet			24 hrs		3days		1 wk.		2 wks		1 mth		2 mth	
					24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
21	Miranol FBS	Disodium cocoamphopropionate(Amphoteric)	Rhone-Poulenc	amepho	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM			
8	MIRANOL JS CONC.	Sodium cocoamphoxypropylsulfonate	Rhodia, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
7	MIRANOL CS CONC.	Sodium cocoamphoxypropylsulfonate	Rhodia, Inc.	anionic	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
54	Miratain BET-D 33	Not Available(Amphoteric)	Rhone-Poulenc	amphoteric	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM			
31	Mirataine BB	Laury/myristylamido propyl betain	Rhone-Poulenc	amphoteric	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
34	Mirataine BET-O 30	Oleamido propyl betain	Rhone-Poulenc	amphoteric	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
33	Mirataine BET-W	Cocoamido propyl betain	Rhone-Poulenc	amphoteric	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
32	Mirataine COB	Coco/oleamido propyl betain	Rhone-Poulenc	amphoteric	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
198	Neodol 1-3	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	8.7	0	40%	50%	55%				0	60	80	85							
199	Neodol 1-5	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	11.2	15%	75%	85%	85%				15	50	60	60							
200	Neodol 1-7	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	12.8	10%	70%	85%	85%				15	50	70	70							
134	Neodol 1-7	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	12.8	10%	60%	75%	80%	81%	82%		10	45	60	65	70						
201	Neodol 1-9	C11 linear primary alcohol ethoxylate	Norman, Fox & Co	13.9	0	10%	80%	40%				0	5	65	80							
132	Neodol 23-6.5	C12-13 linear primary alcohol ethoxylate	Norman, Fox & Co	12.1	10%	25%	70%	85%	92%	95%		10	3	80	85	90						
202	Neodol 23-6.5	C12-13 linear primary alcohol ethoxylate	Norman, Fox & Co	12.1	5%	15%	60%	60%				0	20	45	85							
133	Neodol 25-3	C12-15 linear primary alcohol ethoxylate	Shell Chemicals	7.8	30%	70%	85%	90%	95%	95%		30	60	80	90	90						
135	Neodol 25-3S	(Not available)	Shell Chemicals	n/a	0	5%	10%	20%	25%	30%		0	0	0	5	10						
136	Neodol 25-7	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	12.3	25%	55%	65%	85%	87%	90%		24	35	40	60	70						
203	Neodol 25-7	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	12.3	10%	45%	55%	70%				15	20	25	60							
204	Neodol 25-9	C12-15 linear primary alcohol ethoxylate	Norman, Fox & Co	13.1	0	30%	65%	55%				0	30	70	70							
210	NEODOX 23-6	(Not available)	Westhollow Tech.	n/a	85%	90%	95%	96%				75	87	90	90							
212	NEODOX 25-11	(Not available)	Westhollow Tech.	n/a	35%	65%	65%	65%				30	40	40	40							
211	NEODOX 25-6	(Not available)	Westhollow Tech.	n/a	80%	85%	90%	90%				40	40	45	45							
213	NEODOX 91-5	(Not available)	Westhollow Tech.	n/a	75%	85%	85%	85%				25	30	30	40							
214	NEODOX 91-7	(Not available)	Westhollow Tech.	n/a	70%	75%	75%	75%				20	25	25	40							
205	Norfox F-221	Complex fatty amido ester	Norman, Fox & Co	5.0	0	0	0	0				0	0	0	0							
197	Octyl Stearate	Octyl Stearate	CRODA	n/a	10%	45%	70%	83%				5	10	10	20							
175	Pluronic 17R2	Block copolymers of propylene, ethylene oxides	BASF	n/a	0	0	0	0	0			0	0	0	0				0			
163	Pluronic F 38	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	30.0	10%	15%	25%	30%	50%			0	5	5	5	10						
164	Pluronic F 77	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	24.0	0	0	0	0	0			0	0	0	0	0						
179	Pluronic F-108	Block copolymers of propylene, ethylene oxides	BASF	27.0	0	0	0	0	0			0	0	0	0	0						
176	Pluronic F-68	Block copolymers of propylene, ethylene oxides	BASF	29.0	0	0	0	0	0			0	0	0	0	0						
177	Pluronic F-87	Block copolymers of propylene, ethylene oxides	BASF	24.0	0	0	0	0	0			0	0	0	0	0						
178	Pluronic F-88	Block copolymers of propylene, ethylene oxides	BASF	28.0	0	0	0	0	0			0	0	0	0	0						
170	Pluronic L 101	Block copolymers of propylene, ethylene oxides	BASF	1.0	5%	20%	30%	45%	70%			0	15	16	17	18						
171	Pluronic L 103	Block copolymers of propylene, ethylene oxides	BASF	n/a	0	0	0	0	0			0	0	0	0	0						
172	Pluronic L 121	Block copolymers of propylene, ethylene oxides	BASF	5.0	0	15%	20%	25%	40%			0	10	10	15	18						
173	Pluronic L 122	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	4.0	10%	20%	30%	65%	85%			5	10	30	30	30						
166	Pluronic L 42	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	8.0	0	5%	15%	25%	40%			0	0	5	5	10						
167	Pluronic L 43	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	12.0	5%	10%	30%	50%	75%			0	5	10	15	20						
168	Pluronic L 44	Block copolymers of propylene, ethylene oxides	BASF	16.0	0	0	5%	10%	20%			0	0	0	5	10						
169	Pluronic L 63	Block copolymers of propylene, ethylene oxides	BASF	11.0	0	0	5%	8%	15%			0	0	0	5	10						
184	Pluronic L-31	Block copolymers of propylene, ethylene oxides	BASF	5	0	0	0	0	0			0	0	0	0	0						
185	Pluronic L-44	Block copolymers of propylene, ethylene oxides	BASF	16	0	0	0	0	0			0	0	0	0	0						
186	Pluronic L-61	Block copolymers of propylene, ethylene oxides	BASF	16	0	0	0	0	0			0	0	0	0	0						
187	Pluronic L-62	Block copolymers of propylene, ethylene oxides	BASF	7	0	0	0	0	0			0	0	0	0	0						
188	Pluronic L-64	Block copolymers of propylene, ethylene oxides	BASF	15	0	0	0	0	0			0	0	0	0	0						
189	Pluronic L-72	Block copolymers of propylene, ethylene oxides	BASF	6.5	0	0	5%	10%	15%			10	10	10	10	10						
190	Pluronic L-81	Block copolymers of propylene, ethylene oxides	BASF	2	0	0	0	5%	10%			5	5	5	5	5						
191	Pluronic L-92	Block copolymers of propylene, ethylene oxides	BASF	5.5	0	0	0	0	5%			5	5	5	5	5						

WETTABILITY ALTERATION

No.	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Area% of oil-wet to						Crude oil contact angle on calcite surface (deg. 0 = spreading, 180 = non-wet to oil)											
					water-wet			water-wet			24 hrs		3days		1 wk.		2 wks		1 mth		2 mth	
					24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
165	Pluronic P 104	Block copolymers of propylene, ethylene oxides	Wyandotte Chem	13.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
182	Pluronic P-103	Block copolymers of propylene, ethylene oxides	BASF	9	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
183	Pluronic P-123	Block copolymers of propylene, ethylene oxides	BASF	8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
180	Pluronic P-84	Block copolymers of propylene, ethylene oxides	BASF	14.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
181	Pluronic P-85	Block copolymers of propylene, ethylene oxides	BASF	16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
39	Rhodacal 330	Isopropylamine branched alkylbenzene aryl sulfonate	Rhodia, Inc.	anionic	0%	20%	30%	32%	36%	45%	0	10	15	15	20							
40	Rhodacal IPAM	Isopropylamine salt of linear alkylbenzene sulfonic acid	Rhodia, Inc.	anionic	0%	0%	0%	2%	5%	5%	0	0	0	0	0							
47	Rhodameen OA-910	PEG-30 oleamine(Cationic)	Rhone-Poulenc	16.4	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM			
48	Rhodameen PN-430	PEG-5 hydrogenated tallow amine(Cationic)	Rhone-Poulenc	cationic	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM			
41	Rhodamoxb LO	Lauryl dimethylamine oxide (nonionic/cationic)	Rhodia, Inc.	non/cat	10%	20%	25%	35%	40%	40%	5	10	10	15	20							
42	Rhodapex CD-128	Ammonium capryleth sulfate (Anionic)	Rhone-Poulenc	anionic	15%	40%	60%	70%	75%	80%	10	25	35	50	60							
43	Rhodapex CO-436	Ammonium nonoxynol-4 sulfate(Anionic)	Rhone-Poulenc	anionic	0	0	0	0	0	0	0	0	0	0	0							
45	Rhodaquat DAET-90	Not Available(Cationic)	Rhone-Poulenc	cationic	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM			
46	Rhodaquat M242C/29	Cetrimonium chloride(Cationic)	Rhone-Poulenc	cationic	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM			
44	Rhodaquat T	Ditalow imidazolinium(Cationic)	Rhone-Poulenc	cationic	10%	35%	45%	55%	65%	67%	10	20	30	35	40							
53	RHODOPOL 23	Xanthan gum	Rhone-Poulenc	n/a	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM	TBM			
103	SDS	Sodium dodecyl sulfonate	Aldrich	anionic	0	0	0	0	0	0	0	0	0	0	0							
85	SIL WET® L-7001	Silicone glycol copolymer	Union Carbide	5-8	25%	50%	65%	72%	74%	75%	15	35	45	50	55							
83	SIL WET® L-720	Silicone glycol copolymer	Union Carbide	5-8	23%	50%	70%	76%	80%	82%	12	15	16	17	18							
84	SIL WET® L-722	Silicone glycol copolymer	Union Carbide	5-8	25%	55%	68%	73%	75%	75%	15	20	20	20	20							
86	SIL WET® L-7500	Silicone glycol copolymer	Union Carbide	5-8	25%	50%	55%	60%	65%	70%	20	3	35	40	45							
87	SIL WET® L-7600	Silicone glycol copolymer	Union Carbide	5-8	30%	66%	74%	82%	85%	88%	25	35	38	39	39							
88	SIL WET® L-7602	Silicone glycol copolymer	Union Carbide	5-8	30%	65%	70%	80%	85%	85%	18	32	40	45	52							
89	SIL WET® L-7605	Silicone glycol copolymer	Union Carbide	5-8	30%	55%	75%	80%	84%	87%	20	24	26	28	30							
90	SIL WET® L-7607	Silicone glycol copolymer	Union Carbide	5-8	35%	60%	70%	81%	83%	85%	20	30	32	34	35							
91	SIL WET® L-7614	Silicone glycol copolymer	Union Carbide	5-8	0	0	5%	5%	5%	10%	0	0	0	5	6							
82	SIL WET® L-77	Silicone glycol copolymer	Union Carbide	5-8	30%	75%	80%	85%	90%	92%	10	16	18	20	20							
92	SPAN® 20	Sorbitan monolaurate	ICI Chemicals	8.6	20%	35%	40%	52%	60%	66%	20	40	60	70	75							
93	SPAN® 40	Sorbitan monopalmitate	SIGMA	6.7	10%	25%	40%	45%	50%	52%	5	25	30	35	45							
94	SPAN® 60	Sorbitan monostearate	ICI Chemicals	4.7	10%	20%	30%	40%	45%	50%	5	15	15	17	18							
95	SPAN® 80	Sorbitan monooleate	ATLAS Chemicals	4.3	0	0	0	0	0	0	0	0	0	0	0							
96	SPAN® 83	Not Available	Aldrich	n/a	0	0	0	5%	5%	5%	0	0	0	0	0							
97	SPAN® 85	Sorbitan trioleate	ICI Chemicals	1.8	10%	25%	30%	40%	47%	50%	10	15	15	20	20							
229	Surfactant 190	(Not available)	Dow Corning	n/a	0	0	0	10%			0	0	0	10								
230	Surfactant 193	(Not available)	Dow Corning	n/a	0	0	0	40%			0	0	0	10								
231	Surfactant 5103	(Not available)	Dow Corning	n/a	0	0	0	0			0	0	0	0								
234	Surfadone LP-100	Caprylyl pyrrolidone	ISP Corp.	6.0	0	0	0	0			0	0	0	0								
235	Surfadone LP-300	Lauryl pyrrolidone	ISP Corp.	3.0	20%	65%	80%	83%			10	30	40	40								
141	Surfynol® 2502	(Not available)	Air Products	n/a	0	0	0	5%	5%	8%	0	0	0	0	5							
139	Surfynol® 440	PEG-3.5 tetramethyl decyenediol	Air Products	8	0	0	0	0	0	0	0	0	0	0	0							
140	Surfynol® 465	PEG-10 tetra- methyl decyenediol	Air Products	13	0	0	5%	5%	8%	8%	0	0	0	5	5							
142	Surfynol® SE-F	Surfactant blend	Air Products	4 - 5	0	0	0	0	0	0	0	0	0	0	0							

WETTABILITY ALTERATION

No.	Surfactant (Trade Name)	Chemical Description	Manufacturer	HLB	Crude oil contact angle on calcite surface (deg. 0 = spreading, 180 = non-wet to oil)											
					Area% of oil-wet to			water-wet								
					24 hrs	3days	1 wk.	2 wks	1 mth	2 mth	24 hrs	3days	1 wk.	2 wks	1 mth	2 mth
110	Tergitol [®] 15-S-12	C12-C14 secondary alcohol ethoxylate	Union Carbide	14.7	60%	75%	80%	86%	88%	90%	50	65	65	70	70	
111	Tergitol [®] 15-S-20	C12-C14 secondary alcohol ethoxylate	Union Carbide	14.7	40%	60%	70%	82%	84%	85%	35	35	40	45	50	
106	Tergitol [®] 15-S-3	C12-C14 secondary alcohol ethoxylate	Union Carbide	8.3	25%	30%	40%	45%	50%	55%	12	15	20	25	30	
112	Tergitol [®] 15-S-40	C12-C14 secondary alcohol ethoxylate	Union Carbide	16.4	40%	55%	65%	80%	82%	85%	20	25	30	35	35	
107	Tergitol [®] 15-S-5	C12-C14 secondary alcohol ethoxylate	Union Carbide	10.6	75%	80%	90%	95%	98%	100%	80	80	90	120	150	
108	Tergitol [®] 15-S-7	C12-C14 secondary alcohol ethoxylate	Union Carbide	12.4	65%	80%	84%	90%	93%	95%	60	70	80	88	90	
109	Tergitol [®] 15-S-9	C12-C14 secondary alcohol ethoxylate	Union Carbide	13.3	58%	75%	80%	82%	84%	85%	50	70	75	80	83	
104	Tergitol [®] MIN FOAM 1X	Propoxylated & ethoxylated fatty acids, alcohols	Union Carbide	n/a	75%	80%	85%	90%	95%	95%	70	90	90	91	92	
105	Tergitol [®] MIN FOAM 2X	Propoxylated & ethoxylated fatty acids, alcohols	Union Carbide	n/a	70%	80%	85%	90%	95%	95%	70	85	85	90	90	
116	Tergitol [®] NP-10	Ethoxylated nonylphenol, nonoxynol-10	Union Carbide	13.2	50%	70%	80%	86%	88%	90%	40	55	60	70	80	
117	Tergitol [®] NP-13	Ethoxylated nonylphenol, nonoxynol-13	Union Carbide	13.9	10%	25%	35%	40%	40%	40%	5	15	20	25	25	
113	Tergitol [®] NP-4	Ethoxylated nonylphenol, nonoxynol-4	Union Carbide	8.9	0	0	0	5%	5%	5%	0	0	0	0	0	
114	Tergitol [®] NP-6	Ethoxylated nonylphenol, nonoxynol-6	Union Carbide	10.9	35%	50%	65%	70%	75%	75%	15	15	20	23	25	
143	Tergitol [®] NP-9	Ethoxylated nonylphenol, nonoxynol-9	Union Carbide	12.9	20%	50%	60%	85%	90%	95%	15	45	60	85	90	
115	Tergitol [®] NP-9.5	Ethoxylated nonylphenol, nonoxynol-9.5	Union Carbide	13.1	45%	60%	70%	82%	82%	85%	40	50	65	70	80	
174	Tetronic 701	Block copolymers of propylene, ethylene oxides	BASF	3.0	5%	10%	20%	30%	40%		0		10	15	20	
75	Trimethyl amm bromide	Trimethyl(tetradecyl) ammonium bromide	SIGMA	cationic	35%	82%	88%	95%	98%	98%	40	70	90	120	150	
144	Triton H-66	Phosphate ester, potassium salt	Union Carbide	anionic	20%	40%	50%	75%	80%	80%	10	15	20	30	30	
126	Triton X-100	Ethoxylated octylphenol, octoxynol-9	Rohm & Hass	13.4	40%	55%	80%	88%	90%	92%	25	50	75	85	90	
127	Triton X-114	Ethoxylated octylphenol, octoxynol-8	Aldrich	12.3	40%	60%	82%	90%	91%	93%	30	50	78	85	89	
128	Triton X-165	Ethoxylated octylphenol, octoxynol-16	Rohm & Hass	15.5	40%	55%	75%	85%	90%	90%	25	30	60	70	80	
129	Triton X-405	Ethoxylated octylphenol, octoxynol-40	Aldrich	17.6	15%	24%	30%	38%	43%	45%	10	12	14	15	16	
125	Triton X-45	Ethoxylated octylphenol, octoxynol-5	Union Carbide	9.8	20%	35%	50%	60%	66%	70%	20	30	35	45	50	
130	Triton X-705	Ethoxylated octylphenol, octoxynol-70	SIGMA	18.4	15%	20%	30%	35%	38%	40%	10	10	15	15	20	
131	Triton XL-80N	Propoxylated & ethoxylated fatty acids, alcohols	Union Carbide	n/a	40%	80%	84%	88%	90%	92%	35	65	75	80	85	
118	Triton [™] BG-10	Alkylpolyglucoside	Dow Chemicals	n/a	58%	80%	90%	95%	96%	97%	50	75	85	90	90	
120	Triton [™] CF-87	Alkylaryl ether, modified	D.C. Atkins Son	12.7	45%	65%	80%	85%	88%	90%	50	67	80	85	90	
119	Triton [™] CG-110	Alkylpolyglucoside	Dow Chemicals	n/a	55%	75%	88%	90%	92%	93%	50	70	75	80	80	
121	Triton [™] N-101	(Not available)	Union Carbide	n/a	45%	65%	85%	90%	91%	92%	45	70	82	87	88	
122	Triton [™] QS-44	Phosphate surfactant in free acid form	Union Carbide	n/a	0	0	0	0	0	0	0	0	0	0	0	
123	Triton [™] X-15	Ethoxylated octylphenol, octoxynol-1	Union Carbide	4.9	35%	50%	60%	70%	75%	75%	15	20	20	30	30	
124	Triton [™] X-35	Ethoxylated octylphenol, octoxynol-3	Rohm & Hass	7.8	0	0	0	0	0	0	0	0	0	0	0	
98	Tween [®] 21	POE (4) Sorbitan monolaurate	ICI Chemicals	13.3	40%	60%	70%	80%	85%	86%	45	60	60	65	70	
99	Tween [®] 60	POE (20) Sorbitan monostearate	Unknown	14.9	10%	25%	30%	35%	38%	40%	5	10	10	15	15	
100	Tween [®] 61	POE (4) Sorbitan monostearate	ATLAS Chemicals	9.6	0	0	5%	8%	9%	10%	0	0	0	0	5	
101	Tween [®] 81	POE (5) Sorbitan monooleate	ICI Chemicals	10.0	70%	80%	90%	92%	94%	95%	70	75	80	90	92	
102	Tween [®] 85	POE (20) Sorbitan trioleate	Aldrich	11.0	30%	50%	55%	60%	68%	70%	25	35	40	40	45	

Note: TBM= to be determined

APPENDIX B.

**LIST OF CALCITE CHIP – McELROY CRUDE OIL
CLEANING RESULTS WITH SURFACTANTS**

Wettability Alteration Test for McElroy Crude Oil in 2%wt. NaCl Solution

Calcite Crystals aged in McElroy Crude Oil at 85 °C for **24 hours**

March 8, 2005

Surfactant Name	HLB	Area% from Oil-wet to Water-wet						Solution appearance
		1 hour	2 hours	8 hours	24 hours	3 days	1 week	
Igepal® CO-530	10.8	75%	85%	92%	95%	96%	96%	slightly yellow
Igepal® CO-630	13	65%	65%	80%	80%	82%	85%	clear
Igepal® CO-710	13.6	70%	75%	80%	80%	85%	86%	clear
Neodol® 1-7	12.8	85%	90%	90%	92%	93%	95%	clear
Neodol® 1-9	13.9	72%	75%	80%	80%	83%	85%	clear
Neodol® 25-7	12.3	85%	90%	90%	90%	90%	90%	clear
Neodol® 25-9	13.1	80%	80%	85%	85%	92%	92%	clear
NEODOX® 25-6	n/a	50%	50%	65%	70%	80%	82%	clear
NEODOX® 25-11	n/a	70%	75%	78%	80%	80%	80%	clear
Tergitol® 15-S-5	10.6	72%	72%	90%	90%	90%	90%	slightly yellow
Tergitol® 15-S-7	12.4	85%	90%	92%	95%	92%	92%	clear
Tergitol® 15-S-9	13.3	85%	87%	90%	92%	93%	93%	clear
Tergitol® 15-S-12	14.7	77%	80%	85%	85%	85%	85%	clear
Tergitol® 15-S-20	14.7	65%	65%	70%	70%	70%	70%	clear
Triton X-100	13.4	50%	55%	65%	70%	70%	72%	clear
Triton X-114	12.3	65%	70%	80%	85%	85%	85%	slightly yellow
Triton X-165	15.5	60%	65%	70%	75%	80%	80%	clear
Triton X-405	17.6	50%	50%	60%	70%	75%	75%	clear
SIL WET® L-77	n/a	80%	80%	80%	80%	83%	83%	clear
Triton™ BG-10	n/a	5%	5%	10%	10%	20%	30%	clear
Agrimul® PG 2067	13.6	0%	0%	5%	10%	20%	30%	clear
ALCODET SK	12.7	80%	85%	85%	85%	86%	85%	slightly yellow
ALCODET 218	13.6	75%	80%	86%	85%	85%	85%	clear
ARQUAD T-50	n/a	15%	20%	45%	65%	70%	70%	slightly yellow
C ₁₀ -triphenyl-bromide	n/a	0%	0%	0%	0%	0%	0%	clear
SIMULSOL AS 48	n/a	0%	0%	0%	0%	0%	0%	clear
SIMULSOL SL 4	n/a	15%	15%	15%	20%	30%	40%	clear
SIMULSOL SL 55	n/a	0%	0%	0%	10%	25%	25%	cloudy

Wettability Alteration Test for McElroy Crude Oil in McElroy **Synthetic Brine**

Calcite Crystals aged in McElroy Crude Oil at 85 °C for **24 hours** March 8, 2005

Surfactant Name	HLB	Area% from Oil-wet to Water-wet						Solution appearance
		1 hour	2 hours	8 hours	24 hours	3 days	1 week	
Igepal® CO-530	10.8	55%	55%	65%	70%	70%	70%	slightly yellow
Igepal® CO-630	13	65%	65%	75%	80%	80%	80%	clear
Igepal® CO-710	13.6	20%	30%	40%	50%	80%	80%	clear
Neodol® 1-7	12.8	80%	85%	87%	90%	90%	92%	clear
Neodol® 1-9	13.9	70%	70%	75%	80%	85%	85%	clear
Neodol® 25-7	12.3	55%	65%	70%	75%	82%	87%	clear
Neodol® 25-9	13.1	60%	65%	76%	80%	82%	82%	clear
NEODOX® 25-6	n/a	50%	50%	70%	75%	78%	78%	clear
NEODOX® 25-11	n/a	30%	40%	50%	60%	60%	60%	clear
Tergitol® 15-S-5	10.6	75%	75%	80%	80%	85%	86%	slightly cloudy
Tergitol® 15-S-7	12.4	80%	85%	90%	90%	92%	92%	clear
Tergitol® 15-S-9	13.3	75%	78%	80%	85%	90%	90%	clear
Tergitol® 15-S-12	14.7	50%	50%	60%	70%	75%	75%	clear
Tergitol® 15-S-20	14.7	45%	45%	50%	55%	70%	75%	clear
Triton X-100	13.4	50%	75%	80%	80%	85%	85%	clear
Triton X-114	12.3	90%	92%	92%	93%	95%	95%	slightly yellow
Triton X-165	15.5	50%	50%	60%	60%	65%	70%	clear
Triton X-405	17.6	50%	55%	55%	65%	70%	73%	clear
SIL WET® L-77	n/a	70%	80%	80%	85%	88%	88%	clear
Triton™ BG-10	n/a	0%	0%	0%	10%	20%	30%	clear
Agrimul® PG 2067	13.6	0%	0%	0%	5%	15%	30%	clear
ALCODET SK	12.7	50%	75%	85%	85%	90%	92%	slightly yellow
ALCODET 218	13.6	40%	40%	60%	70%	70%	70%	clear
ARQUAD T-50	n/a	15%	15%	60%	75%	75%	75%	slightly yellow
C ₁₀ -triphenyl-bromide	n/a	0%	0%	0%	0%	10%	15%	clear
SIMULSOL AS 48	n/a	0%	0%	0%	0%	10%	15%	clear
SIMULSOL SL 4	n/a	0%	0%	0%	5%	15%	30%	clear
SIMULSOL SL 55	n/a	0%	0%	0%	0%	5%	20%	cloudy

Wettability Alteration Test for McElroy Crude Oil in 2.0wt.% NaCl Solution

Calcite **Crystals aged** in McElroy Crude Oil at 85 °C for **7 days**

Surfactant Name	HLB	Solution appearance	Area% from Oil-wet to Water-wet				
			24 hours	3 days	1 week	2 weeks	1 month
Igepal® CO-530	10.8	cloudy	0%	2%	7%	15%	40%
Igepal® CO-630	13	clear	0%	0%	2%	5%	10%
Igepal® CO-710	13.6	clear	0%	0%	0%	3%	8%
Neodol® 1-7	12.8	clear	0%	0%	0%	3%	10%
Neodol® 1-9	13.9	clear	0%	0%	2%	5%	15%
Neodol® 25-7	12.3	clear	0%	0%	5%	10%	20%
Neodol® 25-9	13.1	clear	0%	0%	0%	5%	10%
NEODOX® 25-6	n/a	clear	0%	0%	5%	15%	35%
NEODOX® 25-11	n/a	clear	0%	0%	0%	0%	0%
Tergitol® 15-S-5	10.6	slightly cloudy	0%	2%	10%	20%	50%
Tergitol® 15-S-7	12.4	clear	0%	2%	6%	15%	30%
Tergitol® 15-S-9	13.3	clear	0%	0%	0%	3%	10%
Tergitol® 15-S-12	14.7	clear	0%	0%	0%	0%	2%
Tergitol® 15-S-20	14.7	clear	0%	0%	0%	0%	2%
Triton X-100	13.4	clear	0%	0%	2%	4%	10%
Triton X-114	12.3	cloudy	0%	0%	0%	0%	3%
Triton X-165	15.5	clear	0%	0%	0%	0%	0%
Triton X-405	17.6	clear	0%	0%	0%	3%	6%
SIL WET® L-77	n/a	slightly cloudy	0%	0%	0%	0%	2%
Triton™ BG-10	n/a	clear	0%	0%	0%	0%	0%
Agrimul® PG 2067	13.6	clear	0%	0%	0%	0%	0%
ALCODET SK	12.7	clear	0%	0%	0%	0%	3%
ALCODET 218	13.6	clear	0%	0%	0%	0%	0%
ARQUAD T-50	n/a	clear	0%	0%	0%	0%	0%
C ₁₀ -triphenyl-bromide	n/a	clear	0%	0%	0%	0%	0%
SIMULSOL AS 48	n/a	clear	0%	0%	0%	0%	0%
SIMULSOL SL 4	n/a	clear	0%	0%	2%	5%	0%
SIMULSOL SL 55	n/a	cloudy	N/A	N/A	N/A	N/A	N/A

Wettability Alteration Test for McElroy Crude Oil in McElroy Synthetic Brine							
Calcite Crystals aged in McElroy Crude Oil at 85 °C for 7 days							
Surfactant Name	HLB	Solution appearance	Area% from Oil-wet to Water-wet				
			24 hours	3 days	1 week	2 weeks	1 month
Igepal® CO-530	10.8	cloudy	0%	0%	0%	0%	0%
Igepal® CO-630	13	clear	0%	0%	0%	0%	5%
Igepal® CO-710	13.6	clear	0%	0%	0%	0%	3%
Neodol® 1-7	12.8	clear	0%	0%	0%	3%	10%
Neodol® 1-9	13.9	clear	0%	0%	0%	0%	3%
Neodol® 25-7	12.3	clear	0%	3%	10%	20%	45%
Neodol® 25-9	13.1	clear	0%	5%	15%	30%	70%
NEODOX® 25-6	n/a	clear	0%	0%	0%	0%	0%
NEODOX® 25-11	n/a	clear	0%	0%	0%	0%	0%
Tergitol® 15-S-5	10.6	slightly cloudy	0%	0%	0%	0%	0%
Tergitol® 15-S-7	12.4	clear	0%	0%	0%	2%	10%
Tergitol® 15-S-9	13.3	clear	0%	0%	0%	3%	10%
Tergitol® 15-S-12	14.7	clear	0%	0%	5%	10%	20%
Tergitol® 15-S-20	14.7	clear	0%	0%	0%	5%	15%
Triton X-100	13.4	clear	0%	0%	2%	6%	12%
Triton X-114	12.3	cloudy	0%	0%	0%	0%	0%
Triton X-165	15.5	clear	0%	2%	10%	20%	40%
Triton X-405	17.6	clear	0%	3%	7%	12%	25%
SIL WET® L-77	n/a	slightly cloudy	0%	0%	0%	0%	2%
Triton™ BG-10	n/a	clear	0%	0%	0%	0%	0%
Agrimul® PG 2067	13.6	clear	0%	0%	0%	0%	0%
ALCODET SK	12.7	clear	0%	0%	0%	0%	2%
ALCODET 218	13.6	clear	0%	0%	0%	0%	6%
ARQUAD T-50	n/a	clear	0%	0%	0%	0%	0%
C ₁₀ -triphenyl-bromide	n/a	clear	0%	0%	0%	0%	0%
SIMULSOL AS 48	n/a	clear	0%	0%	0%	0%	0%
SIMULSOL SL 4	n/a	clear	0%	0%	2%	5%	15%
SIMULSOL SL 55	n/a	cloudy	N/A	N/A	N/A	N/A	N/A