

**THE EFFECTS OF SURFACE ROUGHNESS ON CONTACT  
ANGLE WITH SPECIAL REFERENCE TO PETROLEUM  
RECOVERY**

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# The Effects of Surface Roughness On Contact Angle With Special Reference to Petroleum Recovery

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## Abstract

*The effect of surface roughness on contact-angle hysteresis was investigated through a study of capillary rise in PTFE (polytetrafluoroethylene) tubes. Systems were chosen to give intrinsic contact angles (contact angles measured at a smooth PTFE surface) covering the complete range from 0 to 180 degrees. Advancing and receding contact angles were determined before and after deliberately roughening the insides of the tubes by abrasion with particulate solids. These angles showed systematic dependence on intrinsic angle and were independent of tube diameter. With sufficient roughening, there was a marked change in the general nature of the observed contact-angle hysteresis. Results for the well-roughened tubes were reasonably consistent and showed no dependence on the particle size of the powder used to roughen the tubes or on further roughening. Relationships between intrinsic contact angle and advancing and receding contact angles were used in a test of the Wenzel theory of surface roughness. Applications of results and of contact-angle studies in general to the complex problems of reservoir wetting behaviour are discussed. When considering contact angles which are operative during oil recovery, distinction should be drawn between imbibition and drainage, which respectively correspond to advancing and receding conditions. For systems of intermediate wettability, it appears that oil recovery by low-interfacial-tension flooding will be adversely affected, because contact-angle hysteresis will tend to increase the capillary forces which resist displacement.*

## Introduction & Background

WETTABILITY determines the distribution of commingled fluids within reservoir rocks and directly affects the microscopic mechanism of oil recovery. Contact angle, for example as exhibited by the sessile drops of water in oil shown in Figure 1 (a) and (b), provides a basic measure of the wetting properties of reservoir fluids with respect to selected mineral surfaces. Preparation of a smooth solid surface is recognized to be an important factor in obtaining reproducible results. However, as may be seen from the electron micrographs shown in Figure 1 (c) through (f), the surfaces of pores which determine wetting behaviour within reservoir rocks are generally rough and extremely complex in character because of cementation and other diagenetic effects. Mixed mineral composition, surface roughness, pore geometry and adsorption effects can all be expected to influence reservoir wetting and hence the capillary forces which control recovery. The development of a sound understanding of the significance of observed contact angles with respect to recovery mechanisms requires that each of these factors be studied systematically. The present investigation concerns the effect of surface roughness on contact angle.

The circumstances under which contact angle provides a single valued and unambiguous measure

of wettability are somewhat restrictive and do not generally apply to reservoir systems. The requirements are that fluids (say a liquid, l, and gas, g) are free of polar impurities and that the surface of the solid (s) is smooth, nondeformable and homogeneous with respect to surface energy. Contact angle is then a fundamental property of the system and is referred to as the intrinsic angle  $\theta_K^{1-3}$ . The intrinsic angle,  $\theta_K$ , measured through the liquid phase is related to the interfacial tensions,  $\sigma$  (solid-liquid, solid-gas and gas-liquid), acting at the three-phase line of contact by Young's equation<sup>(1)</sup>,

$$\sigma_{sg} = \sigma_{sl} + \sigma_{gl} \cos \theta_E \dots \dots \dots (1)$$

Zisman and co-workers have shown that the conditions for observation of intrinsic contact angles are met closely by liquids against air on smooth surfaces of a number of organic polymers<sup>(1,4)</sup>. Such surfaces exhibit reproducible contact angles which are clearly related to the surface tension of the liquid. For a given solid, a plot of surface tension against  $\cos \theta_K$  for a homologous series of fluids can be used to predict a critical surface tension below which the contact angle will be zero and spreading can be expected. Three types of solids have specific surface energies of the same order of magnitude as most liquids (< 100 ergs/sq.cm) and are described as low-energy solids.

The minerals which comprise reservoir rocks belong to classes of hard solids with specific surface energies in the range of 500 to 5,000 ergs/sq.cm and are referred to as high-energy solids<sup>(5)</sup>. Provided the surfaces are clean, most liquids will spread against gas on high-energy solids and water will spread against a non-polar hydrocarbon. The spreading condition corresponds to complete water wetting for a hydrocarbon reservoir. Departure from complete wetting can

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arise through modification of the mineral surface by adsorption of polar material or the deposition of organic matter. Because the wetting behaviour of a surface is largely determined by the nature and orientation of the outermost layer of molecules at that surface, it may be appreciated that many uncertainties arise in attempts to maintain or reproduce the wetting behaviour of a reservoir. These uncertainties are such that the wetting behaviour of any reservoir can not yet be considered to be properly understood. A wide range of contact angles have been observed for water against various reservoir crude oils at smooth mineral surfaces<sup>(7)</sup>. It can therefore be inferred that a broad spectrum of wettability conditions of various types, ranging from strongly water-wet to strongly oil-wet, may be encountered in oil production.

Development of a definitive knowledge of the effects of wettability on oil recovery requires that displacement studies be conducted under controlled conditions. Even with unrestricted choice of chemicals, difficulties were experienced in gaining satisfactory wettability control at high-energy surfaces<sup>(8)</sup>. The suitability of low-energy solids for controlling the wettability of porous media was recognized by Stegemeier and Jensen<sup>(9)</sup>. These solids have been found to provide good wettability control and are well suited for the investigation of several aspects of the wettability problem<sup>(10)</sup>. The low-energy solid polytetrafluoroethylene (PTFE) was used in the present study of surface roughness.

From previous studies of roughness effects<sup>(11-16)</sup> on contact angle, it can be expected that, for a system of a given intrinsic angle, the contact angles which are operative under drainage and imbibition conditions will depend on microscopic roughness. These operative angles cannot be measured directly for porous media.

The objective of the present work was to determine the relationship between intrinsic contact angle and the contact angles which are operative at rough surfaces under drainage and imbibition conditions. The approach taken was to study capillary rise in PTFE tubes before and after deliberately roughening the insides of the tubes with an abrasive powder. Bartell and Shepard reported that attempts to prepare roughened surfaces by abrasion gave rise to experimental difficulties and the results showed

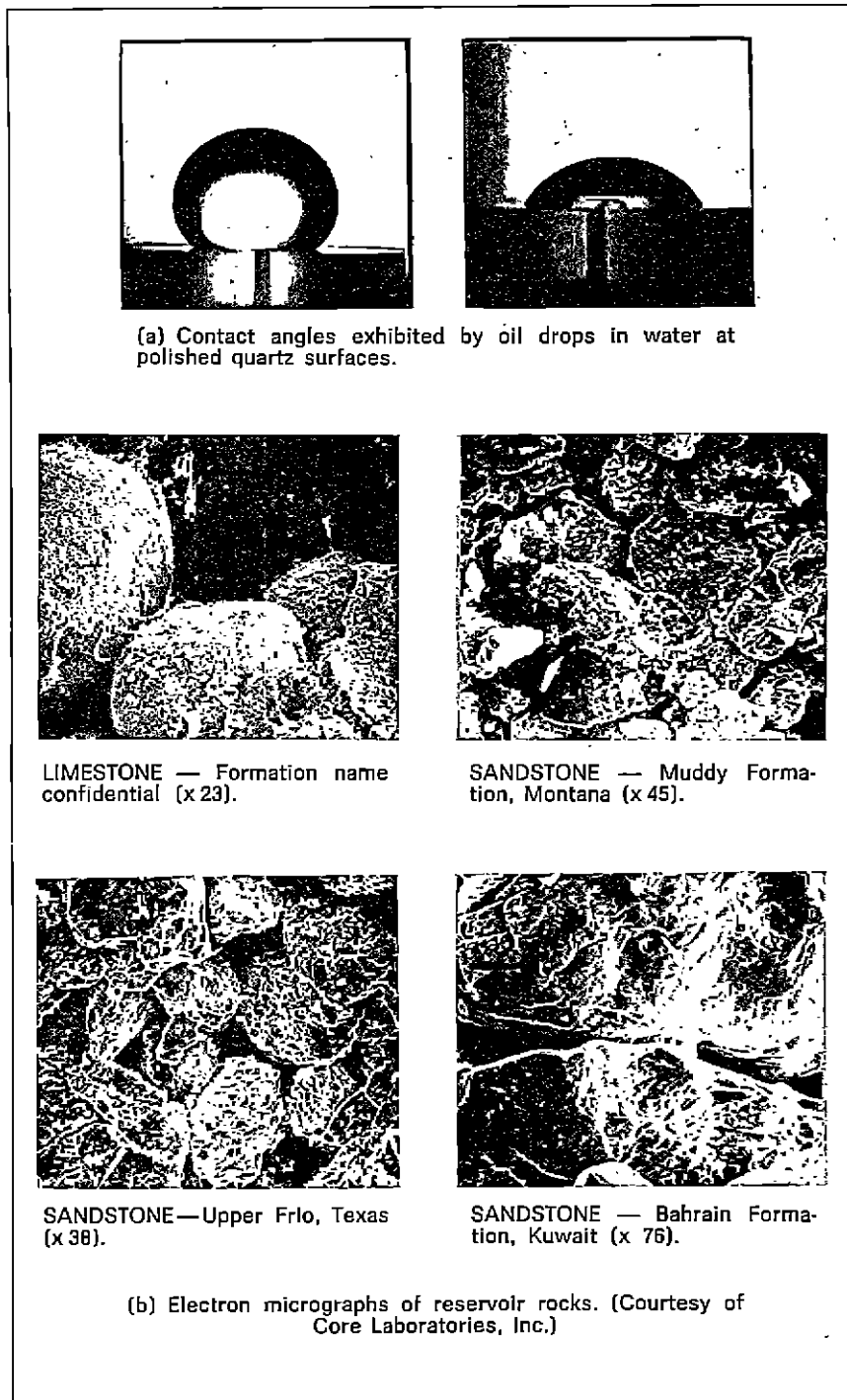


FIGURE 1 — Photographs showing smooth surfaces at which contact angles are measured and electron micrographs showing the surface roughness of reservoir rocks.

poor reproducibility<sup>(13)</sup>. It is believed that these difficulties have been largely overcome in the present work, mainly because of the advantages of determining contact angle from capillary rise. A large number of measurements can be made quickly and accurately and scatter is greatly reduced over that given by direct observation of the contact angle, because each measurement corresponds to an average value for the interface perimeter.

## Experimental

PTFE tubing, with the range of radii listed in Table 1, was obtained from Chromatographic Specialties, Ltd. The radii of the tubes used in experimental work were determined by measuring the weight and length of a mercury thread which could be held in each tube.

Several methods of cleaning the tubes were tested. The most effective

ive, as judged from reproducibility in measurements of capillary rise at finite contact angles, was to soak the tubes in warm (50-60°C) chromic acid for 30 minutes, followed by a rinse with distilled water. The tubes were then soaked in warm distilled water for 30 minutes and finally dried in an oven at 80°C.

Liquids used in the measurement of capillary rise are listed in Table 2, together with their sources. Values of intrinsic contact angles at smooth Teflon surfaces were found to be in substantial agreement with values reported by Zisman and co-workers<sup>(4-6)</sup>. The test liquid was held in a glass reservoir 8.5 cm in diameter. Teflon tubes were held straight by placing them

in glass tubes which had previously been cleaned with chromic acid. The reservoir was covered by a clean glass plate between readings. All experiments were conducted at a temperature of  $24 \pm 1^\circ\text{C}$ .

A cathetometer, which measured heights reproducibly to within  $\pm 0.004$  cm, was used to measure capillary rise with respect to the surface of the liquid held in the reservoir. As capillary rise in the reservoir itself could be safely neglected away from the walls of the reservoir, hydrostatic pressure was taken to be zero at the reference level given by the liquid in the reservoir. Capillary rise was measured for advancing and receding conditions by lowering or raising the tube with respect to

the reservoir. Measurements were usually reproducible to within  $\pm 0.01$  cm. When the contact angle was close to 90 degrees, the meniscus became obscured by liquid held at the reservoir wall by capillary rise. A clear view of the meniscus within the tube could be obtained by holding the tube against the reservoir wall by means of a grooved Teflon block.

The internal surfaces of the tubes were roughened by packing them with dolomite powder and then rolling them between two flat plates. Further details of roughening procedures are given with the results. After removing most of the dolomite powder, the tubes were soaked in concentrated hydrochloric acid and then cleaned in the manner described above, before measuring capillary rise. Small lengths of tube were slit open and mounted for study by electron microscope. Electron micrographs were taken for visual comparison of the internal surfaces of the tubes before and after roughening.

Independent checks of tube radii were provided by capillary-rise measurements for pentane. Pentane gives a contact angle of 0 degrees, its interfacial tension being less than the critical surface tension of PTFE<sup>(6)</sup>. Any observed hysteresis for pentane can therefore be ascribed to the non-uniformity in bore of the PTFE tube. Hysteresis at zero contact angle caused by such non-uniformities will be called hydrostatic hysteresis. From the radii determined by capillary rise for advancing and receding conditions, it can be seen (Table 1) that hys-

TABLE 1—Specified and Measured Internal Radii of Teflon Tubes (cm)

Tube Ref. No.	Based on Manufacturers' Specifications			Mercury-Thread Method	Determined From Capillary Rise of Pentane ( $\theta = 0$ )			
	Min.	Nominal	Max.		Min. Average Max. (6 READINGS) Before Roughening		After Roughening	
1	.128	.135	.142	.1355	1341	.1354	.1378	.1443
2								.1455
3	.103	.108	.113	.1083	1094	.1109	.1127	—
4	.092	.097	.102	.0938	.0946	.0950	.0954	.0959
5	.073	.075	.085	.0766	.0757	.0764	.0775	.0780
6	.065	.068	.078	.0687	.0681	.0683	.0687	—
7	.057	.060	.069	.0618	.0615	.0624	.0628	.0625
8	.046	.049	.055	.0497	.0471	.0473	.0473	.0497
9	.041	.043	.050	.0461	.0461	.0466	.0469	.0465
10	.032	.035	.041	.0352	.0352	.0354	.0356	—
11	.026	.028	.035	.0306	.0305	.0306	.0307	—
12	.021	.023	.028	.0228	.0221	.0222	.0223	—

Wall thickness of tubes 1 to 9:  $0.0305 \pm 0.008$  cm.

Wall thickness of tubes 10 to 12:  $0.0228 \pm 0.005$  cm

TABLE 2—Contact Angles at Smooth PTFE Surfaces.

Pure Liquid — Air	Source	Surface Tension (dyne/cm)	Density (g/cc)	Intrinsic Contact Angle ( $\theta_g$ ) (degrees)	Complementary Angle ( $180 - \theta_g$ ) (degrees)
N-Pentane	Phillips Petroleum Co. (Pure Grade)	15.6	0.621	0	180
n-Hexane	Phillips Petroleum Co. (Pure Grade)	18.4	0.668	7	173
n-Heptane	Phillips Petroleum Co. (Pure Grade)	18.89	0.680	22	158
n-Octane	Phillips Petroleum Co. (Pure Grade)	21.22	0.699	26	154
n-Decane	Phillips Petroleum Co. (Pure Grade)	23.35	0.726	35	145
n-Dodecane	Phillips Petroleum Co. (Pure Grade)	24.9	0.743	42	138
n-Tetradecane	Phillips Petroleum Co. (Pure Grade)	26.16	0.759	44	136
Diocetyl Ether	Eastman Kodak Co.	27.3	0.802	49	131
Heptanoic Acid	Eastman Kodak Co.	27.9	0.909	49	131
Hexachlorobutadiene	Eastman Kodak Co.	36.0	1.682	60	120
$\alpha$ -Bromonaphthalene	Fisher Scientific Co. (Reagent grade)	43.0	1.174	73	107
Ethylene Glycol	Fisher Scientific Co. (Certified)	47.7	1.108	90	90
Water		70.6	0.977	108	72
Alcohol/Water Mixture — Air (See Reference 17)					
80 vol. % EtOH		24.99	0.849	42.5	137.5
41.5 vol. % EtOH		30.25	0.936	73	107
22.5 vol. % EtOH		37.5	0.965	90	90
12.7 vol. % EtOH		45.63	0.979	100	80

teresis observed for pentane was extremely small and within the limits of experimental error. When tube radii determined by the mercury-thread method were used to determine contact angles for pentane, average advancing and receding angles were 5.8 and 5.1 degrees respectively. It may be noted that the difference between the cosines of these angles and 1.0 ( $\cos 0^\circ$ ) is less than 0.5%. Constancy of tube diameter was also checked from the variation in length with position along a tube of an approximately 1.5-cm length of mercury thread. Variation in tube diameter was less than  $\pm 0.4\%$ .

Contact angles for the unroughened or slightly roughened tubes were calculated from capillary rise using tube radii measured by the mercury-thread method. After roughening the tubes, hysteresis in the capillary rise of pentane still remained insignificant. However, results indicated that the roughening procedure caused a small increase in tube radius of up to 7% (see Table 1), and this was taken into account when determining contact angles from capillary rise in the roughened tubes.

### Calculation of Contact Angles From Capillary Rise

The weight of liquid,  $w$ , supported in a tube of radius  $r$ , above a plane liquid surface, defines a mean peripheral contact angle,  $\theta$ , given by

$$w = \frac{2\pi r \sigma \cos \theta}{g} \quad (2)$$

where  $\sigma$  is the surface tension and  $g$  is the acceleration due to gravity. The weight,  $w$ , is obtained from the measured height of rise,  $h$ . A correction must be applied for the amount of liquid held in the region of the meniscus above the measured height of rise. Let us define a height,  $h'$ , in the region of the meniscus, such that

$$w = \pi r^2 h' \Delta \rho \quad (3)$$

where  $\Delta \rho$  is the density difference of the two fluids.

The shape of the meniscus will depend on the ratio of gravity to capillary forces, expressed by the Bond Number,  $(\Delta \rho g r^2)/\sigma$ , and also the contact angle. At low Bond Numbers, the meniscus approaches the shape of a spherical cap and  $h'$  is given by  $h''$  where,

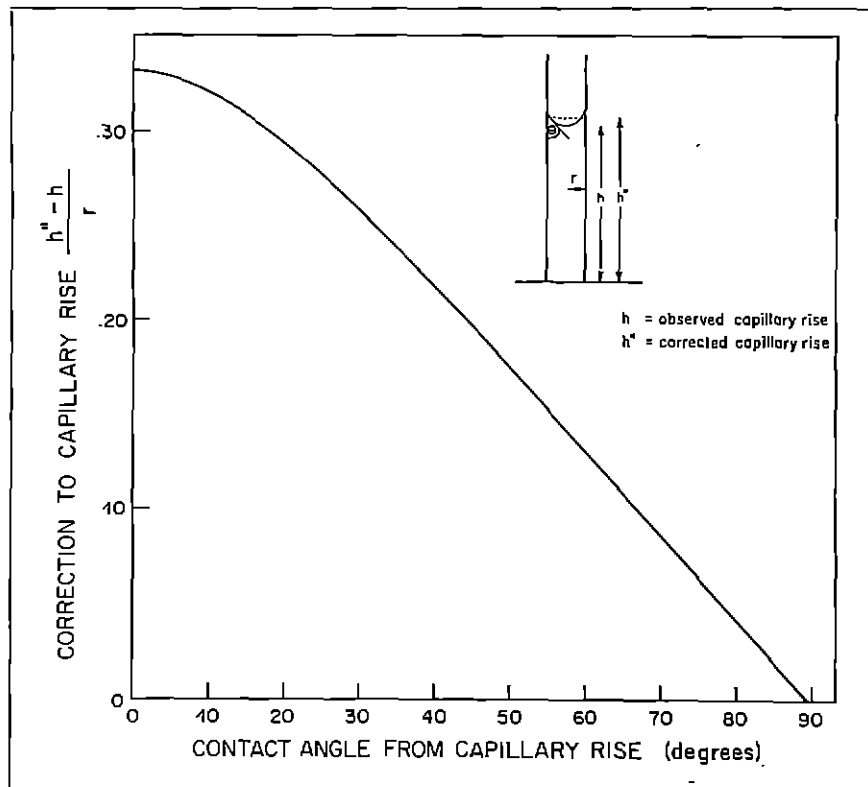


FIGURE 2—Correction to capillary rise.

$$h'' = h + \left( 1 - \frac{(1 - \sin \theta)(2 + \sin \theta)}{3 \cos^2 \theta} \right) \left( \frac{1 - \sin \theta}{\cos \theta} \right) r \quad (4)$$

A plot of  $(h'' - h)/r$  versus  $\theta$  is given in Figure 2. With an increase in Bond Number, the meniscus tends to flatten because of gravity, until the limiting case where an essentially plane interface is reached away from the walls of the tube. The properties of the meniscus in a vertical cylindrical tube over the complete range of Bond Numbers and contact angles have been reported by Concus<sup>(18)</sup>. In the present work, most of the results were obtained for systems having Bond Numbers of 0.4 and less. For such systems, the error which arises from assuming the meniscus to be a spherical cap is much smaller than the accuracy of measurement in the present work. The error which arises from the assumption of a spherical interface decreases as contact angle increases, and becomes zero for the trivial case where the contact angle is 90 degrees and  $h''$ ,  $h'$  and  $h$  are all equal. For capillary rise of octane in the largest tube (radius 0.1346 cm), the error in the correction to  $h$ , expressed as  $(h'' - h)/(h' - h)$ , is less than 10% (about 0.003 cm). This was at the limit in accuracy of reading the cathetometer, but sig-

nificantly smaller than the general accuracy of repeating a capillary rise measurement in a given tube ( $\pm 0.01$  cm). It was therefore considered satisfactory to determine contact angles from adjusted heights obtained by using the correction given by Equation (4). For a given liquid, an initial value of contact angle,  $\theta_1$ , was obtained from an average value for the three narrowest tubes, using the equation

$$h = \frac{2\sigma}{\Delta \rho g} \cos \theta_1 \quad (5)$$

Values of  $\theta$  were obtained by iteration on the contact angle between Equations (4) and (5) until the change in  $\theta$  was less than  $1/2$  degree.

Contact-angle hysteresis at specially prepared smooth PTFE surfaces has been shown to be extremely small (of the order of 1-2 degrees)<sup>(4)</sup>. Thus, the intrinsic angle,  $\theta_E$ , observed under these circumstances provides an essentially unambiguous measure of wettability which depends on the chemical constitution of the given system. The choice of phase through which  $\theta_E$  is measured is then arbitrary; a system of wettability  $\theta_E$  with respect to one fluid phase can alternatively be regarded as a system of wettability  $(180 - \theta_E)$  with respect to the other phase. Thus, an interchange of receding and advancing angles measured at roughened sur-

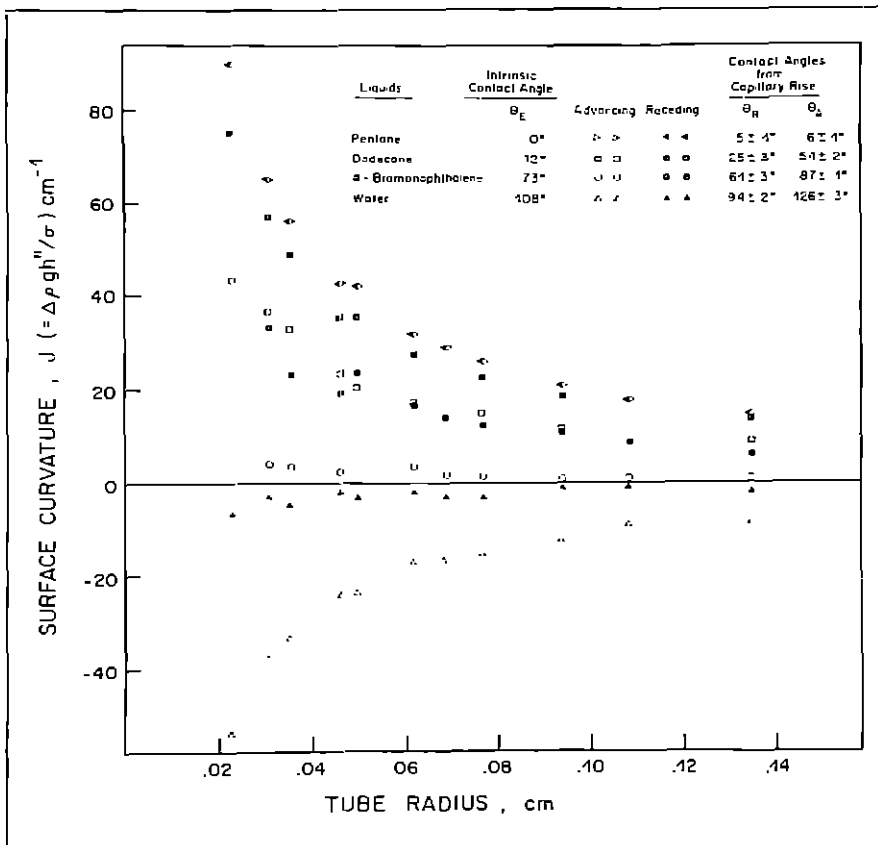


FIGURE 3—Surface curvature determined from capillary rise under advancing and receding conditions versus tube radius (tubes as supplied).

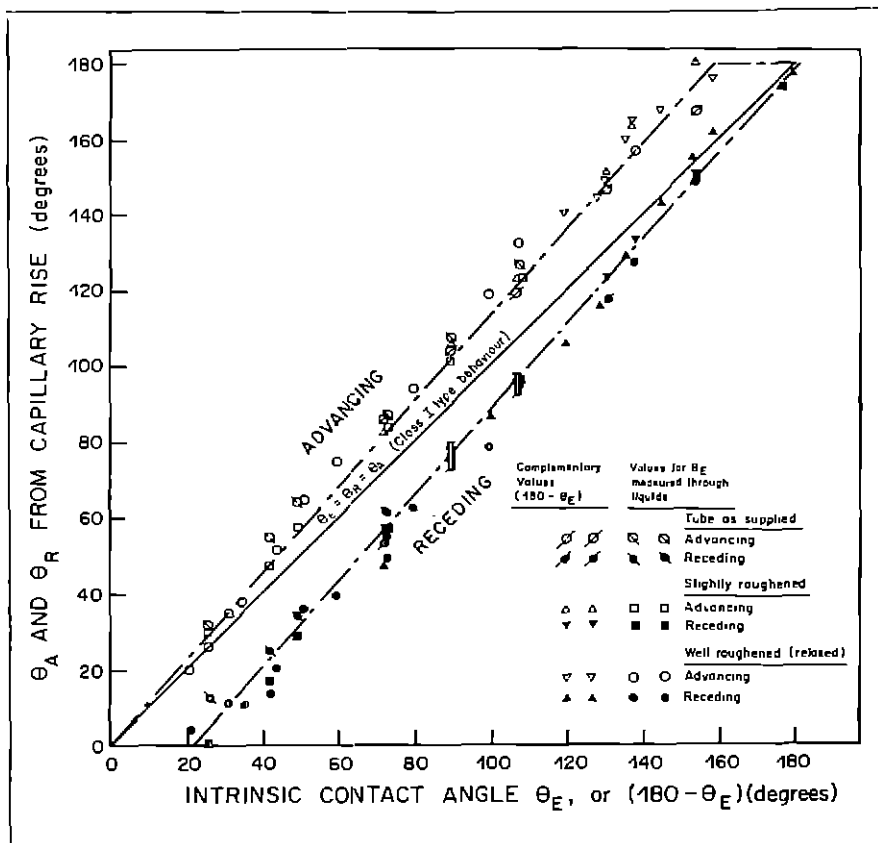


FIGURE 4 — Results exhibiting Class II behaviour.

faces for a system with intrinsic wettability,  $\theta_E$ , provides results for the same system, but with wettability redefined as  $(180 - \theta_E)$ . On this basis, hysteresis data observed for liquids giving intrinsic angles in the range of 0 to 108 degrees were re-interpreted as results for systems having intrinsic angles in the range of 72 to 180 degrees.

### Results For Non-Roughened Tubes

Contact angles from capillary rise were first determined for tubes as supplied by the manufacturers. For liquids exhibiting finite intrinsic angles, a definite hysteresis was observed. Example results for four liquids and eleven tubes are given in Figure 3. The four liquids (pentane, dodecane,  $\alpha$ -bromonaphthalene and water) gave intrinsic contact angles of 0, 42, 73 and 108 degrees respectively. Results are shown as plots of  $(h''\Delta\rho g)/\sigma$  versus tube radius. Constancy of the dimensionless group,  $(h''\Delta\rho g r)/\sigma$ , showed that the effect of contact angle on capillary rise was reasonably consistent from one tube to the next; i.e. there was no over-all systematic trend with respect to tube radius.

Readings were taken at a number of positions along each tube. Each data point shown in Figure 3 is an arithmetic average of from 5 to 20 measurements of capillary rise. An increasing number of data points were taken as the absolute magnitude of the observed capillary rise decreased. Values of contact angle calculated for each tube for six different liquids are shown in Table 3, together with arithmetic average values for all tubes and their standard deviations. The two sets of data given for dioctyl ether were measured independently. Data of the type shown in Figure 3 were further condensed to give plots of advancing and receding contact angle versus intrinsic angle, as shown in Figure 4.

The very small contact-angle hysteresis observed at smooth PTFE surfaces implies that if the internal surfaces of the tubes under study had been manufactured with the same smoothness, capillary rise would be essentially independent of whether it was measured under advancing or receding conditions. Under these circumstances, a plot of contact angle determined from capillary rise versus the intrinsic contact angle would fall on the 45-degree line included in Figure 4.

The form of results obtained in

the present work are such that it is convenient to discuss relationships between contact angles measured by capillary rise and intrinsic contact angles in terms of three classes of behaviour. The hypothetical relationship for smooth surfaces represented by the 45-degree line ( $\theta_E = \theta_R = \theta_A$ ) will be referred to as Class I type.

Contact angles measured for tubes as supplied by the manufacturer gave contact-angle hysteresis with advancing and receding angles of about  $12 \pm 5$  degrees, respectively, higher and lower than that of the intrinsic angle of a given system (see Fig. 4). This was referred to as Class II type behaviour. Class II behaviour can be represented by the following straight-line relationships, which are included in Figure 4.

**Advancing Contact Angles — Class II**

$$0^\circ < \theta_E < 158^\circ \quad \theta_A = 1.14 \theta_E \dots (6)$$

$$158^\circ < \theta_E < 180^\circ \quad \theta_A = 180^\circ \dots (7)$$

**Receding Contact Angles — Class II**

$$0^\circ < \theta_E < 22^\circ \quad \theta_R = 0 \dots (8)$$

$$22^\circ < \theta_E < 180^\circ \quad \theta_R = 1.14 (\theta_E - 22^\circ) \dots (9)$$

**Results For Roughened Tubes**

Previous studies have demonstrated the importance of the degree of roughening on contact-angle results<sup>(11-16)</sup>. In the present work, attempts to control the degree of roughness were first made by packing five of the tubes with dolomite powder (-200 + 340 mesh). The packed tubes were rolled a distance of about 4 in., five times, between

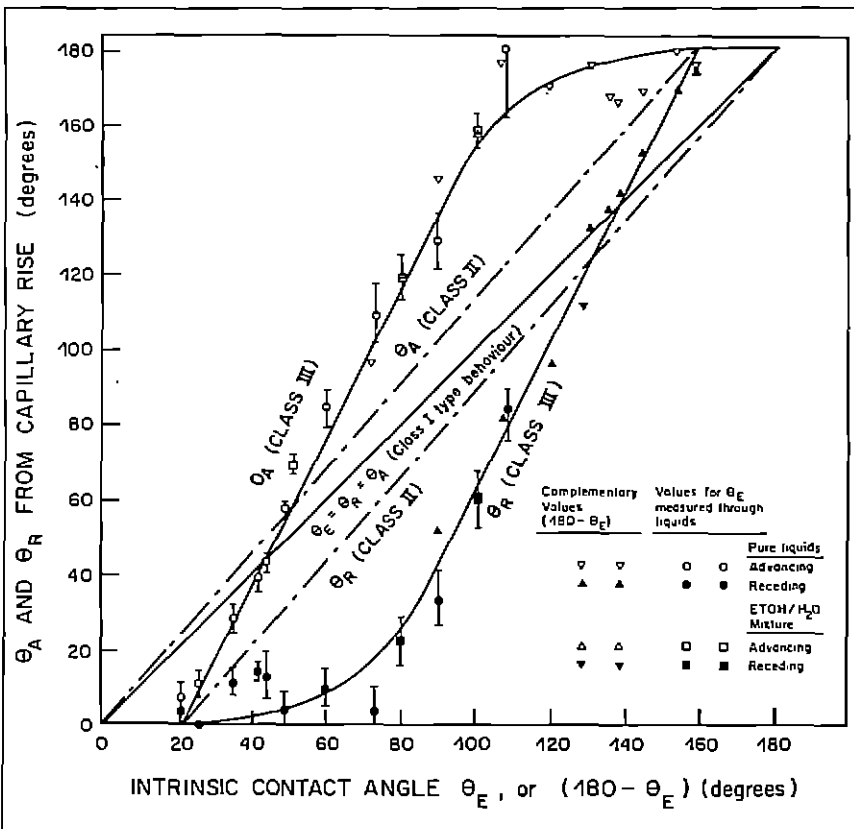


FIGURE 5 — Results exhibiting Class III behaviour obtained after roughening.

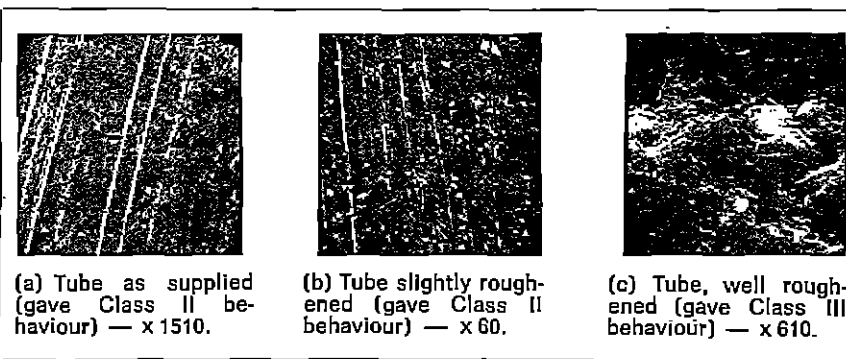


FIGURE 6 — Electron micrographs of PTFE.

TABLE 3 — Advancing and Receding Contact Angles Calculated From Capillary Rise — Examples of Class II Results

Inside Radius of Tube (cm)	n-Octane		n-Dodecane		Diocetyl Ether				$\alpha$ -Bromo Naphthalene		22.5% Ethyl Alcohol-Water		Water	
	$\theta_R$	$\theta_A$	$\theta_R$	$\theta_A$	(a)	(b)	(a)	(b)	$\theta_R$	$\theta_A$	$\theta_R$	$\theta_A$	$\theta_R$	$\theta_A$
					$\theta_R$	$\theta_R$	$\theta_A$	$\theta_A$						
0.1346	8	32	19	51	—	—	—	—	66	86	—	—	97	127
0.1083	12	32	—	—	31	39	60	67	62	86	77	109	92	120
0.0938	10	29	25	54	27	35	59	67	59	88	78	108	93	128
0.0766	16	33	25	52	28	38	59	66	62	86	81	109	97	127
0.0687	16	34	—	—	34	39	62	64	61	87	—	—	96	127
0.0618	11	35	27	53	33	35	64	64	59	84	82	99	93	123
0.0497	9	33	22	58	25	33	66	67	54	90	—	—	94	128
0.0461	17	32	31	55	34	39	63	64	63	87	—	—	93	125
0.0352	15	34	26	52	36	38	62	62	65	86	80	111	95	127
0.0306	—	—	25	54	—	35	—	64	59	86	74	109	92	127
0.0228	—	—	26	59	36	—	62	—	—	—	—	—	94	130
Average	12.7	32.7	25.1	54.2	31.6	36.8	61.9	65.0	61.0	86.7	78.7	107.5	94.3	126.3
Standard Deviation	3.2	1.6	3.1	2.4	3.8	2.0	2.2	1.7	3.4	1.4	2.7	4.0	1.6	2.5

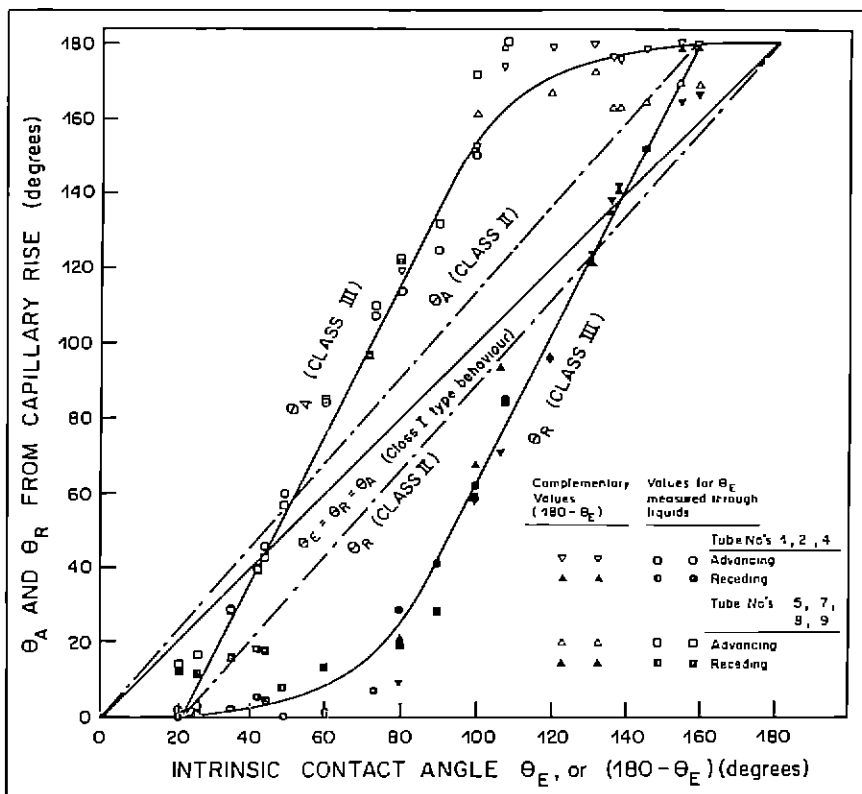


FIGURE 7—Comparison of results for two sets of tubes roughened with different sizes of powder.

two flat plates, using about 10 lb of force on the plates. Contact angles determined for these tubes are included in Figure 4. It is seen that the roughening procedure had little effect; the tubes still gave Class II behaviour. Electron micrographs confirmed (c.f. Fig. 6a and 6b) that the roughening procedure had not had much effect on the appearance of the internal surfaces of the tubes.

#### OBSERVATIONS OF CLASS III BEHAVIOUR

In the next series of experiments, the same five tubes were subjected to a more severe roughening procedure. They were packed with the same dolomite powder and rolled between the plates about 50 times using about 45 lbs pressure. Capillary-rise measurements on these tubes gave results of the form shown in Figure 5. Results of this form will be referred to as Class III type behaviour. Repeat measurements were also made on two tubes for which Class III behaviour had been observed in preliminary studies conducted 10 months earlier; the Class III behaviour was reproduced.

The relationships between  $\theta_E$ ,  $\theta_R$  and  $\theta_A$ , which are included in Figure 5, correspond to the following equations.

#### Advancing Angles — Class III

$$0^\circ < \theta_E < 21.6^\circ$$

$$\theta_A = 0^\circ \dots \dots \dots (10)$$

$$21.6^\circ < \theta_E < 92.4^\circ$$

$$\theta_A = 2(\theta_E - 21.6^\circ) \dots \dots \dots (11)$$

$$92.4^\circ < \theta_E < 158.4^\circ$$

$$\theta_A = 181.5 - 4.051e^{-0.05\theta_E} \dots \dots \dots (12)$$

$$158.4^\circ < \theta_E < 180^\circ$$

$$\theta_A = 180^\circ \dots \dots \dots (13)$$

#### Receding Angles — Class III

$$0^\circ < \theta_E < 21.6^\circ$$

$$\theta_R = 0^\circ \dots \dots \dots (14)$$

$$21.6^\circ < \theta_E < 87.6^\circ$$

$$\theta_R = 0.5e^{0.05\theta_E} - 1.5 \dots \dots \dots (15)$$

$$87.6^\circ < \theta_E < 158.4^\circ$$

$$\theta_R = 2(\theta_E - 68.4^\circ) \dots \dots \dots (16)$$

$$158.4^\circ < \theta_E < 180^\circ$$

$$\theta_R = 180^\circ \dots \dots \dots (17)$$

#### EVIDENCE OF RELAXATION OF SURFACE ROUGHNESS

Four months after making the observations described above for all seven tubes, an attempt was made to extend measurements to a larger number of wetting conditions. It was found that results for all seven tubes mentioned above had reverted to Class II type behaviour (Fig. 4). These results were quite unexpected. In view of the fact that two of the seven tubes had given reproducible results of

the Class III type over a time interval of 10 months, it seems unlikely that this apparent relaxation of roughness was simply due to change with time. Possibly the tubes were inadvertently overheated during drying. In subsequent studies of roughened surfaces, no further evidence of relaxation was observed and this aspect of the work was not deliberately pursued. It seems noteworthy, however, that the observed change was from Class III to Class II behaviour, rather than to something intermediate with respect to these two classes.

#### FURTHER OBSERVATIONS OF CLASS III BEHAVIOUR

The same seven tubes were next subjected to a similar but even more severe roughening procedure. Tubes 1, 2 and 4 were packed with 20-32 mesh dolomite and tubes 5, 7, 8 and 9 with 60-80 mesh dolomite. The number of times the tubes were rolled by the plate was doubled from 50 to 100. Electron micrographs taken before and after this roughening procedure showed a marked change in the appearance of the tube surfaces (c.f. Figs. 6a and 6c). It was found that the tubes gave Class III behaviour once again. The condensed results for all seven tubes are given in Figure 5. Results for tubes roughened with 20-32 mesh dolomite and for tubes roughened with 60-80 mesh dolomite are presented separately in Figure 7. It is seen that the size of particle used to roughen the tube surface has little influence on the results, except that the tubes roughened with the finer (60-80 mesh) powder gave consistently higher receding angles for systems with intrinsic angles of 73 degrees and less. However, when compared on the basis of the cosines from which these angles were derived, this difference in behaviour observed for the two sets of tubes is less than 5%.

The effect of further roughening was studied using tubes 1, 2, 4 and 5. The roughening procedure was as described above, except that the tubes were rolled about 200 times. Change in the internal surfaces of the tubes caused by further roughening was apparent from the distinctly increased opacity of the tubes. However, these tubes still exhibited Class III behaviour (Fig. 8), showing the determined advancing and receding angles to be essentially independent of further roughening.



## TEST FOR COMPOSITE SURFACE EFFECTS

It is often pointed out that contact angles observed at roughened surfaces can be markedly influenced by fluid held by capillarity in grooves or pockets of the solid surface. Surfaces of this type are sometimes referred to as composite surfaces and their influence on wetting behaviour has been considered in some detail<sup>(9,10)</sup>.

As a test for possible composite surface effects in the present work, measurements of capillary rise were repeated using liquids giving intrinsic angles of 108 degrees (water) and 90 degrees (water/ethanol mixture). The four tubes (1, 2, 4, 5) which had been subjected to the most severe roughening, to give the results shown in Figure 8, and the three narrower tubes (7, 8 and 9), which had not been subjected to further roughening, were immersed in liquid and the pressure was raised to 1000 psi. From the results included in Figure 8 it is seen that both sets of tubes still gave Class III behaviour. This indicated that composite surface effects were not of great significance in the present work.

## Discussion

### WENZEL'S THEORY

Data obtained in the present work can be used to test a theory of the effect of surface roughness on contact angle which was proposed by Wenzel<sup>(13)</sup>. A surface-roughness ratio,  $r$ , was used as a quantitative measure of surface roughness, where

$$r = \frac{\text{actual surface}}{\text{geometric surface}} \dots \dots \dots (18)$$

(The actual surface is the surface area of a region of a rough surface and the geometric surface is that which would be given if this region were smooth.) Wenzel introduced the concept of "effective adhesion tensions" to obtain a modified form of Young's equation, in which roughness changed the effective solid-gas and solid-liquid tensions in proportion to the roughness factor,  $r$ . By combining Young's equation and its modified form, a relationship was obtained between the intrinsic angle,  $\theta_E$ , and the angle observed at a rough surface,  $\theta'$ :

$$\cos \theta' = r \cos \theta_E \dots \dots \dots (19)$$

In reporting experimental measurements on materials being tested for water repellency, Wenzel com-

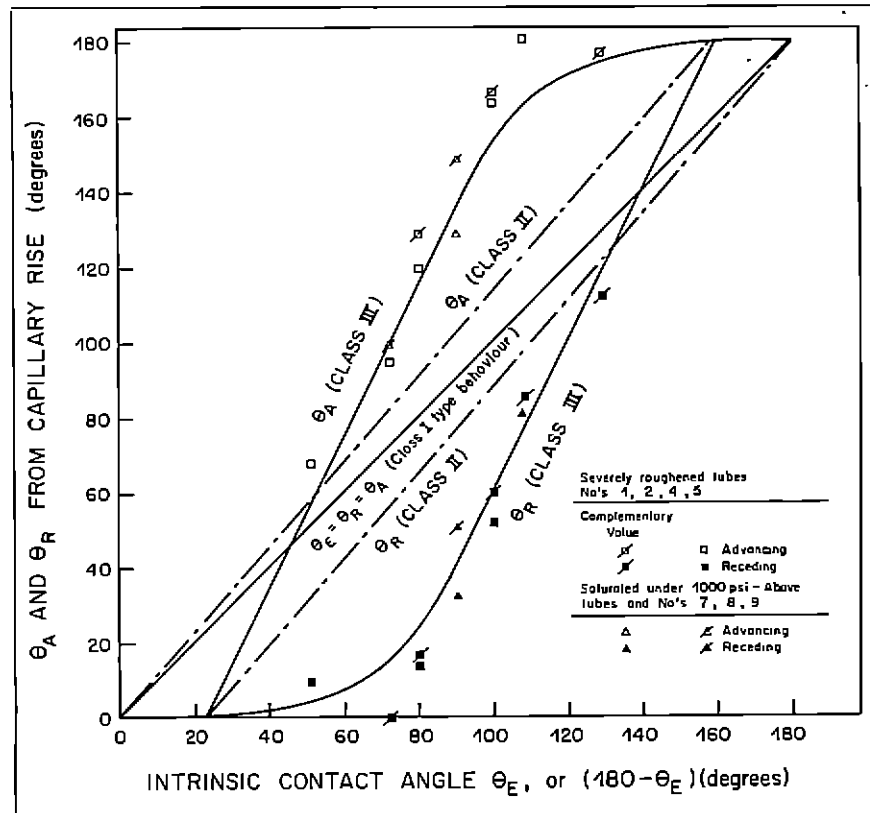


FIGURE 8 — Results of Class III observed for severely roughened tubes and for tubes saturated with liquid under pressure.

mented on the necessity of measuring contact angles under water-advancing conditions in order to obtain results which were reproducible and relevant to the problem in hand. (It may be noted that the hysteresis exhibited by contact angles at roughened surfaces poses a fundamental objection to a theory of surface roughness based on equilibrium concepts.) Wenzel ascribed variation in  $\theta'$  to local variation in the roughness ratio.

The roughness ratio,  $r$ , as defined by Equation (18), is a property of the solid and should be some number,  $> 1$ , which is independent of the intrinsic angle, as illustrated in Figure 9 for a roughness ratio of 1.5. The advancing contact-angle values obtained in the present work were substituted in Equation (19) for the Class III behaviour to obtain the values of roughness ratio,  $r$ , as shown in Figure 9. It is seen that the roughness ratio,  $r$ , so obtained, is highly dependent on intrinsic angle. In this respect, the present work supports the findings of Shepard and Bartell<sup>(11)</sup>, who also concluded that Wenzel's theory is not reliable. Values of  $r$  determined for Class III receding values and both advancing and receding values for Class II behaviour are included in Figure 9.

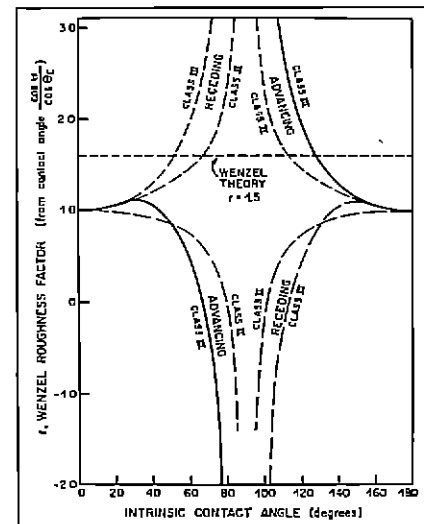


FIGURE 9 — Test of the Wenzel theory — variation of Wenzel roughness factor with intrinsic angle.

### COMPARISON WITH EARLIER ROUGHNESS STUDIES

Shepard and Bartell<sup>(11-13)</sup> studied contact-angle hysteresis on paraffin wax surfaces formed by cutting two sets of parallel v-shaped grooves at right angles to each other to give a regular array of equal pyramids. Advancing and receding contact angles were measured for surfaces of varying pyramid height,  $h$ , and

varying angle of inclination,  $\phi$ , of the sides of the pyramids. It was found that results were independent of height,  $h$ , but varied with  $\phi$ , the angle of inclination. The results obtained by Shepard and Bartell for values of  $\phi$  of 30, 45 and 60 degrees are presented in Figure 10 together with the Class III behaviour obtained in the present work. Bearing in mind the considerable differences in nature of the surfaces studied by Shepard and Bartell and the randomly rough surfaces of the present work, there is good qualitative agreement, with the results for  $\phi = 60$  degrees being closest to the Class III behaviour. However, the data of Shepard and Bartell lack the self-consistency of the data of the present work, in that when the angle observed at a smooth surface is replaced by its complement, and advancing and receding angles are interchanged, the results do not overlap the curves given by the results in their original form.

The independence of Shepard and Bartell's results with respect to pyramid height,  $h$ , seems consistent with the observation of the present work that the size of particles used to induce roughness has little effect on the results. In connection with the influence of height of surface asperities, it is interesting to note that Tamai and Aratani recently

reported advancing contact angles for mercury on silica plates (intrinsic angle 130 degrees)<sup>(20)</sup>. The originally smooth plates were roughened with various grades of abrasive. It was found that the advancing angle increased from 130 to  $158 \pm 2$  degrees for all plates, even though the various methods of roughening gave up to ten-fold variation in the average heights of surface asperities from one plate to another. Another interesting feature of this work was that polishing of the plates so that the asperities were gradually flattened, until a smooth surface was restored, gave a series of contact angles between 158 and 130 degrees (i.e., in the transition region between Class I and Class III behaviour), according to the degree of polishing.

Fox and Zisman<sup>(4)</sup> mentioned that contact angles (presumably advancing) decreased with increasing surface roughness and that roughness caused liquids of low interfacial tension to spread on Teflon. They commented that these observations were consistent with the conclusions of Wenzel<sup>(15)</sup> and Cassie and Baxter<sup>(16)</sup> for intrinsic angles of less than 90 degrees. They are also consistent with Class III behaviour reported in the present work, but only for intrinsic angles of up to about 45 degrees. Above this angle, advancing contact angles

at roughened surfaces were greater than those observed at smooth surfaces (see Fig. 5). Because Fox and Zisman did not provide details of their results, no further comparison can be made.

## ROUGHNESS EFFECTS AT HIGH-ENERGY SURFACES

At smooth high-energy mineral surfaces, finite contact angles arise when the surface character of the mineral is altered by some form of surface deposition such as adsorption. Under these circumstances, such systems do not give a single valued contact angle. A range of stable or slowly changing contact angles may be observed which are bounded by advancing and receding values, say  $\theta_A^1$  and  $\theta_R^1$  respectively. In application to reservoir engineering, emphasis has been placed on obtaining water-advancing contact angles,  $\theta_A^1$ , because of their relevance to waterflooding. Because values of  $\theta_A^1$  and  $\theta_R^1$  are dependent on adsorption processes, times of up to several thousand hours may elapse before the system is judged to have reached an equilibrium<sup>(7)</sup>. When the mineral surfaces are rough, as is the case for reservoir rocks, the operative contact angles within the pore spaces can be expected to exhibit a greater degree of hysteresis than that observed at the smooth surfaces.

Obviously, a systematic study of roughness effects at high-energy solids is needed. However, difficulty in finding pure chemicals which provide accurate and stable wettability control presents an obstacle to carrying out this type of investigation<sup>(8)</sup>. An alternative approach to obtaining wettability control is the use of various crude oils. However, results obtained using this approach are not always consistent. Furthermore, the disadvantage of not being able to properly specify the system is an obvious drawback with regard to the objective of developing a reproducible body of knowledge on wetting behaviour.

In the absence of direct information for high-energy surfaces, it is suggested that roughness effects be assumed to be of the Class III type observed for low-energy surfaces and that such roughness effects be treated as additive with respect to adsorption effects. Thus, the results which have been obtained for low-energy solids would be applied by assuming

$$\theta_E = \theta_A^1 \dots \dots \dots (20)$$

for imbibition, and

$$\theta = \theta_{ER}^1 \dots \dots \dots (21)$$

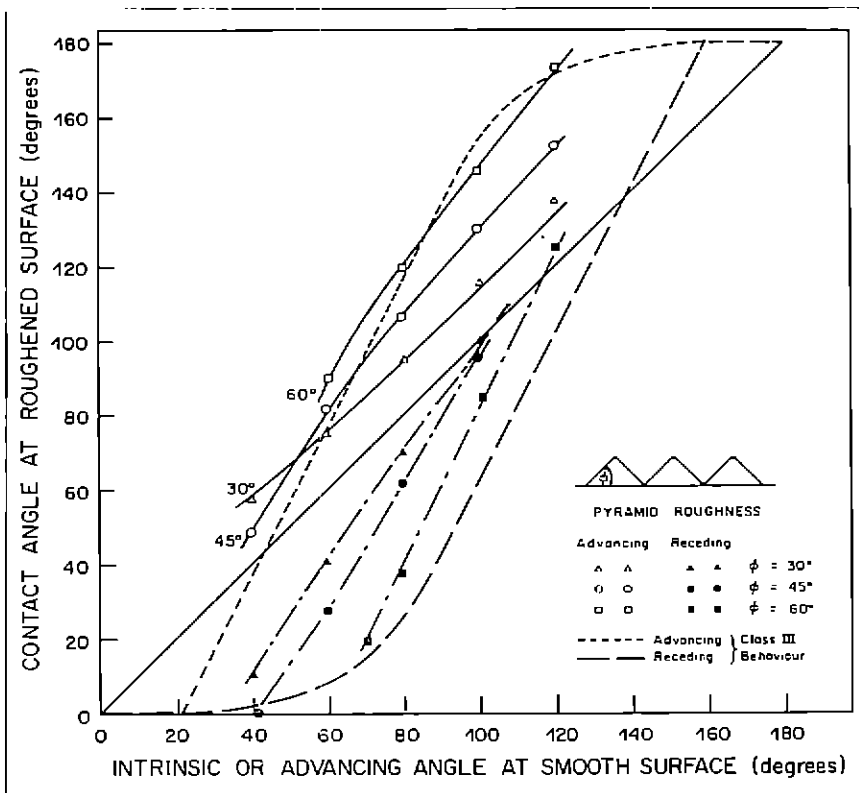


FIGURE 10 — Comparison of advancing and receding angles on regular (pyramidally) rough surfaces with Class III behaviour observed in the present work.

for drainage. Thus, if the advancing contact angle at a smooth mineral surface,  $\theta_a$ , was observed to be 60 degrees and the receding angle,  $\theta_r$ , was 25 degrees, then the operative angles at roughened surfaces for imbibition and drainage are estimated from equations (20) and (11), and (21) and (15), as 77 degrees and 1 degree respectively. These estimates suggest that the system would behave as if completely water wet under drainage and weakly water wet under imbibition.

## CONTACT ANGLE AND RESERVOIR WETTABILITY

As with porous media in general, contact angle cannot be measured directly for reservoir systems. Determination of reservoir wettability from contact-angle measurements for reservoir fluids at smooth mineral surfaces might be regarded as a grossly oversimplified approach to a complex problem. A major difficulty is that of selecting a surface which will correctly represent the reservoir rock surface.

In practice, advancing angles have been measured for reservoir fluids on minerals which, from examination of thin sections of the reservoir rock, are judged to be predominant at the pore walls. Treiber *et al.* found that wettability, as determined from contact-angle measurements on smooth crystal surfaces, was qualitatively consistent with wettability as judged by relative-permeability measurements. Contact-angle data were reported for 55 reservoirs, and these indicate that a wide range of wettability conditions may be encountered. These results are in distinct contrast to the once-held view that most reservoirs are preferentially water wet<sup>(21)</sup>.

Because of heterogeneity of surface energy arising from mixed mineral composition or other possible causes, it may not always be appropriate to discuss wettability in terms of a single contact angle. Several aspects of the effect of surface heterogeneity on contact angle have been investigated theoretically<sup>(7)</sup>. For reservoir systems, contact-angle measurements for a given reservoir crude will give an indication of the likely importance of surface heterogeneity arising from mixed mineralogical composition. For 6 of the 55 crude oils studied by Treiber *et al.*, contact-angle measurements were reported for both quartz and calcite<sup>(7)</sup>. In three cases, the respective angles in degrees were: 140, 145; 125, 145;

160, 135; indicating that mixed mineralogical composition would not be a highly significant factor in wetting behaviour. In the three other cases, however, the respective angles were: 15, 145; 100, 150; 45, 125. More extensive data of this type are needed to evaluate this aspect of the so-called mixed wettability problem.

In view of the divergence of opinion as to types of wetting behaviour that are operative in reservoirs and the fact that Treiber *et al.* considered that there was significant bias in the selection of the reservoirs which they studied, there is a clear need for more contact angle and other wettability-related data for reservoir systems. For example, a study of contact angle for fluids taken from different wells in a given reservoir would be of particular interest. If contact angle were found to be constant, then the basis for treating wettability as a definitive variable for a given reservoir would be much improved.

Apart from the work of Treiber *et al.*, there is very little reported contact-angle data for reservoir systems. At present, it does not seem to be generally accepted that measurement of contact angle provides a basic and powerful approach to investigating many of the recognized problems of reservoir wettability. In addition to those already mentioned, other examples, several of which have been investigated by imbibition studies<sup>(22)</sup>, are: determining the effect of compositional changes (live versus dead crude or the use of synthetic brine); the effect of pressure and temperature change and, in particular, the effect of temperature lowering which occurs during recovery of samples; development of satisfactory methods of preservation and testing of reservoir samples; identification of the causes of wettability and wettability alteration; assessing the effect of drilling muds or corrosion inhibitors on reservoir wettability in the vicinity of the well bore; screening chemical additives for ability to induce favourable wettability changes; measuring the wettability of low-interfacial-tension systems; testing wettability reversal agents; studying the kinetics of adsorption of reservoir or injected fluids; investigating possible relationships between reservoir wettability and the mechanism of migration of hydrocarbons from source rocks and their subsequent accumulation in the reservoir.

An apparatus which could be used to investigate aspects of these problems through contact-angle measurement was recently described by McCaffery<sup>(23)</sup>. Considerable time and great care is needed to obtain satisfactory data. Development of rapid and reliable methods of contact-angle measurement would greatly speed advances in the basic understanding of many of the problems of reservoir wettability.

## CONTACT-ANGLE HYSTERESIS AND IMPROVED RECOVERY BY LOW-INTERFACIAL-TENSION FLOODING

Mobilization of residual oil has been shown to depend on increasing the ratio of viscous to capillary forces<sup>(24)</sup>. Capillary forces which develop after breakdown of micro-emulsion slugs are evidenced by sensitivity of oil recovery to flooding rate<sup>(25)</sup>. Surfactant systems may alter capillary forces through both change in interfacial tension and wettability<sup>(26)</sup>. The present work on the effect of surface roughness on the contact angle has relevance to the effects of wettability on the mobilization of residual oil.

On the basis of model calculations of capillary numbers for displacement of residual oil in sphere packings, Melrose and Brandner<sup>(27)</sup> concluded that strongly water-wet conditions would be optimum. The physical basis of the model calculations was that onset of displacement of a residual oil ganglia involved drainage at the leading front and imbibition at the rear. The capillary force resisting displacement is given by the difference of the drainage and imbibition capillary pressures. It was assumed that there was no contact-angle hysteresis. The calculated increase in capillary forces resisting displacement with an increase in contact angle from 0 degrees was due to the manner in which pore geometry and contact angle interact to determine drainage and imbibition displacement pressures.

If contact-angle hysteresis is taken into account, receding contact angles will be operative at the drainage front of the ganglia and advancing angles will be operative at the rear. For the simple case of a cylindrical tube, there is no resistance to displacement unless there is contact-angle hysteresis, in which case the capillary force,  $\Delta P$ , resisting displacement of a liquid

slug in a tube of radius  $r$  would be given by<sup>(28)</sup>:

$$\Delta P = \frac{2\sigma}{r} (\cos \theta_R - \cos \theta_A) \dots \dots (22)$$

A plot of  $(\cos \theta_R - \cos \theta_A)$  vs  $\theta_E$  is given in Figure 11 for both Class II and Class III behaviour. Resistance to displacement because of wettability effects is at a maximum when the intrinsic contact angle of the system is 90 degrees. For porous media with pores of non-uniform cross section, it is necessary to take into account the interaction of pore geometry and operative contact angles which determine the drainage and imbibition displacement pressures<sup>(29)</sup>. However, results of the present study indicate that resistance to the mobilization of residual oil because of the superimposed effects of contact-angle hysteresis will have an adverse effect on recovery by low-interfacial-tension flooding. On this basis, it would appear that one criteria for the selection of surfactant systems should be that they maintain or induce strongly water-wet conditions.

## Summary

1. Observation of capillary rise in PTFE tubes provided a convenient method of investigating the effect of surface roughness on contact-angle hysteresis over a wide range of wettability conditions as defined by intrinsic contact angle.

2. In contrast to smooth PTFE surfaces, which give essentially no contact-angle hysteresis (Class I behaviour), the tubes as supplied by the manufacturer exhibited contact-angle hysteresis of a type described as Class II behaviour. Slight roughening of the tubes did not change this behaviour.

3. With sufficient roughening of the internal surfaces of the tubes, the Class II type of contact-angle hysteresis was markedly increased to give what was described as Class III behaviour. This behaviour was obtained for a variety of roughness conditions. It was found to be essentially independent of the particle size of the abrasive used in roughening, the extent of further roughening and possible composite surface effects.

4. These results are probably of relevance to the wetting behaviour of surfaces of porous reservoir rocks which are generally of extremely complex character. Contact-angle measurements for reservoir fluids at smooth mineral surfaces exhibit contact-angle hysteresis because of adsorption effects. In estimating the magnitude of operative contact angles within a reservoir, it is suggested that roughness effects at reservoir rock surfaces be taken into account by superimposing Class III behaviour on the advancing and receding contact angles observed at smooth surfaces.

5. Contact-angle hysteresis will increase the capillary forces which oppose the mobilization of residual oil during low-tension flooding. Strong water wetting appears to be the optimum wettability condition for this type of recovery process.

6. Wenzel's theory of the effect of surface roughness on contact angle does not appear to be generally valid. The Wenzel roughness ratio, although defined as a property of the solid surface, was found, when determined from contact-angle data, to be highly dependent on intrinsic contact angle.

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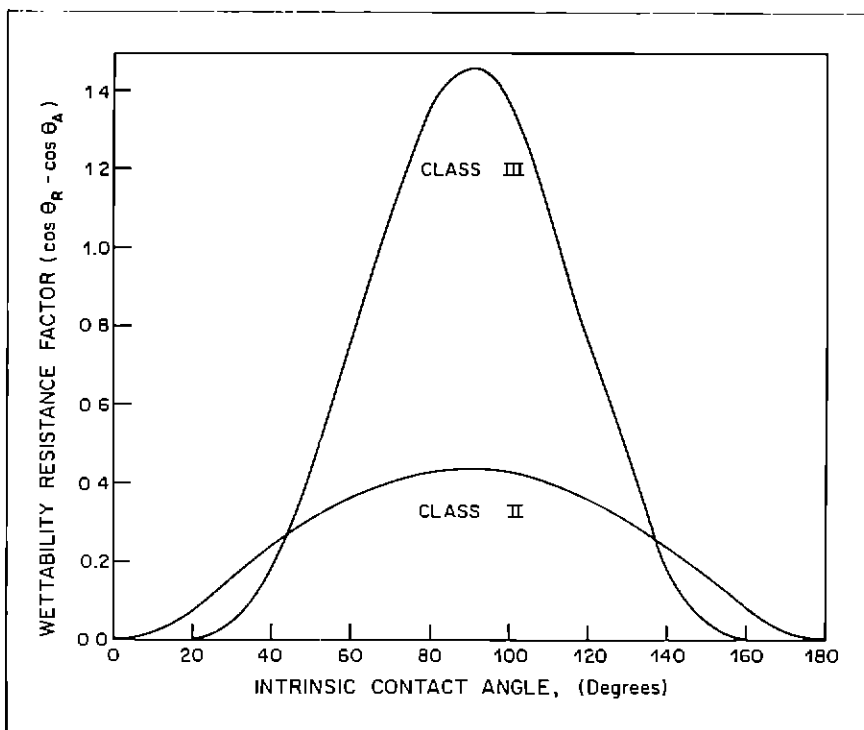


FIGURE 11 — Wettability resistance factor versus intrinsic contact angle for the displacement of liquid slugs in cylindrical capillaries.

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