Recommended Practices for Laboratory Evaluation of Surface Active Agents for Well Stimulation

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RECOMMENDED PRACTICES FOR LABORATORY TESTING OF SURFACE ACTIVE AGENTS FOR WELL STIMULATION

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RECOMMENDED PRACTICES FOR LABORATORY TESTING OF SURFACE ACTIVE AGENTS FOR WELL STIMULATION

SCOPE

A. Surface active agents are frequently added to treating fluids for stimulation of oil, gas, and injection wells to perform one or more of the following functions:

1. prevent or minimize emulsification of treating fluid with formation fluid,

2. reduce water saturation,

3. alter wettability,

4. suspend fine particles dislodged by the treatment for removal or redistribution, and

5. stabilize foam or emulsion in the treating fluid.

B. This diversity of function has resulted in the availability of a large number of products for use in petroleum production operations. Testing of surface active agents as described herein is primarily for qualitative comparison of performance and for general screening related to preceding Paragraph A, items 1-4. Procedures are given for the following:

1. emulsion and sludge tests,

2. measurement of fluid flow through cores,

3. measurement of interfacial tension, and

4. measurement of wettability.

C. Since chemical activity of a surface active agent (surfactant) depends on its chemical environment, pressure, temperature, and time, the user is advised to test the surface active agent in the presence of all additives to be used in a field treatment at their appropriate concentration. Production batch and shelf life may effect variations in surface active agents' properties, so that in many cases even these items must be considered in evaluating a surface active agent.

SECTION 1
EMULSION TESTS FOR CHARACTERIZATION OF SURFACE ACTIVE AGENTS IN ACID, BRINE, OR OIL

USE AND PURPOSE OF EMULSION TESTS

1. The purpose of the emulsion test is to indicate the tendency of a surface active agent to increase or decrease the emulsification of a particular oil-brine or acid-oil system. These tests are designed to indicate the tendency of a system to emulsify but do not determine whether emulsification actually occurs or persists during well stimulation operations. Since the stability of emulsions can be enhanced by the presence of finely divided solids often created in well stimulation processes, all testing of surface active agents includes use of finely divided particles as a component.

EQUIPMENT AND MATERIALS

2. The equipment and materials for emulsion testing include the following:

a. High speed stirrer (mixer) [Hamilton-Beach Model 936, or equivalent, with standard disc head or Sargent-Welch agitator S-76695].

b. 400 ml tall form beakers for mixing.*

c. 100 ml graduated cylinders.*

d. Stopwatch or timer.

e. Syringes one milliliter, graduated.*

f. Acid solution containing corrosion inhibitor and other additives.

g. Crude oil.

h. Surface active agent, demulsifier.

i. Formation cores, when available, or silica flour (approximately 85-95% passing a 325-mesh sieve analysis) and bentonite (Wyoming sodium bentonite, cement-type, untreated).

PROCEDURE

Sandstone Acidizing Tests

3. Prepare partially spent acid by reacting two liters of acid with one liter of formation sand. The acid solution should contain 3 weight percent hydrofluoric acid (HF), 12 weight percent hydrochloric acid (HCl), the recommended concentration of corrosion inhibitor, and any other additives to be evaluated in the actual treatment. If formation sand is unavailable, use one liter of a 50 weight percent silica flour — 50 weight percent bentonite mixture to spend the acid and provide solids content. Allow acid

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*Note: Use plastic containers for solutions that contain hydrofluoric acid.

solution to remain in contact with solids for at least 24 hours.*

4. Decant spent acid solution and store in plastic container for testing.

5. Disperse 2.5 grams of pulverized formation fines or 2.5 grams of a 50 weight percent silica flour — 50 weight percent bentonite mixture in 25 ml of spent acid.

6. Add 75 ml of crude oil to this spent acid solution. Emulsify the solution with mixer at 14,000 to 18,000 rpm for 30 seconds. Pour emulsion immediately into 100 ml graduated cylinder and record volume of water breakout at 15 minutes, 1 hour, and 24 hours. Tests are usually conducted at ambient laboratory temperature.

7. Repeat procedures in Pars. 5 and 6 omitting the demulsifier for control.

Carbonate Acidizing Test—Live Acid Test

8. Use an acid solution which includes all the additives in the same concentration as prescribed for the field treatment. It may be necessary to run a series of screening tests to select the most effective non-emulsifying system. Disperse 2.5 grams of a 90 weight percent silica flour—10 weight percent bentonite mixture in 50 ml of acid solution.

9. Add 50 ml of crude oil to the acid dispersion. Emulsify the solution with the mixer at 14,000 to 18,000 rpm for 30 seconds. Pour emulsion immediately into 100 ml graduated cylinder and record volume of water breakout at elapsed time intervals indicated in Figure 1 (refer to Par. 15). Tests are usually conducted at ambient laboratory temperature.

10. Repeat steps in Pars. 8 and 9 omitting the demulsifier for test control.

11. Repeat preparation of test solution in Par. 8 but use 25 ml of the acid dispersion with 75 ml of crude oil in the test described in Pars. 9 and 10.

Carbonate Acidizing Test—Spent Acid Test

12. Spend the acid solution containing all additives except demulsifier on an excess of crushed formation rock. Spending should be complete in 24 hours. If time imposes limitations, allow the acid to contact formation solids until effervescence ceases. Gently swirl the mixture to disperse fines; decant the acid with suspended fines into another container for testing.

13. If no formation rock is available, prepare a synthetic spent acid solution from reagent grade calcium chloride and water at a concentration equivalent to the chloride concentration in live acid. The solution should contain all other additives to be used for field treatment, each at its recommended concentration. Adjust the pH to a value between 1 and 5 using hydrochloric acid. If an acid solution other than hydrochloric acid is simulated, use the appropriate calcium salt. Disperse 2.5 grams of a 90 weight percent silica flour — 10 weight percent bentonite mixture in 50 ml of acid solution.

14. Prepare the emulsion with spent acid as described in Pars. 9 through 11 and record data.

REPORTING TEST RESULTS

15. Data should be recorded on the form shown in Figure 1. Results are reported as volume percent of original aqueous phase such that 100 percent represents complete water breakout. In addition to recording the degree of water breakout, include information in the remarks column, such as, volume of sediment layer, quality of the interface (e.g., sharp, diffuse), and whether the oil adheres to sides of the cylinder in the water layer.

16. An optional but valuable record can be obtained by taking color photographs of the emulsion system at the completion of the test period.

ACID SLUDGE TEST

17. Some crude oils in contact with acid yield precipitates referred to as sludges, even though the system may not exhibit emulsion tendency. The test described in Pars. 18-21 is a useful procedure to demonstrate the tendency of sludge to form at laboratory conditions. Whether or not the tendency exists at field conditions or whether the anti-sludge agent performs satisfactorily under those conditions may not be determined by this method.

Equipment and Materials

18. The following equipment and materials are required for the acid sludge test:

a. Surface active agent, acid sludge preventive agent.

b. Acid solution containing corrosion inhibitor and all additives except sludge preventive surface active agent.

c. Crude oil.

d. Water bath, temperature controlled.

e. Bottles with screw caps.*

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*Note: Use plastic containers for solutions that contain hydrofluoric acid.

FIG. 1
ACID-OIL EMULSION TESTS DATA SHEET

OPERATOR:
WELL:
FIELD:
FORMATION:
DEPTH:
COUNTY:

SUBMITTED BY:
SOURCE OF SAMPLE:
DATE SAMPLED
DATE RECEIVED:

CONC. AND TYPE OF ACID.
CONC. OF INHIBITOR:
TYPE & CONC. OF SOLIDS:
TEST TEMPERATURE
ANALYSIS BY.

PERCENTAGE OF ORIGINAL ACID SEPARATED AT VARIOUS TIME INTERVALS AFTER EMULSIFYING

OIL/ACID RATIO																
ADDITIVES																
CONCENTRATION,%																
GAL/1000 GAL ACID																
SETTLING TIME	UNSPENT	SPENT	UNSPENT	SPENT	UNSPENT	SPENT	UNSPENT	SPENT	UNSPENT	SPENT	UNSPENT	SPENT	UNSPENT	SPENT	UNSPENT	SPENT
1(MIN)																
2																
4																
6																
8																
10																
15																
30																
60 (1 HOUR)																
180 (3 HOURS)																
1440(24 HOURS)																
% EMUL. END																
VOL. EMUL. END																
SOLIDS*																
INTERFACE**																
VOL. SEDIMENT																

REMARKS:

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*Preferential wetting of solids. OB=oil wet bottom. OO=oil-wet oil phase. WB=water wet bottom
**Interface. S=sharp. R=ragged. D=diffuse.

[illegible]

f. 100-mesh stainless steel screen, 3-inch square.

g. Wash bottle filled with Soltrol 130 (Phillips Petroleum Co.).

h. Wash bottle filled with water.

Procedure

19. Pour acid into a clean bottle. Add an equal volume of crude oil, free of solids and emulsion. Cover bottle and shake vigorously. Place the mixture in a water bath at formation temperature and let stand quiescent for at least four hours, preferably 24 hours. Carefully pour the mixture through a clean, 100-mesh stainless steel wire screen. If no solids remain on the screen no sludge has been formed.* If solids are present, wash the screen alternately with warm water and Soltrol 130. This will remove emulsions and paraffins but will not remove sludge caused by acid. Describe the amount of sludge according to the list below. Report the result in the remarks section on the form shown in Figure 1.

No sludge — no solid particles retained on the screen.

Trace — a very few small particles on the screen.

Moderate — particles obviously present.

Heavy — many large particles.

20. Repeat Par. 19 procedures using the acid sludge preventive agent at the concentration specified by the supplier.

21. Anti-sludging agents may influence emulsion tests. If an anti-sludge agent is to be employed in a well treating solution, emulsion tests should include the agent as a part of the test system.

SECTION 2

SURFACE ACTIVE AGENT EVALUATION BY FLOW TEST IN CORES

22. This test procedure may be used as an indication of the ability of a surface active agent to remove a fluid block from a formation using representative core samples. Connate fluid saturations are established in the core appropriate to the type of well being simulated. In sequence, a fluid block is induced and then treated with the surface active agent solution. Finally, the mobile fluid appropriate to the simulated well is allowed to flow through the core. Permeability is measured at each stage as follows:

a. before the fluid block is induced,

b. after the fluid block is formed but prior to surface active agent treatment, and

c. after surface active agent treatment.

Comparison of these permeability measurements and the rate of change indicates the effectiveness of the surface active agent.

MATERIALS

23. Core. A core sample from the formation to be treated is preferred. When such core material is not available, substitute another core of suitable permeability and similar lithology. Use a core two inches long and one inch in diameter.

24. Water. Use a prepared brine solution to establish connate water saturation in the core and to measure permeability to brine. Prepare the solution with pure chemicals, so that either (a) the synthesized brine has the same chemical composition as the actual formation water, or (b) the brine contains 9.0 weight percent sodium chloride and 1.0 weight percent calcium chloride. Prior to use, filter the brine thoroughly and deaerate by vacuum pump for fifteen minutes. Minimize contact of the prepared brine with air to prevent precipitation of calcium carbonate.

25. Reference Oil. Use a clean, nonplugging oil with a viscosity convenient for laboratory testing or representative of formation oil. Commercially available oils employed for this purpose are Soltrol 130 (Phillips Petroleum Co.) and Dispersol (Shell Oil Co.). Prior to use, filter the reference oil through silica gel (200-mesh) to remove surface active agents. Then deaerate oil by vacuum pump for two hours.

26. Gas. Use nitrogen gas to establish gas saturation in the core and to measure permeability to gas.

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*Precipitates may form that pass through the 100-mesh screen. While not classified as sludge, the particles can be detected by flow tests using cores outlined in Section 2.

27. Surface Active Agent. Prepare the surface active agent solution according to supplier's instructions. Some surface active agents can be stored for long periods after preparation without significant change; others must be used shortly after preparation. Follow supplier's recommendations on shelf life and method of storage for surface active agents and solution.

EQUIPMENT

28. Core Holder. Mount the core so that fluid does not bypass the core. A rubber sleeve type holder is recommended for this purpose.

29. Flow Apparatus. The apparatus for this test must provide:

a. manifolding flow of reference oil, water, gas, and surface active agent solution into either end of the core, and

b. measurement of pressure, flow rate, and cumulative volume of fluid. A schematic flow diagram incorporating these requirements is shown in Figure 2. All flow lines between fluid vessels and core face must be absolutely clean. Precautions must be taken to avoid contamination of the system with treating fluid, reaction products, or solids.

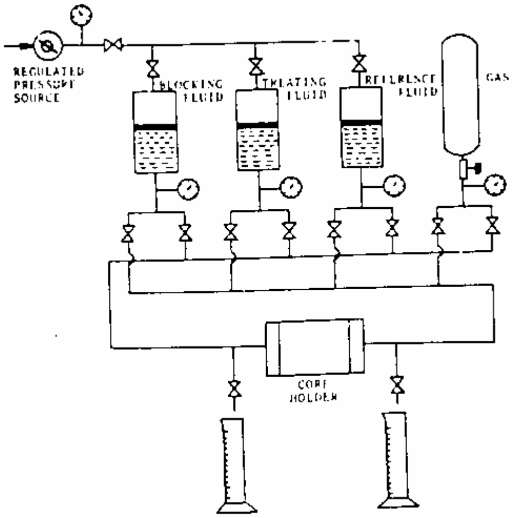

FIG. 2
SCHEMATIC FLOW DIAGRAM FOR CORE TEST

30. Pumping Equipment. The method of pumping is not specified. Pumping equipment must be able to force each fluid through the flow system at a constant specified pressure without contamination or aeration of the injected fluid. Do not use a system where test fluids are in direct contact with a gas under pressure. One type of pump suitable for these tests consists of a free piston and a cylinder. The free piston segregates the driving fluid from the pumped fluid. An alternative type of pump uses a bladder or a diaphragm to separate the fluids. (In a system where fluids are pumped directly by gas, the fluid becomes saturated with gas under inlet pressure. As the fluid flows through the core, the pressure drops and gas may come out of solution to reduce the permeability of the core to the reference fluid.)

PROCEDURE

31. Clean core thoroughly. Core cleaning procedures are described in *API RP 27: Recommended Practice for Determining Permeability of Porous Media*. Dry core in an oven at 200-220 F for at least two hours. Cool and weigh the core.

32. Measure permeability of the core to the gas at a differential pressure, preferably less than 10 psi, and at room temperature. For cores of low permeability, it may be necessary to increase the differential pressure so that the flow rate of gas is fast enough to be measureable in a reasonable length of time. The selected differential pressure should preclude turbulent flow within the core in this test.

33. Evacuate the core for at least one hour with a vacuum pump at a pressure below 1 mm mercury. Next, introduce brine slowly into the evacuated container. Let the brine imbibe slowly into the core. When the core is completely covered with brine, vent the container to the atmosphere immediately. Allow the core to stand for at least one hour before removing it.

34. Remove the saturated core from the brine and blot off excess water. Weigh the core. The pore volume of the core is equal to the weight of the brine (i.e., weight of wet core less weight of dried core) divided by the brine density.

35. Measure the permeability of the core to brine at a differential pressure, preferably less than 100 psi; flow at least 10 pore volumes of brine through the core before making permeability measurement. Continue flow of brine until equilibrium permeability is attained. Equilibrium permeability is defined in this procedure as the permeability at which flow of ten additional pore volumes produces less than 5 percent change in permeability.

Establish Appropriate Initial Fluid Saturation

36. The type of well being simulated will dictate the fluid saturations of the core prior to surface active agent treatment. To simulate an oil well, use a core that contains oil and residual water. Other well conditions require the following saturations:

a. Dry gas well — gas and residual water.

b. Water injection well — water and residual oil.

c. Gas injection well — gas, residual water, and residual oil.

d. Water supply well — water only.

Methods of saturation are described in the following paragraphs.

Establishing Oil Saturation.

37. Water content of the core is reduced to connate water saturation by flowing reference oil, preferably at a differential pressure of 100 psi, across the core. Flow oil in the direction to simulate production of fluid from the formation until an equilibrium permeability value is reached. During the operation, permeability should continue to increase until equilibrium is reached as a result of decreasing water saturation. If permeability decreases at this stage, it suggests that contaminants are plugging the core. Terminate flow. Refilter and evacuate the oil, clean all flow lines. Repeat the procedure with another core.

Establishing Gas Saturation.

38. Flow gas saturated with water through the core in the appropriate direction to simulate production or injection as required. Stop gas flow when visible production of liquid ceases. Measure equilibrium permeability at a differential pressure low enough to avoid turbulent flow within the pore space, but sufficient to provide a measurable flow rate of gas.

Establishing Water Saturation.

39. Flow water through core preferably at a differential pressure of 100 psi across the core in the appropriate direction to simulate production or injection. Flow water until equilibrium permeability is reached.

Measuring Reference Fluid Permeability.

40. The value of equilibrium permeability measured in Pars. 37, 38, or 39 is the reference permeability depending upon whether the mobile fluid in the simulated well is oil, gas, or water, respectively.

Establish Fluid Block

41. Flow ten pore volumes of water, oil, or other fluid of interest at a convenient pressure through the core to establish a fluid block. The direction of flow should simulate flow of the anticipated source of the blocking fluid. Let core stand for at least six hours.

42. Flow fluid used in establishing reference permeability through core at a differential pressure less than that used in establishing the reference permeability. Continue flow at that same differential pressure until equilibrium permeability is reached. For liquid flow, use a differential pressure of 25 psi. For gas flow the differential pressure should be the same as was used in Par. 38 to establish equilibrium permeability. The permeability thus measured is referred to as the *damaged permeability*.

Inject Surfactant Treating Fluid.

43. Flow ten pore volumes of the surface active agent treating fluid through the core at a convenient differential pressure not exceeding 25 psi. Flow should be in the injection direction. Allow to stand for at least six hours.

Measure Final Permeability After Treatment.

44. Flow the fluid used in establishing the reference permeability through the core at the same differential pressure set forth in Par. 42 until an equilibrium permeability is attained. The permeability thus measured is the *final permeability*. Record permeability versus pore volume throughput to determine rate of cleanup after treatment.

REPORTING TEST RESULTS

45. Test results shall be reported as percent recovery of initial reference (undamaged) permeability as a function of pore volume throughput. In addition, report the name of the surface active agent along with the concentration of surface active agent used, core properties, and any deviations from the test procedure.

SECTION 3
INTERFACIAL TENSION AND WETTABILITY

46. To measure interfacial tension of a system where the value is greater than 1 dyne per centimeter, use the duNouy tensiometer. For more precise measurement and to have the added capability of measuring values of very low interfacial tension, use either the pendent drop, sessile drop, or spinning drop method. Both the sessile drop and spinning drop methods can be used for time-dependent systems. One advantage of the sessile drop method is that the contact angle can be calculated from drop dimensions. This is most useful when conditions are such that the contact angle is not well defined. Wettability is determined by the contact angle between a drop and a clean surface surrounded by an immiscible phase of different density. In addition to calculating contact angle from drop dimensions, it can be measured directly when the angle is well defined. Qualitative determination of wettability can be made by observing the dispersive tendency of solid particles in oil and aqueous phases, but for some systems such determinations are indeterminant.

INTERFACIAL TENSION MEASUREMENT

duNouy Tensiometer—Ring Method

47. The ring method for determining interfacial or surface tension is based on measuring the force required to detach a ring from the surface of a liquid or from the interface between two liquids. Recommended procedures are contained in manuals supplied with commercial instruments and are found in *ANSI/ASTM D971: Method of Test for Interfacial Tension of Oil Against Water by the Ring Method,** Part 17, "Petroleum Products, Fuel, Solvents, Lubricating Oils, Cutting Oils, Grease". The duNouy tensiometer is widely used within the petroleum industry. Several points are listed below to aid in precise measurement.

a. Instrument calibration should be checked daily, or before measurement if used less frequently.

b. Do not use a ring bent out of plane (slight distortion of the circular portion can be tolerated).

c. All interfaces in a series of measurements should be aged for the same length of time and that time should be reported *(ANSI/ASTM D971** recommends 30 seconds).

d. The ring must move from the liquid phase that completely wets the ring to the other phase (for interfacial tension).

e. This method loses reliability at readings less than 1 dyne/cm.

f. Correction factors must be applied to obtain absolute values. Such factors are provided in graphical form in instrument manuals based on the data by Harkins and Jordan.[1]

Pendent Drop Method

48. The pendent drop method for determining interfacial tension is based upon the formation of a drop of liquid on a tip, the drop being slightly smaller than that which will spontaneously detach itself from the tip. See references 2 through 11. A hypodermic syringe is frequently used to form the droplet. The pendent drop is either photographed and the dimensions of the image measured or direct measurement of the drop is made with a cathetometer. Refer to Figure 3. Interfacial tension is calculated from the dimensions of the drop by the following equation:

$$\sigma = \Delta\rho g d_e^2/H \qquad (1)$$

where:

σ = interfacial tension, dyne/cm

$\Delta\rho$ = difference in density between the droplet and the phase surrounding it, gm/cm^3

g = gravitational constant, cm/sec^2

d_e = maximum (equatorial) diameter of the unmagnified drop, cm

H = shape correction factor, dimensionless.

Values for $1/H$ are given in Table 1 as a function of d_e and d_s. The diameter, d_s, is measured at the selected plane shown in Figure 3. Table 1 is from Niederhauser, Andreas, et al.[5] Tables of values can be found in references by Andreas,[2] Fordham,[3] and Mills.[4]

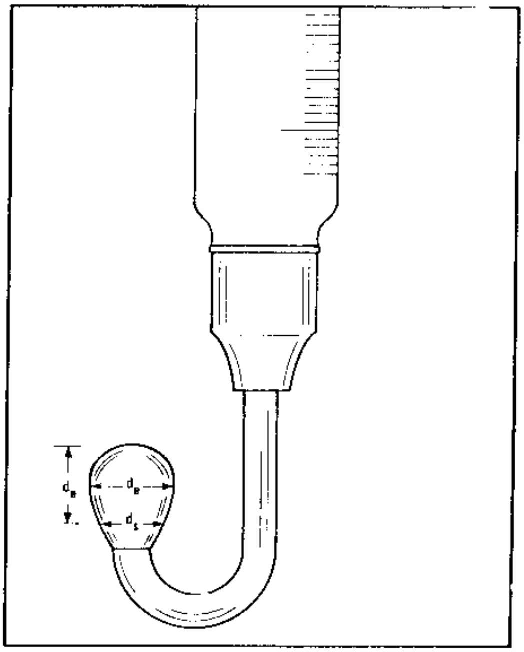

FIG. 3
PENDENT DROP CONFIGURATION

Sessile Drop Method

49. The sessile drop technique for calculating interfacial tension for a system such as oil and water consists of placing a small drop of oil on

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*Available from American National Standards Institute, 1430 Broadway, New York, NY 10018.

TABLE 1[5]
PENDENT DROP SHAPE CORRECTION FACTORS FOR INTERFACIAL TENSION CALCULATION

(After Niederhauser and Bartell, reference 5.)

d_s/d_e	Values for 1/H*									
	0	1	2	3	4	5	6	7	8	9
0.67	.90174	.89822	.89471	.89122	.88775	.88430	.88087	.87746	.87407	.87069
0.68	.86733	.86399	.86067	.85736	.85407	.85080	.84755	.84431	.84110	.83790
0.69	.83471	.83154	.82839	.82525	.82213	.81903	.81594	.81287	.80981	.80677
0.70	.80375	.80074	.79774	.79477	.79180	.78886	.78593	.78301	.78011	.77722
0.71	.77434	.77148	.76864	.76581	.76299	.76019	.75740	.75463	.75187	.74912
0.72	.74639	.74367	.74097	.73828	.73560	.73293	.73028	.72764	.72502	.72241
0.73	.71981	.71722	.71465	.71208	.70954	.70700	.70448	.70196	.69946	.69698
0.74	.69450	.69204	.68959	.68715	.68472	.68230	.67990	.67751	.67513	.67276
0.75	.67040	.66805	.66571	.66338	.66107	.65876	.65647	.65419	.65192	.64966
0.76	.64741	.64518	.64295	.64073	.63852	.63632	.63414	.63196	.62980	.62764
0.77	.62550	.62336	.62123	.61912	.61701	.61491	.61282	.61075	.60868	.60662
0.78	.60458	.60254	.60051	.59849	.59648	.59447	.59248	.59050	.58852	.58656
0.79	.58460	.58265	.58071	.57878	.57686	.57494	.57304	.57114	.56926	.56738
0.80	.56551	.56364	.56179	.55994	.55811	.55628	.55446	.55264	.55084	.54904
0.81	.54725	.54547	.54370	.54193	.54017	.53842	.53668	.53494	.53322	.53150
0.82	.52978	.52808	.52638	.52469	.52300	.52133	.51966	.51800	.51634	.51470
0.83	.51306	.51142	.50980	.50818	.50656	.50496	.50336	.50176	.50018	.49860
0.84	.49702	.49546	.49390	.49234	.49080	.48926	.48772	.48620	.48468	.48316
0.85	.48165	.48015	.47865	.47716	.47568	.47420	.47272	.47126	.46980	.46834
0.86	.46690	.46545	.46401	.46258	.46116	.45974	.45832	.45691	.45551	.45411
0.87	.45272	.45134	.44996	.44858	.44721	.44585	.14449	.44313	.44178	.44044
0.88	.43910	.43777	.43644	.43512	.43380	.43249	.43118	.42988	.42858	.42729
0.89	.42600	.42472	.42344	.42216	.42089	.41963	.41837	.41711	.41586	.41462
0.90	.41338	.41214	.41091	.40968	.40846	.40724	.40602	.40481	.40361	.40241
0.91	.40121	.40001	.39882	.39764	.39646	.39528	.39411	.49294	.39178	.39062
0.92	.38946	.38831	.38716	.38602	.38488	.38374	.38260	.38147	.38035	.37922
0.93	.37810	.37699	.37588	.37477	.37367	.37256	.37147	.37037	.36928	.36819
0.94	.36711	.36603	.36495	.36387	.36280	.36173	.36067	.35960	.35854	.35749
0.95	.35643	.35538	.35433	.35328	.35224	.35120	.35016	.34913	.34809	.34706
0.96	.34604	.34501	.34398	.34296	.34195	.34093	.33991	.33890	.33789	.33688
0.97	.33587	.33487	.33386	.33286	.33186	.33086	.32986	.32887	.32787	.32688
0.98	.32588	.32489	.32390	.32290	.32191	.32092	.31992	.31893	.31793	.31694
0.99	.31594	.31494	.31394	.31294	.31194	.31093	.30992	.30891	.30790	.30688
1.00	.30586	.30483	.30379							

*Linear interpolation warranted.

the underside of a flat plate in a cell filled with water and measuring the maximal dimension of a magnified image. The required drop dimensions are shown in Figure 4. Apparatus and procedure to measure drop dimensions are more fully described in Pars. 57 and 58. To calculate the interfacial tension, use the following equation:

$$\sigma = \frac{g}{2} \Delta\rho f_{90} h^2 \qquad (2)$$

where:

σ = interfacial tension, dyne/cm

g = gravitational constant, cm/sec^2

$\Delta\rho$ = density difference between droplet and the phase surrounding it, gm/cm^3

h = height of drop from equatorial plane to apex, cm

f_{90} = shape correction factor, dimensionless. The value of f_{90} is read from Figure 4 as a function of the shape factor given by the ratio of h to r.

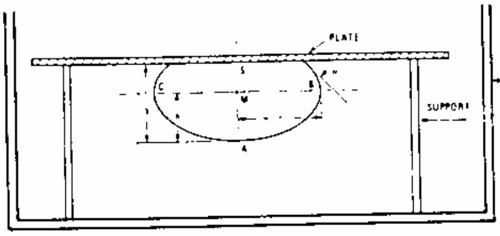

FIG. 4
SESSILE DROP CONFIGURATION AND CELL DESIGN

Data for construction of curves similar to that in Figure 5 are available in references 12, 13, and 14. The curve in Figure 5 is according to Brandner and Melrose.[15]

50. Equation (2) and Figure 5 are applicable only if the following conditions are met:

a. The drop must be symmetrical, that is, have the same shape when viewed from any direction parallel to the plate on which the drop rests. If this condition is not met, the drop will appear to wet the plate to a different degree around the boundary of the drop. This may be due to nonuniformity in plate smoothness or to surface contamination. In either case, the remedy is to select another plate and avoid exposure of the plate to the laboratory atmosphere after cleaning and before immersion in the aqueous phase.

b. The contact angle, θ, must be less than 90°. When this condition does not exist, a plate of different surface energy can be tried. For example, if the oil wets glass or quartz, a teflon plate may be useful. If the oil is sufficiently transparent, water and oil phases can be interchanged. For contact angles greater than 90°, generalized curves and formulae are available in reference 15.

c. The system is at equilibrium, that is, temperature and pressure are constant, and h and r are constant. It is best to thoroughly equilibrate the bulk oil and water phases prior to the experiment.

51. A good approximation for a large drop is given by Healy and Reed[16] and has the form:

$$\sigma = \frac{g\,(\Delta\rho)h^2}{2(1 + 0.306\,\frac{h}{r})^2} \qquad (3)$$

where:

σ = interfacial tension, dyne/cm

g = gravitational constant, cm/sec^2

$\Delta\rho$ = density difference between droplet and the phase surrounding it, gm/cm^3

h = height of drop from equatorial plane to apex, cm

r = radius of drop at the equatorial plane, cm

When the value of h/r is less than or equal to 0.23, the error incurred in calculating interfacial tension from equation (3) is one percent or less.

Spinning Drop Method

52. The spinning drop method for determining interfacial tension is based on measuring the shape of a drop of liquid or a gas bubble in a more dense liquid contained in a rotating horizontal tube (refer to references 17, 18, and 19). This method depends on attaining gyrostatic equilibrium, i.e., there must be no relative motion between the various fluid surfaces. To assure gyrostatic equilibrium for most systems, high rotational speeds (in excess of 6,000 rpm) are required. A capillary tube is filled completely with the more dense phase, and the less dense phase is injected with a microliter syringe. The filled tube is then placed onto the shaft of the instrument. For very low values of interfacial tension, very small volumes (10^{-3} cm^3 or less) of the less dense phase are required. Drop dimensions are usually measured using a traveling microscope. Rotational speeds in the range of at least 1,000 to 10,000 rpm are required. For drop sizes such that the length, L, is at least eight times drop radius, R, the following equation

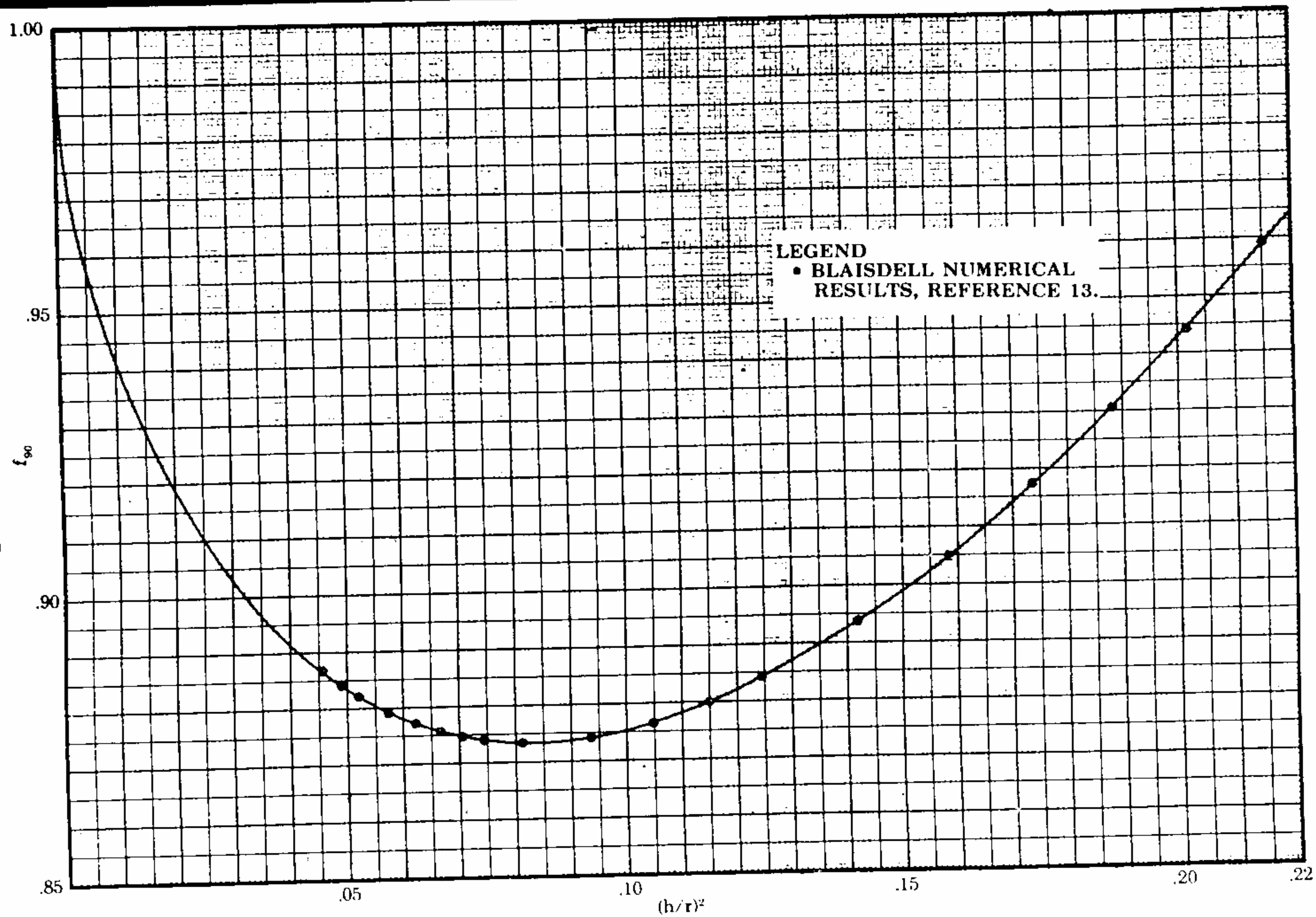

FIG. 5[15]

SESSILE DROP SHAPE CORRECTION FACTORS FOR INTERFACIAL TENSION CALCULATIONS

(After Brandner and Melrose, reference 15.)

may be used to calculate interfacial tension (refer to reference 17):

$$\sigma = \frac{\Delta\rho\, w^2\, R^3}{4} \qquad (4)$$

where:

σ = interfacial tension, dyne/cm

$\Delta\rho$ = difference in density between the drop and the surrounding phase, gm/cm^3

w = angular velocity, radians/sec

R = radius of cylindrical part of the drop, cm

Equations for calculating interfacial tension of other drop shapes and sizes are given in references 18 and 19. The spinning drop method for measuring low interfacial tensions is relatively simple compared to other methods. This method has the advantage of not involving a third (solid) phase in contact with the fluids. However, for valid results using the spinning drop method, *gyrostatic equilibrium must be obtained.*

CONTACT ANGLE CALCULATION

Sessile Drop Method

53. Contact angle can be calculated by measurement of one or more drop dimensions in addition to those required for interfacial tension. In the case where the contact angle, θ, is less than 90°, this dimension is k, the total height of the drop from the solid surface to the apex of the drop (refer to Figure 4). The equation for contact angle is:

$$\theta = \cos^{-1}\left[f_\theta\left(\frac{k}{h}\right)^2 - 1\right] \qquad (5)$$

where:

θ = contact angle, degrees

k = total drop height from solid surface to apex, cm

h = drop height above equatorial plane, cm

f_θ = shape correction factor.

The shape correction factor, f_θ, is read from Figure 6, where f_θ is given as a function of shape parameter, h/r, for a family of curves based on the k to h ratio. For contact angles greater than 90°, more generalized shape factor corrections are given in reference 15.

WETTABILITY

Wettability and Contact Angle

54. The wetting properties of uncontaminated reservoir fluids are measured using polished mineral surfaces. The degree that a droplet will preferentially wet the mineral surface depends on adsorption of surface active agents present. If a droplet does not wet the mineral surface under simulated reservoir conditions, then it will probably not wet the same minerals in the reservoir and the opposite is also probably true.

55. The wettability test is performed by placing a droplet such as oil on a mineral surface in the presence of water or oil or both. The equilibrium angle measured through the water phase between the mineral surface and the oil-water interface at the point of oil-water-solid contact is the contact angle. The contact angle can be calculated by drop measurement as described in Par. 53. Contact angles less than 75° are normally considered to indicate preferentially water-wet systems, and contact angles greater than 105° are normally considered to indicate preferentially oil-wet systems. Equilibrium contact angles between 75° and 105° normally indicate intermediate wettability conditions.

56. The polished mineral surfaces used in tests differ depending upon the reservoir. Polished quartz is normally used for sandstone reservoirs and polished calcite for limestone reservoirs, however, selenite and siderite can be used in place of calcite.

MEASURING DROP DIMENSION AND CONTACT ANGLE

Equipment

57. A small rectangular glass cell is used, having two clear parallel ends on opposite sides, a glass lid, and two small supports for the polished mineral plate. Polytetrafluoroethylene (PTFE) or other inert material is used as a support (refer to Figure 4). For measurement at reservoir conditions, a special glass-PTFE apparatus for measuring contact angles is described by Leach, et al.[20] A modified apparatus to permit measurement of contact angles at reservoir temperatures using degassed crude oils and brines has been developed by Treiber, et al.[21]

Procedures

58. As an example, consider measurement of contact angle of an oil droplet on a mineral plate immersed in water as follows:

a. Position the polished mineral slab on its supports in a thoroughly clean cell.

b. Fill the cell with water until the mineral is immersed. Permit the cell to age for at least 36 hours.

c. Using a hypodermic syringe, place one or

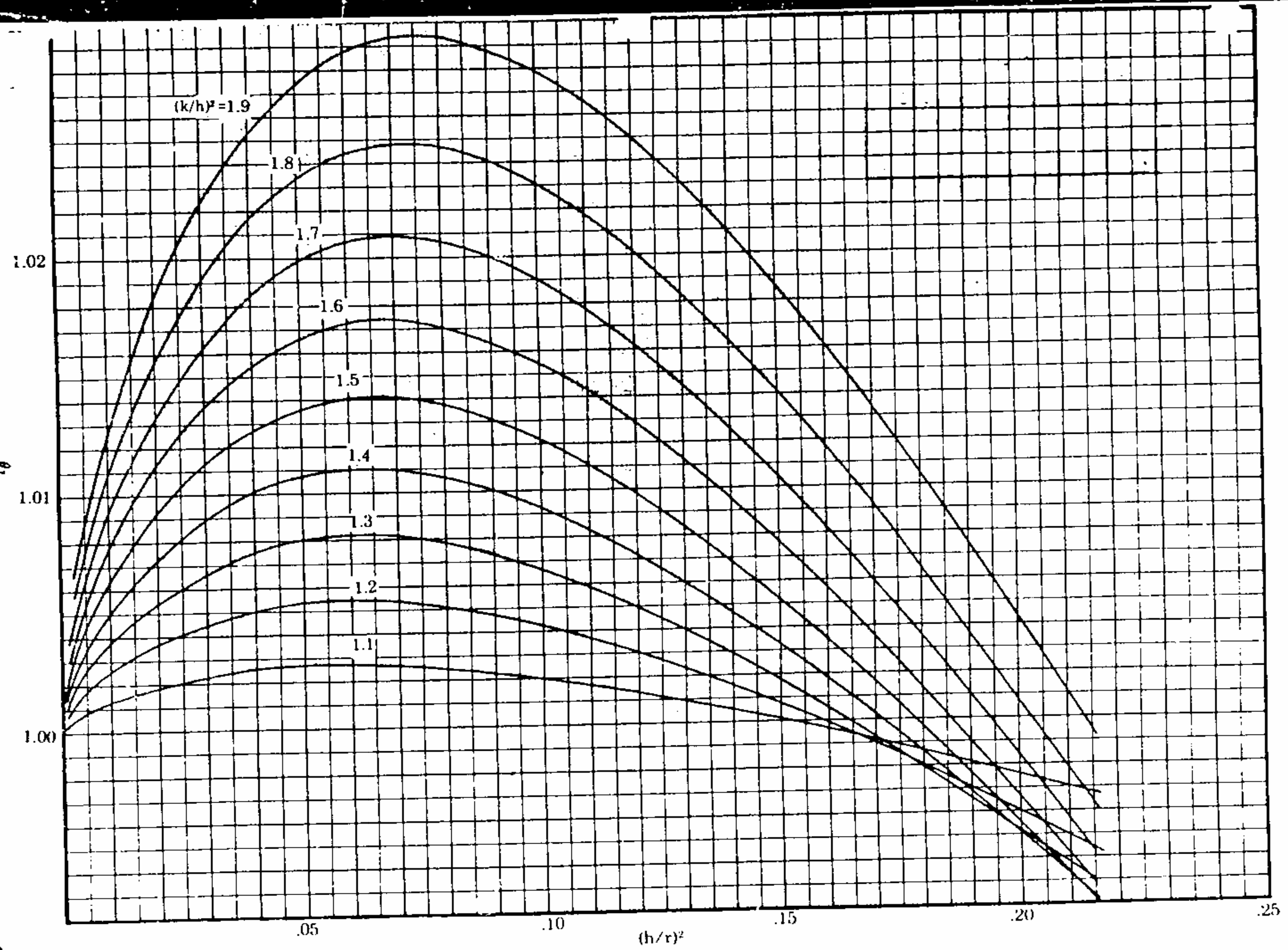

FIG. 6[15]
SESSILE DROP SHAPE CORRECTION FACTORS FOR OBTUSE CONTACT ANGLES
(After Brandner & Melrose, reference 15.)

more droplets of oil on the underside of the mineral so that each drop can be seen through both of the clear sides of the cell. As an alternative, if the oil used in the test is a transparent oil, then the cell can be filled with oil and a water droplet placed on the top of the mineral.

d. Measure the required drop dimension with a cathetometer or take a photograph of the drop. A goniometer may be used to measure contact angle through the water phase between the solid and the oil-water interface.

Drop dimensions required for interfacial tension and for contact angle calculation are described in Pars. 49 and 53. Periodic measurements will indicate when equilibrium conditions are reached. Normally, refined oils and brines attain equilibrium within 24 hours; some systems have required 600 hours or more to reach equilibrium.

59. The procedures outlined in Par. 58 can be easily adapted to test agents designed to alter wettability or interfacial tensions. These agents should be introduced into the appropriate phase and resultant contact angles measured.

VISUAL WETTABILITY TEST

60. This method provides a simple and rapid procedure for qualitatively determining the wetting tendencies of surface active agent solutions. If water-wetting or oil-wetting tendency is great, it can be easily distinguished. Intermediate degrees of wetting are not easily characterized. For quantitative measurements, use sessile drop or contact angle methods described in Paragraphs 53, 57, and 58.

Equipment and Materials

61. The following equipment and materials should be used for visual wettability tests:

a. 4 oz wide mouth bottles or 150 ml beakers.

b. Kerosine and/or crude oils (filter kerosine as described in Par. 25).

c. Aqueous test fluid (water, brine, or acid).

d. Clean sand and/or limestone particles, 40-60 mesh

PROCEDURE

Oil Soluble or Dispersible Surface Active Agents

62. Place 50 ml of oil containing the surface active agent at the desired concentration (usually 1 percent or less for use in well stimulation) in a bottle and add 10 cm^3 of test sand. After 30 minutes, slowly pour 50 ml of water into the bottle, taking care to prevent excessive mixing and emulsification.

63. Observe the relative dispersibility of the particles or their tendency to form clumps in both aqueous and oil phases by lifting a small quantity of sand with a semi-micro spoon spatula into the oil phase and allowing it to fall back into the water.

Water Soluble or Water Dispersible Surface Active Agents

64. Place 50 ml of a water solution containing the surface active agent at the desired concentration in a bottle and add 10 cm^3 of test sand. After 30 minutes decant solution into another bottle and carefully add 50 ml of oil on top of the solution. Sift the treated sand slowly into the bottle allowing it to fall through the oil and water. Observe the relative dispersibility or tendency to form clumps as described in Par. 63.

Acid Solutions

65. Place 50 ml of acid containing surface active agent and/or corrosion inhibitor to be tested in a bottle and add 10 cm^3 of sand. Proceed as described in Par. 64.

66. Observe the appearance of the sand grains in acid, decant the acid, and rinse the sand with formation or synthetic brine. Cover the sand with 50 ml of brine and 50 ml of oil. Again observe condition of sand grains.

INTERPRETATION OF OBSERVATIONS

67. The basis for interpretation of the wetting observations is similar to that used for determination of emulsion type by dilution. Oil-internal, water-external phase emulsions disperse in water; water-internal, oil-external phase emulsions disperse in oil. Particles that are completely water-wet disperse readily in an aqueous phase, but agglomerate or clump in an oil phase. Particles that are completely oil-wet behave in an opposite manner. Since wettability exists in different degrees between the extremes of being either completely water-wet or oil-wet, observations of intermediate systems are difficult to distinguish and describe.

68. Other factors should be considered in addition to dispersion or agglomeration. For instance, when a dark colored crude oil is used, oil-wet sand should approach the color of the crude. If a crude oil tends to form an emulsion spontaneously on contact with aqueous surface active agent solutions, the sand may have the same appearance as if it were oil-wet. A microscope can be used to detect emulsion in some cases.

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