

noted. A small geared turbogenerator caused the breakdown of former oil fills in a few hundred hours of operation. After thorough application of a special cleaner, the interfacial tension of the new oil charge decreased by only 0.5 dyne per cm. in 24 hours and has remained practically unchanged during several thousand hours of subsequent operation.

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## Ring Method for the Determination of Interfacial Tension

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THE ring method for the determination of surface and interfacial tension has come into common use during the past decade or so. Interfacial tension may be used in studying small changes in concentration of impurities during the refining of petroleum (5, 7, 8) that are difficult to detect by other means. It is likewise useful in following the deterioration of hydrocarbon oil, either in accelerated stability tests or in actual service (5, 8, 9, 10). In applications of this nature the ring method is usually chosen on account of its simplicity.

Harkins and Jordan (4) have pointed out that values obtained by the ring method according to the simple equation  $S = \frac{P'}{4\pi R}$  may be in error by as much as 30 per cent, or even more. In this equation  $S$  is the surface or interfacial tension in dynes per centimeter,  $P'$  is the maximum pull on the ring in dynes, and  $R$  is the radius of the ring in centimeters. These investigators have worked out, upon an empirical basis, factors which can be used to correct such values. These correction factors depend upon the density of the liquid or liquids, the maximum pull on the ring, and the dimensions of the ring. Freud and Freud (2) have substantiated this work from a fundamental standpoint.

Harkins and Jordan have prepared tables of their factors which are conveniently used for surface tension work. However, for interfacial tension measurements, the tables are in-

adequate except for the cases of very low scale readings and/or very great differences between the densities of the two phases. To handle the cases most generally met in the measurement of interfacial tension at hydrocarbon-water interfaces, it has been necessary to extend the data of Harkins and Jordan considerably.

The method employed consisted of a mathematical analysis of the tabulated data to ascertain whether they obeyed any "natural" mathematical relation which might constitute a reliable basis for extrapolation. It has been found that, for a given ring, the correction factor is determined by the relation:

$$(F - a)^2 = \left(\frac{4b}{\pi^2} \cdot \frac{1}{R^2}\right) \times \frac{P}{D - d} + C \quad (1)$$

TABLE I. AGREEMENT BETWEEN DATA OF HARKINS AND JORDAN AND CALCULATED FROM EQUATION 1

$R/r$	$P/(D-d)$	$F$ (H and J)	$F$ (Equation 1)	$R/r$	$P/(D-d)$	$F$ (H and J)	$F$ (Equation 1)
30	105.36	1.012	1.016	50	105.36	1.054	1.053
	79.017	0.967	0.972		79.017	1.013	1.014
	52.678	0.921	0.918		52.678	0.970	0.969
40	105.36	1.038	1.040	60	79.017	1.022	1.023
	79.017	0.996	0.999		63.213	0.998	0.998
	52.678	0.950	0.951		52.678	0.981	0.980

where  $F = \frac{S}{P}$  = correction factor

$S$  = interfacial or surface tension, dynes per cm.

$P$  = maximum pull on ring, dynes per cm.

$D$  and  $d$  = densities of the lower and upper phases, respectively (liquid-air, water-oil), etc.

and for the case of a given ring the following quantities are constant:

$R$  = the radius of the ring

$C$  = a constant, which depends upon the ratio  $r/R$ , where  $r$  = radius of the wire of the ring, in the following manner:

$$C = 0.04534 - 1.679 \frac{r}{R} \quad (2)$$

and  $a = 0.7250$  and  $b = 0.0009075$  are universal constants for all rings.

It is apparent from Equation 1 that the dependence of  $F$  upon the quantity  $P/(D-d)$  obeys a parabolic law for any given ring. The ability of Equations 1 and 2 to evaluate the data of Harkins and Jordan is illustrated in Table I. This satisfactory agreement in conjunction with the simple and standard mathematical form of Equation 1 provides reasonable certainty for extrapolating the data of Harkins and Jordan to the considerable degree required for application of the ring method to interfacial tension measurements.

Figure 1 presents the correction factor,  $F$ , as a function of the quantity  $P/(D-d)$ . Two sets of curves are given, the upper set applicable to a ring of circumference equal to 4 cm. and the lower set to one of 6 cm. Individual curves in each set apply to cases of definite values of  $R/r$  in the following manner:

For the lowest curves in each set,  $R/r = 30$

For the second lowest curves in each set,  $R/r = 40$

For the third curves from bottom in each set,  $R/r = 50$

For the top curves in each set,  $R/r = 60$

The curves were calculated from Equations 1 and 2.

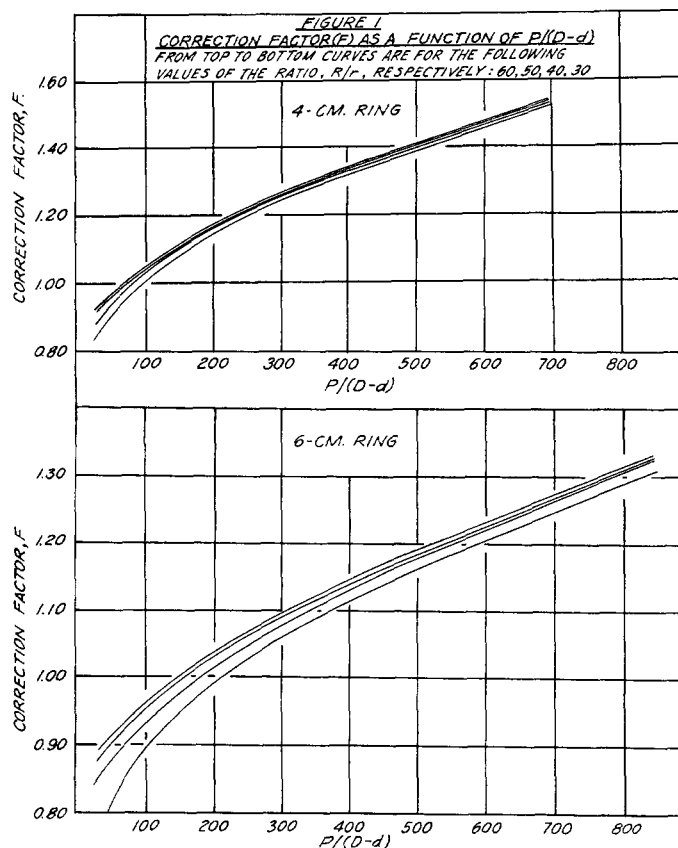
It is indicated by the curves of Figure 1 that the correction values for a 6-cm. ring are much smaller than those for the 4-cm. ring. Upon this basis it follows that, in the interests of greater precision, the larger ring should be used, since the required degree of extrapolation for the correction factor is considerably less than for the smaller ring and the actual magnitudes of  $F$  are also smaller.

TABLE II. OILS USED FOR CORRELATION OF INTERFACIAL TENSION BY RING AND CAPILLARY METHODS

Oil	Description	Density at 25° C.
A	Specially treated kerosene cut	0.7825
B	Solvent-extracted transformer oil	0.8501
C	50-50 blend of A and B	0.8171
D	Untreated medium distillate cut from recycled stock taken from cracking unit	0.8469
E	Untreated heavy distillate cut from recycled stock taken from cracking unit	0.9765
F	67-33 blend of D and E	0.8907
G	33-67 blend of D and E	0.9334
H	Solvent-extracted 150 viscosity turbine oil	0.8843
I	Benzene	0.8735

TABLE III. COMPARISON OF RING AND CAPILLARY METHODS FOR DETERMINING INTERFACIAL TENSION OF OIL AGAINST WATER

		(Temperature, 25° C.)							
		S(Uncorrected)				F			
		4-Cm. Ring		6-Cm. Ring		4-cm. ring		6-cm. ring	
Oil		$R/r = 41.7$	$R/r = 38.8$	$R/r = 54.0$	$R/r = 53.4$				
A	42.0	..	45.5	..	..	1.153	1.041	48.4	47.4
B	41.0	..	45.4	..	..	1.233	1.097	50.6	49.8
C	40.4	..	44.9	..	..	1.182	1.064	47.8	47.8
D	30.7	..	34.2	..	..	1.161	1.050	35.6	35.9
E	19.0	..	23.5	..	..	1.642	1.414	31.2	33.2
F	25.1	..	27.0	..	..	1.193	1.067	29.9	28.8
G	22.4	..	25.1	..	..	1.295	1.141	29.0	28.6
H	..	42.4	..	48.8	..	1.311	1.159	55.6	56.6
I	..	29.1	..	32.6	..	1.189	1.072	34.6	34.9



The validity of Equations 1 and 2 has been checked by means of measurements with two du Nöuy tensiometers (using 4- and 6-cm. rings) as well as by an independent method—namely, the capillary method as described by Bartell and Miller (1). Nine oils have been studied. A brief description of these oils is given in Table II, and interfacial tension data are shown in Table III.

These data show good agreement between the results of the capillary method and corrected results obtained by the ring method for 8 of the 9 oils shown above; and in the case of sample E, which has such a high density that  $P/(D-d)$  is 922 and 1141, respectively, for the 4- and 6-cm. rings used, so that the correction factors are extremely high, the agreement is fair. The value for benzene is in good agreement with the value of 34.68 at 25° C. reported in the literature (3). For samples whose density approaches that of water,  $P/(D-d)$  becomes very large and the ring method loses precision. Oils ordinarily encountered usually have a density of less than 0.90 and are nearly always under 0.95, however, and in this range the ring method, modified by the above outlined correction, is capable of reasonably good precision and accuracy.

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