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Experimental technique to determine the wettability of surfaces to lubricating oils

F. G. ARIETA, D. T. GAWNE
Department of Materials Technology, Brunel University, Uxbridge UB8 3PH, UK

A series of lubricating oils on several metallic surface coatings have been found to conform to the equation $A = Ct^w$, where A is the area of liquid spread, t the time, and C and w are characteristic constants of the system. The parameter w is designated the wettability exponent and is directly related to the rate of liquid spread on the solid surface. The experimental data indicate that w is a reproducible measure of the spreading behaviour of the system and is sensitive to changes in the solid surface, liquid and temperature.

1. Introduction

The spreading of liquids over the surface of solids is important in a large number of applications, including lubrication, adhesion, soldering, lithographic printing, waterproofing of textiles, dust control and spraying of foliage. In the case of lubrication, the wettability of surfaces to oils is crucial in minimizing the wear of surfaces and, in this context, the practice of applying surface coatings to engineering components is becoming increasingly important. Surface coating is the last manufacturing operation before service of many parts and thus provides an opportunity to control surface properties such as wettability. For example, the modification of chromium coatings to produce porous structures has been found to increase the service life of cylinder liners and piston rings in internal combustion engines and this is generally attributed to their improved wettability [1, 2]. The work reported in this paper is directed at establishing an experimental procedure to quantify the wettability of surface coatings to lubricating oils.

2. Theory

A drop of liquid placed on a solid surface will either remain as a drop or spread over the surface. The outcome will depend upon the relative magnitude of the surface free energies per unit area (or surface tensions) of the solid–vapour interface, γ_{sv}, solid–liquid interface, γ_{sl}, and liquid–vapour interface γ_{lv}. Spreading of the liquid decreases the area of the solid–vapour interface and increases that of the other two interfaces. If the net change in free energy is negative, the total Gibbs free energy, G, of the system decreases and the liquid tends to spread; otherwise it will tend to cover a minimum area of the solid. These considerations concern small volumes of liquid for which surface factors dominate and gravitational effects may be neglected. The change in Gibbs free energy, dG, caused by the drop spreading is given by:

$$\mathrm{d}G = \gamma_{sl}\delta A_{sl} + \gamma_{lv}\delta A_{lv} + \gamma_{sv}\delta A_{sv} \qquad (1)$$

where δA_{sl}, δA_{lv} and δA_{sv} are the changes of area of the three interfaces with subscripts as before. For a planar surface, the magnitude of these three areas is approximately equal:

$$\delta A_{sl} = \delta A_{lv} = -\delta A_{sv} \qquad (2)$$

and their substitution into Equation 1 gives the free energy change on spreading:

$$\mathrm{d}G = -(\gamma_{sv} - \gamma_{sl} - \gamma_{lv})\delta A \qquad (3)$$

The thermodynamic condition for spreading is $\mathrm{d}G < 0$, and combining this with Equation 3 gives:

$$\gamma_{sv} - \gamma_{sl} > \gamma_{lv} \qquad (4)$$

Equation 4 indicates that spreading will tend to occur if the interfacial energy of the solid–vapour boundary is higher than that of the solid–liquid boundary by at least an amount equal to the interfacial energy of the liquid–vapour boundary.

At equilibrium, the contact angle, θ, subtended at the drop periphery by the liquid surface and the solid–liquid interface, as illustrated in Fig. 1a, is given by Young's equation:

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \qquad (5)$$

This shows that the cosine of the contact angle is given by the ratio of the free energy release from forming unit area of solid–liquid interface to that required to form unit area of the liquid–vapour interface. As illustrated in Figs 1b and c, $\theta > 90°$ and $\theta < 90°$ are generally taken to represent non-wetting and wetting liquids, respectively. Under ideal conditions, θ may thus be regarded as an inherent property of the solid–liquid–vapour system and a measure of its wettability. The measurement of contact angles is a commonly used experimental technique [3]; the wettability of the system being taken as the inverse of the contact angle.

The surface area of a sessile liquid–vapour interface is uniquely smooth and is defined by its planar area. A solid–liquid interface is not perfectly smooth, however, and its surface area is critically dependent upon the nature of the surface. All engineering surfaces are microscopically rough and this violates the assumptions of flatness and homogeneity inherent in Young's

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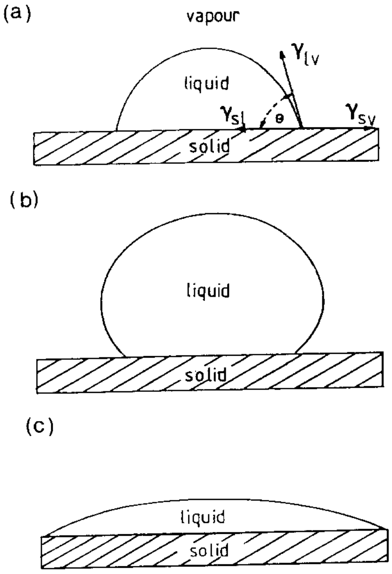

Figure 1 Profiles of liquid drops on a solid surface: (a) definition of parameters; (b) non-wetting liquid; (c) wetting liquid.

equation [4, 5]. Wenzel [4] noted that roughening a solid surface would increase its true surface area by a factor of r over that of a microscopically smooth surface. r is termed the roughness parameter and is the ratio of the true area of the solid surface to its apparent or nominal projected area. The changes in area of the solid–vapour and solid–liquid interfaces caused by the drop spreading are now $r\delta A$ and Equation 3 becomes:

$$dG = -[r(\gamma_{sv} - \gamma_{sl}) - \gamma_{lv}]\delta A \qquad (6)$$

The thermodynamic driving force for the spreading of wetting liquids is thus increased by roughening the solid surface. Similarly, the apparent or measured contact angle θ^* for the rough surface is given by:

$$\cos\theta^* = \frac{r(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} \qquad (7)$$

Combining Equations 5 and 7,

$$\cos\theta^* = r\cos\theta \qquad (8)$$

where θ is the true or thermodynamic equilibrium contact angle, θ^* the apparent contact angle and r the roughness parameter ($r \geqslant 1$). For a microscopically smooth surface, r is unity and θ^* equates with θ. Engineering surfaces exhibit $r > 1$ and for wetting liquids ($\theta < 90°$), the apparent contact angle θ^* will be less than the true contact angle according to Equation 8 and as shown in Fig. 2. Roughening a substrate is thus expected to decrease the contact angles of wetting liquids and increase those of non-wetting liquids so that, in general, the difference between the true angle and 90° is enhanced. Equation 8 also indicates that the difference between the apparent and true contact angles is greatest for wetting liquids (low θ) on rough surfaces (high r). A further property of Equation 8 is that θ has a finite value of $\cos^{-1}(1/r)$ when θ^* is zero for $r > 1$ and, as a consequence, systems with highly wetting liquids on rough surfaces for which $\theta < \cos^{-1}(1/r)$ cannot be evaluated.

The assessment of wettability depends upon the assessment of both r and θ^*, for which the experimental errors are substantial. An insight into the sensitivity of θ to errors in r and θ^* may be obtained by differentiation of Equation 8:

$$\delta\theta = \frac{\cos\theta^*}{r^2\sin\theta}\delta r + \frac{\sin\theta^*}{r\sin\theta}\delta\theta^* \qquad (9)$$

where $\delta\theta$ is the change in θ caused by small increments, δr and $\delta\theta^*$, in r and θ^*, respectively. It is noted that:

$$\sin\theta = \frac{(r^2 - \cos^2\theta^*)^{1/2}}{r} \qquad (10)$$

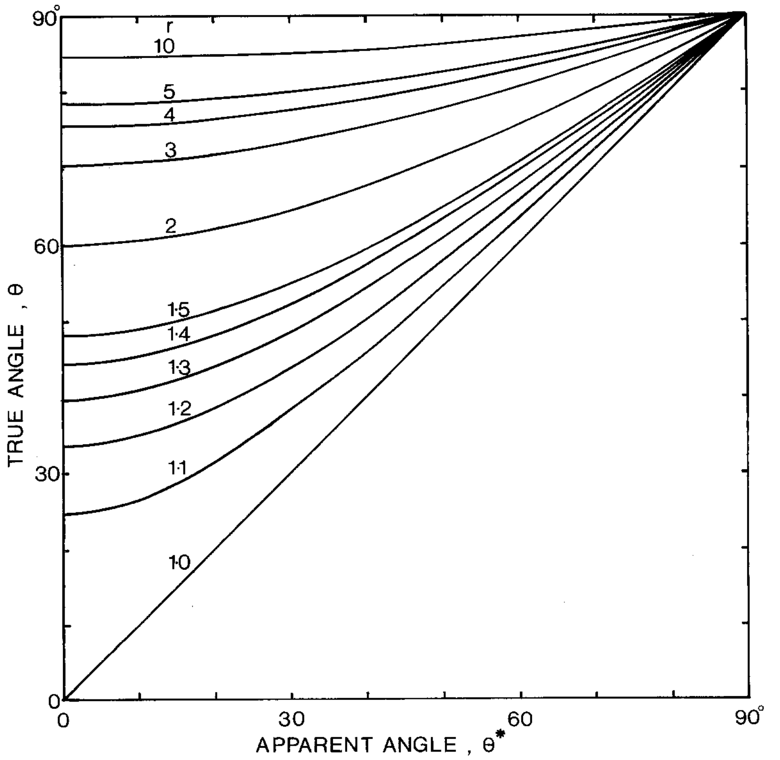

Figure 2 True contact angle θ as a function of the apparent contact angle θ^* for various values of the roughness parameter, r.

and substitution into Equation 9 gives:

$$\delta\theta = \frac{\cos\theta^*}{r(r^2 - \cos^2\theta^*)^{1/2}}\delta r + \frac{\sin\theta^*}{(r^2 - \cos^2\theta^*)^{1/2}}\delta\theta^* \quad (11)$$

Equations 9 and 11 show that θ is particularly sensitive to experimental errors for relatively smooth surfaces (low values of r). Tribological systems tend to consist of relatively smooth engineering surfaces with highly wetting liquids and so the evaluation of their wettabilities by the contact angle technique incurs serious difficulties.

A different approach to the determination of wettability, adopted by a number of workers [6–10], is to use the area of spread of a liquid film on the solid surface as an experimental parameter. This is particularly attractive for tribological systems in which the rate of spreading of highly wetting liquids is a relevant factor. This paper is directed at assessing the suitability of this approach for engineering surface coatings and concerns the measurement of the area of spread of lubricating oils as a function of time and temperature.

3. Experimental procedure

3.1. Materials

Seven surface coatings were used as solid surfaces: low-temperature electrodeposited chromium (A), conventional electrodeposited chromium (B), electroless nickel–8% phosphorus alloy coating (C), sputtered gold deposit (D), electroplated tin (E), conventional electrodeposited chromium (F) and a duplex chromium coating (G). The process conditions used for these coatings are detailed in Table I. The substrate for all samples except E was a plain carbon–manganese steel (080M40 grade) surface ground to a finish with an R_a value of 0.5 to 0.6 μm. The substrate for sample E was a continuously cast cold-rolled and annealed aluminium-killed low carbon steel.

Three different oil lubricants were used in the investigation. The majority of the work was carried out using oil 1, which is a base oil of type SAE30 designated Stanco 150 with an addition of 1.5 vol % zinc dipentyl dithiophosphate (ZDDP – a multifunctional additive with antiwear, antioxidant and anticorrosion roles). The distribution of carbon between aromatic, alkane and cyclo-alkane forms in the base stock was determined by infrared spectrometry to be 10, 67 and 23%, respectively, and the sulphur content was 1.3%. Two other oils were used: XD3-30, a fully formulated commercial lubricant (oil 2) and XD3-30-MoS_2 (oil 3), which is oil 2 with an addition of molybdenum disulphide to improve lubricity. The properties of oils 2 and 3 are broadly similar to each other but appreciably different from oil 1.

3.2. Test method

The apparatus to measure wettability consisted of a 25 ml glass beaker at the bottom of which was attached a horizontal tube (150 mm long and 7 mm inner diameter) with a vertical tap (1.65 mm inner diameter) located 30 mm above the centre of the flat test surface. The beaker and the test surface were placed on electrically heated hot plates. A 35 mm camera (50 mm focal length, f1.4 aperture) with a motorized drive was mounted above the test surface. For work at elevated temperatures, the oil and the test surface were maintained at the same temperature and a thermocouple was inserted in a drilled hole in the substrate of the test specimen, 0.5 mm below its surface. The assembly was placed on a table free from vibrations and sunlight.

The test surfaces were obtained in the clean, as-plated state but in order to standardize conditions, the following cleaning procedure was adopted immediately before testing. The specimen surface was washed with soap and running water, ultrasonically cleaned in distilled water for 1 min, washed in acetone and blow-dried.

A single drop of the test liquid of mass 20 mg was released from the tap and timed from the moment it contacted the test surface. Photographs of the liquid spreading on the surface were taken at pre-determined time intervals and the areas of spread measured with

TABLE I Process conditions for surface coatings

Identity	Coating	Deposition conditions	Deposition temperature (°C)	Current density (kA m^{-2})	Deposition time (sec)
A	Electrodeposited chromium (low deposition temperature)	Chromic acid bath	35	4.6	7.2×10^3
B	Electrodeposited chromium (conventional)	Chromic acid bath	55	4.6	7.2×10^3
C	Electroless Ni–8%P	Acid–hypophosphite bath, pH 4.8	88	–	3.6×10^3
D	Sputtered gold	8 kV, 25 mA, 0.8 torr	–	–	180
E	Electrodeposited tin	Stannous sulphate bath	50	2.5	30
F	Electrodeposited chromium (conventional)	Chromic acid bath	51	3.2	18×10^3
G	Electrodeposited chromium (duplex):	Chromic acid bath			
	topcoat		70	3.2	12.6×10^3
	undercoat		51	3.2	5.4×10^3

an Allbrit planimeter to an accuracy of ±3% on the enlarged prints. The ambient conditions throughout the tests consisted of temperatures of 19 to 25° C and relative humidities of 55 to 71%.

4. Results and discussion

Three independent wettability tests were carried out for oil 1 on the electrodeposited chromium surface A under ambient conditions. The data in Fig. 3 indicate that the results obtained were well behaved and reproducible. Further wettability experiments were performed with the same oil on chromium surface B, electroless nickel C, sputtered gold D, and electrodeposited tin E. Fig. 4 shows that all the surface coatings exhibited a logarithmic relationship between area of spread and time. The experimental data thus show that the systems studied conform to the general equation:

$$\log A = w \log t + K \tag{12}$$

where A is the area of spread of the test liquid on the test surface after time, t, w and K are the gradient and intercept at unit time, respectively, of the plot of log A against log t. w and K are constants for a specific system. Equation 12 may be expressed in the parabolic form as:

$$A = Ct^{w} \tag{13}$$

where C is the antilogarithm of K in Equation 12.

The parameter w is defined as the gradient of the log–log plot of the area of liquid spread against time:

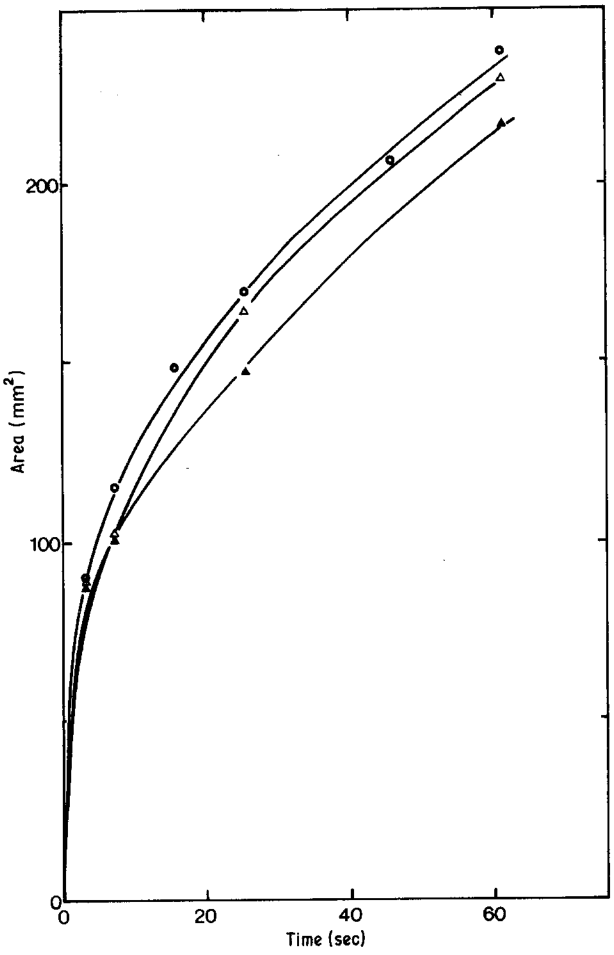

Figure 3 Area of spread of oil 1 on chromium surface A as a function of time at 25° C.

$$w = \frac{\mathrm{d}(\log A)}{\mathrm{d}(\log t)} = \frac{\mathrm{d}(\ln A)}{\mathrm{d}(\ln t)} = \frac{t\,\mathrm{d}A}{A\,\mathrm{d}t} \tag{14}$$

Rearranging,

$$\frac{\mathrm{d}A}{\mathrm{d}t} = w\frac{A}{t} \tag{15}$$

Equation 15 shows that w is directly related to the rate of liquid spread on the solid surface, which is a relevant factor in practice. The parameter w is taken to represent the wettability of a given system and is to be designated as the wettability exponent; the larger the wettability exponent, the higher the wettability of the system.

The wettability exponent was determined for each of the three tests on the chromium surface A with oil 1 (Fig. 3). A mean value of w of 0.309 was obtained with a 95% confidence limit of ±0.007, which indicates satisfactory reproducibility. The values of the wettability exponent together with those of the intercept K are given for the other surface coatings with oil 1 in Table II. The wettability exponent ranges from 0.074 for the electrodeposited tin to 0.309 for chromium surface A. The differences in w between the various surface coatings are clearly significant and demonstrate that the method is sufficiently sensitive to reveal variations between solid materials.

The surface free energies of metals at ambient temperatures lie in the range 1000 to 3500 mJ m^{-2} compared with only 10 to 40 mJ m^{-2} for organic liquids and 73 mJ m^{-2} for water. On the basis of Equations 3 and 5, therefore, these liquids should exhibit zero contact angles and spread indefinitely on metallic surfaces. The fact that this tends not to occur [11] has been attributed by Schrader [12] to atmospheric contamination of the metallic surfaces (e.g. oxidation and adsorption of organic substances from the environment) which markedly reduces their surface energies.

In the current investigation the highest wettability exponent was given by chromium A, followed by gold, chromium B, nickel and tin, the lowest (Table II). The surface free energies of metals reported in the literature [13–17] are notoriously variable but approximate mean values are 2500 mJ m^{-2} for chromium (b c c), 1700 mJ m^{-2} for gold, 2500 mJ m^{-2} for nickel and 1000 mJ m^{-2} for tin. The surface energies of the lubricating oils were measured using the capillary rise

TABLE II Values of the wettability exponent, w, and the intercept, K, for various solid surfaces with oil 1 at ambient temperature

Identity	Coating	Wettability exponent, w	Intercept, K (mm^2)
A	Low temperature chromium	0.309	64
B	Conventional chromium	0.139	49
C	Electroless nickel	0.123	67
D	Sputtered gold	0.259	69
E	Electrodeposited tin	0.074	45

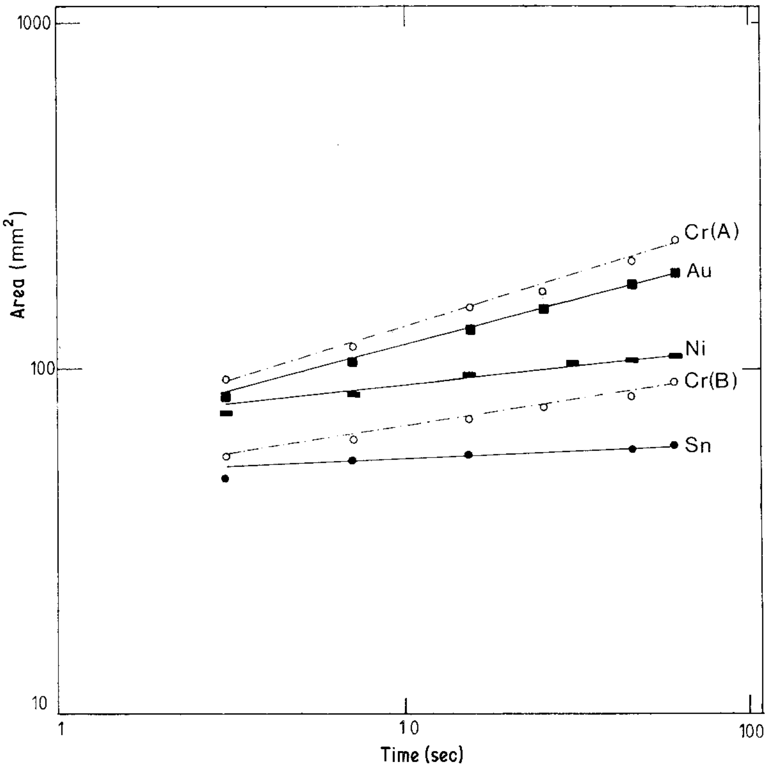

Figure 4 Area of spread of oil 1 on the chromium, nickel, gold and tin surface coatings at 25° C.

method with distilled water as a comparative standard. The results are given in Table III and show a value of 16.0 mJ m^{-2} for oil 1. The low wettability exponent of tin is possibly related to its low surface energy. The high wettability of gold is also possibly related to the fact that it is not oxidized and hence retains a high surface energy. However, chromium A and B are inherently the same material (b c c chromium) but give appreciably different wettability exponents. The implication is that there are other factors besides surface energy that affect wettability.

The theoretical treatment so far considered implicitly assumes that the topography of the solid surface is only of importance through its effect in increasing the surface area and that the individual surface features are negligibly small compared with the drop dimensions. Shuttleworth and Bailey [18] followed by more recent workers [19, 20], however, regard the asperities on rough surfaces as a series of energy barriers that must be overcome as the liquid front advances from one metastable configuration to another. The ability of the liquid to overcome the barriers and spread over the solid surfaces depends upon the relative magnitude of the barriers and the vibrational energy of the liquid. The surface of electrodeposited chromium consist of nodules of approximately 10 μm in height [21] which is significant compared with the thickness of the liquid film. Chromium coatings A and B were prepared under different deposition conditions (Table I) and this is expected to produce different surface topographies owing to, *inter alia*, differences in the nucleation and growth rates of the nodules. Surface topography is likely to be the major cause of the difference in wettability between the two chromium coatings and to have an important influence on the wettability of engineering surface coatings in general.

TABLE III Surface energies of lubricating oils

Identity	Oil type	Surface energy (mJ m^{-2})
1	Stanco 150 + 1.5% ZDDP	16.0
2	XD3–30	29.3
3	XD3–30–MoS$_2$	25.3

Tribological systems such as piston rings and cylinder liners in internal combustion engines, operate at elevated temperatures under lubricated conditions. The variation of wettability with temperature is a practically important factor in these cases. Wettability measurements were carried out at temperatures up to 150° C using the three lubricants: oils 1 to 3 (as described in Section 3.1). A larger drop volume (60 mg) was used in this series of experiments relative to that employed in the previous room temperature tests in order to compensate for the evaporation losses at the elevated temperatures. Two solid surfaces were used: a conventional electrodeposited chromium coating, F, and a duplex chromium coating, G (Table I). The duplex deposit consisted of a conventional chromium undercoat on to which was electrodeposited a crack-free chromium topcoat.

The results of the wettability tests at elevated temperatures are given in Fig. 5. The three oils give significantly different wettabilities with a particularly large difference between oil 1 and the other oils. The wettability exponent rises to a maximum at approximately 80° C and then gradually decreases. The larger volume of oil used in this series of tests increased the wettability exponent for oil 1 on conventional chromium from 0.14 (Table II) to 0.51 (Fig. 6).

Wettability phenomena at elevated temperatures are complicated by the fact that the properties of lubricating oils are temperature-dependent, especially viscosity and composition. Compositional changes occur owing to the preferential evaporation of the more volatile components at elevated temperatures. The viscosities of the oils were measured using a Redwood viscometer (no. 1) and the data are plotted as a function of temperature in Fig. 6. Oil 1 possesses a much lower viscosity than oils 2 and 3, particularly at 25° C. The viscosity of all the oils decreases as the temperature rises, the rate of fall being particularly pronounced between 25 and 80° C. The evaporation losses of the oils were determined by weighing at the temperatures of interest and the results are shown in Fig. 7. The greatest losses occur in oil 1 and all oils experience large increases in evaporation between 80 and 150° C.

The increase in wettability exponent between 25 and 80° C (Fig. 5) is attributed to the large increase in fluidity of the oils over this temperature range (Fig. 6) which promotes spreading over the surface. The subsequent fall in the wettability exponent above 80° C is most likely a result of the influence of evaporation. The rate of evaporation increases markedly above 80° C (Fig. 7) which is expected to increase viscosity due to the preferential removal of the lighter components of the oil. This effect is accentuated by the fact that vaporization on a hot solid surface is expected to take place more rapidly from the thin spreading edge of the liquid film than from the film centre. This will result in the development of a viscosity gradient across the film diameter at elevated temperatures with the most viscous liquid at the advancing periphery.

The duplex chromium coating gave consistently higher wettability exponents than the conventional chromium (Fig. 5). A major factor in this difference is likely to be the change in surface topography arising

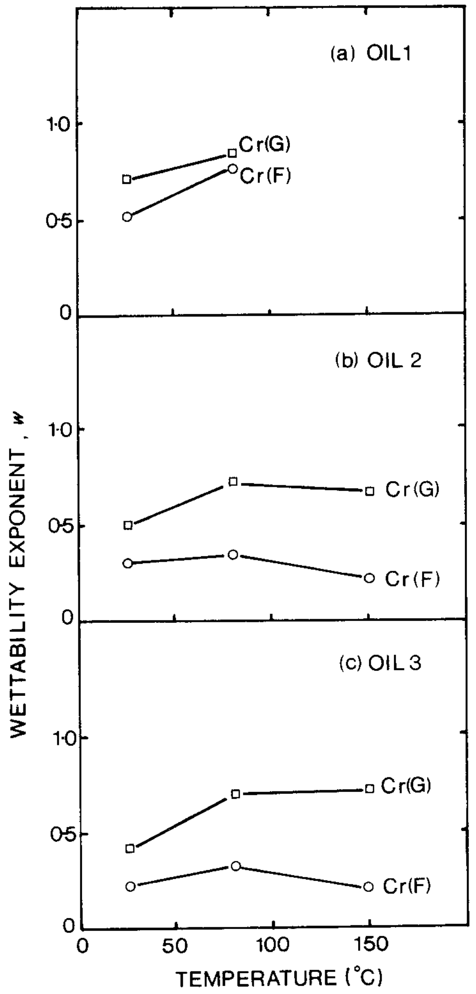

Figure 5 The effect of temperature on the wettability exponent for oils 1 to 3 on conventional electrodeposited coating (F) and duplex chromium coating (G).

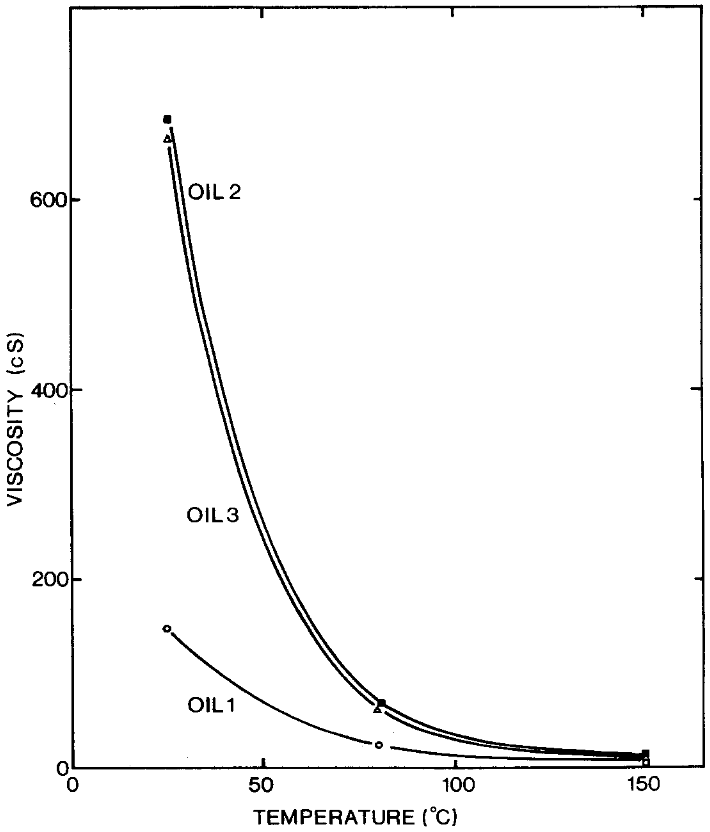

Figure 6 Kinematic viscosity values for oils 1 to 3 as a function of temperature.

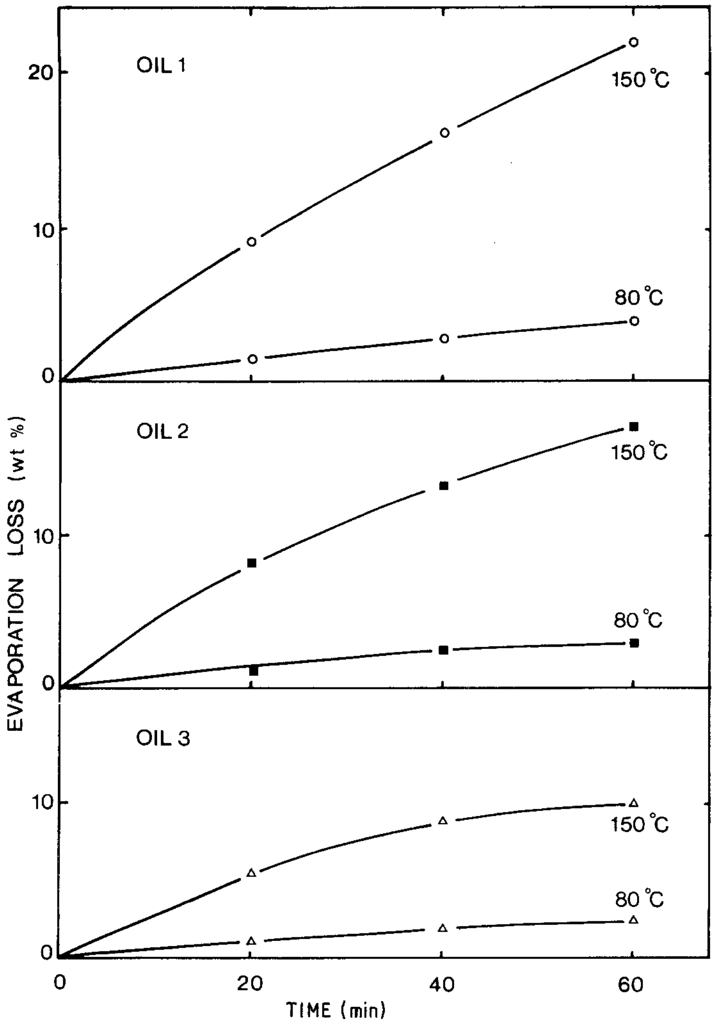

Figure 7 Evaporation losses for oils 1 to 3 as a function of time and temperature.

from the different deposition conditions. In addition, the crack-free chromium surface of the duplex coating has a hexagonal close packed crystal structure [22] (as opposed to the body centred cubic structure of conventional chromium) and this may possibly influence its wettability through its effect on surface energy.

The contact angle technique is directed at determining the equilibrium configuration as a means of evaluating wettability. The areal spread rate technique used in the current investigation measures the kinetics of liquid spreading. The balance of surface energies will dictate whether or not spreading will occur but the kinetics of the process will also be governed by the properties of the entire system rather than material properties alone. Hence, factors such as liquid viscosity, temperature and surface topography will play a major role in spreading behaviour. The present work was carried out under atmospheric conditions whereas practical systems may operate under non-standard pressures and different gas compositions. The experimental range of the present technique may be extended by enclosing the apparatus in a chamber for work under controlled gas compositions and pressures.

5. Conclusions

1. The areal spread, A, of lubricating oils on engineering surface coatings has been found to conform to the equation $A = Ct^w$, where t is the time, C and w are characteristic constants of the system.

2. w is designated the wettability exponent and is directly related to the rate of liquid spread on the solid surface. The experimental data indicate that w is a reproducible measure of the spreading characteristics of a system.

3. Seven surface coatings and three lubricating oils were investigated. The wettability exponent was found to vary appreciably with the type of solid surface and liquid.

4. The wettability exponent reaches a maximum at approximately 80° C and then decreases for the oils tested. This is attributed to the fact that the viscosity of the oils decreases up to 80° C but then increases at the spreading edge of the liquid film owing to compositional changes caused by evaporation.

References

1. J. M. A. VAN DER HORST, *Proc. Amer. Electroplaters Soc.* **31** (1943) 56.
2. R. PYLES, *ibid.* **31** (1943) 136.
3. R. J. GOOD, *Surf. Colloid Sci.* **11** (1979) 86.
4. R. N. WENZEL, *Ind. Eng. Chem.* **28** (1938) 988.
5. W. A. ZISMAN, in "Advances in Chemistry", No. 43, edited by R. F. Gould (American Chemical Society, Washington, 1964) p. 1.
6. C. L. BAKER, *Ind. Eng. Chem.* **23** (1931) 1025.
7. R. BUCKLEY and G. H. S. SNYDER, *J. Amer. Chem. Soc.* **55** (1933) 194.
8. J. HYYPIA, *Anal. Chem.* **20** (1948) 1039.
9. T. HORI, S. HAYASHIDA, S. VEDA and S. KONISHI, *J. Amer. Soc. Lubrication Eng.* **33** (1977) 83.
10. B. P. KRISHNAN, N. RAMON, K. NARAYANASWAMY and P. K. ROHATGI, *Tribology Int.* **14** (1981)

301.
11. H. W. FOX, E. F. HARE and W. A. ZISMAN, *J. Phys. Chem.* **59** (1955) 1097.
12. M. E. SCHRADER, "Fluid–Solid Surface Interactions", Proceedings of the 2nd Symposium, edited by H. J. Lugt (US Naval Ship Research and Development Center, Bethesda, Maryland, 1974) pp. 151–67.
13. V. K. SEMENCHENKO, "Surface Phenomena in Metals and Alloys" (Addison-Wesley, Reading, Mass., 1962).
14. W. R. TYSON, *Can. Metall. Q.* **14** (1975) 307.
15. A. R. MIEDEMA, *Z. Metallkde* **69** (1978) 287.
16. H. JONES, *Met. Sci. J.* **5** (1971) 18.
17. T. A. ROTH, *Mater. Sci. Eng.* **18** (1975) 183.
18. R. SHUTTLEWORTH and G. L. J. BAILEY, *Disc. Faraday Soc.* **3** (1948) 16.
19. C. HUH and S. G. MASON, *J. Colloid Interface Sci.* **60** (1977) 11.
20. R. H. DETTRE and R. E. JOHNSON Jr, *J. Adhesion* **2** (1970) 61.
21. D. T. GAWNE and T. F. P. GUDYANGA, *Tribology Int.* **17** (1984) 123.
22. W. A. SAFRANEK, National Bureau of Standards, Special Publication No. 452, Washington (1976) pp. 56–63.

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