# WETTABILITY OF POROUS SURFACES.

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*Received* 19*th June*, 1944.

## 1. Introductory.

Adam [1] and Wenzel [2] have shown how a rough surface can influence the apparent contact angle at the boundary between a liquid and the surface, and many examples have been given of the difficulty of wetting rough surfaces because of their large apparent contact angles. The wettability or water-repellency of porous surfaces has not been similarly investigated although it is of much importance for the rain resistance of all porous clothing, both natural and artificial. The present paper extends Adam and Wenzel's analysis to porous surfaces.

## 2. Apparent Contact Angle for Porous Surfaces.

If the water is under zero hydrostatic pressure it will come to rest on a porous surface in some position AA, Fig. 1, determined by the advancing smooth surface—water contact angle and the shape of the pores in the surface. The surfaces of practical importance are usually grids formed of roughly cylindrical fibres, and Fig. 1 is a cross-section of such a grid. Let $f_1$ be the total area of solid-liquid interface and $f_2$ be the total area of liquid-air interface in a plane geometrical area of unity parallel to the rough surface. When water spreads over the unit area, a solid-air interface of area $f_1$ is destroyed and an energy $f_1\gamma_{SA}$ is gained, where $\gamma_{SA}$ is the solid-air interfacial energy ; an energy $f_1\gamma_{LS}$ is expended in forming the solid-liquid interface over the same area, where $\gamma_{LS}$ is the liquid-solid interfacial energy. An energy $f_2\gamma_{LA}$ is also expended in forming the air-water surfaces. The net energy, $E_D$, expended in forming unit geometrical area of the interface is, therefore,

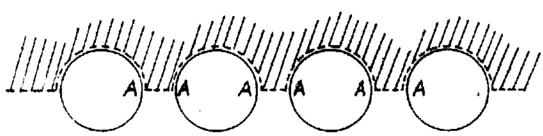


Fig. 1.—Water on cylinders.

$$E_D = f_1(\gamma_{LS} - \gamma_{SA}) + f_2\gamma_{LA} \quad . \quad . \quad . \quad (1)$$

If $\theta_A$ be the advancing contact angle for the solid-liquid interface,[3]

$$\cos\theta_A = (\gamma_{SA} - \gamma_{LS})/\gamma_{LA} \quad . \quad . \quad . \quad . \quad (2)$$

the equation (1) becomes

$$E_D = \gamma_{LA}(f_2 - f_1\cos\theta_A) \quad . \quad . \quad . \quad (3)$$

Equation (2) may be written—

$$\cos\theta_A = -E/\gamma_{LA} \quad . \quad . \quad . \quad . \quad (4)$$

since $(\gamma_{LS} - \gamma_{SA})$ is the energy, $E$, required to form unit area of the solid-liquid interface. An apparent contact angle, $\theta_D$, may be defined for the porous surface by analogy with (4) ; it is

$$\cos\theta_D = -E_D/\gamma_{LA} = f_1\cos\theta_A - f_2 \quad . \quad . \quad . \quad (5)$$

[1] Adam, *Physics and Chemistry of Surfaces*, 3rd ed., p. 186.
[2] Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988.
[3] Adam,[1] p. 178.

When the surface is rough but not porous, $f_2$ is zero, and equation (5) educes to Wenzel's equation [8] for the apparent contact angle of a rough surface with the roughness factor $f_1$.

Equation (5) gives the apparent contact angle for water advancing on to a dry surface. An apparent receding contact angle can be defined in the same way: it is

$$\cos \theta_W = f_1 \cos \theta_R - f_2 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\theta_R$ is the solid-water receding contact angle, and $\theta_W$ is the apparent receding contact angle for the porous surface. It should be noted that $f_1$ and $f_2$ in equation (6) are determined by the advancing contact angle $\theta_A$.

## 3. Calculation of Apparent Contact Angles.

Clothing problems that are amenable to quantitative treatment usually involve surfaces made up of grids of parallel fibres, and $f_1$ and $f_2$ can be derived from the value of $\theta_A$ and the dimensions of the grating. Fig. 2 shows the cross-section of neighbouring fibres in the grating with their axis normal to the paper. Consider unit length of the grating normal to the paper. The plane geometrical area may be taken as OA, when $f_1$ is given by the arc DC divided by OA, and $f_2$ is given by BC/OA. If the fibres are of radius $r$ with their axes $2(r + d)$ apart, then

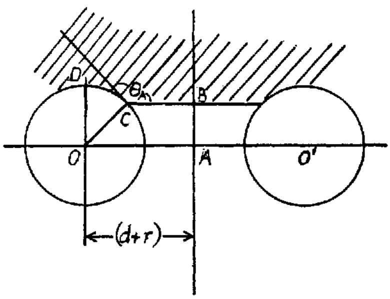


FIG. 2.—Determination of $f_1$ and $f_2$.

$$f_1 = \{(\pi r/(r + d)\}(1 - \theta_A/180°) \quad . \quad . \quad . \quad (7a)$$

and

$$f_2 = 1 - r \sin \theta_A/(r + d) \quad . \quad . \quad . \quad . \quad . \quad (7b)$$

Fig. 3 shows the apparent advancing contact angle derived from equations (5) and (7) for values of $(r + d)/r$ ranging from 1 to 5, and Fig. 4 shows the apparent receding angles for a fibre-water advancing angle of 90°. They show the pronounced effect of porosity on contact angle. Thus, a typical clothing example is a grid with $(r + d)/r$ equal to 3, made of fibres with an advancing fibre-water contact angle of 90°, and a receding angle of 60°. The apparent contact angles given by Figs. 3 and 4 are 130° and 115° respectively. The structure of the surface thus increases the water-repellency very considerably, and water drops formed on it will readily roll off.

## 4. Comparison with Experiment.

The most direct experimental verification of the present analysis was obtained by measuring $\theta_D$ and $\theta_W$ for a wire grating together with $\theta_A$ and $\theta_R$ measured on a flat plate whose surface was identical with the surfaces of the wires. The wires were wound parallel to one another on a brass frame 5 cms. square and 3 mms. thick. The wires completely covered the frame forming a flat cage which could be dipped into water without the water penetrating into it. The wires of the grating were coated with a thin film of paraffin wax by first dipping the grating into a solution of paraffin wax in benzene, then shaking to remove the excess solution which formed films between the wires. On allowing the benzene to evaporate, it was found that the paraffin wax had been deposited in large crystals on the wires and in many cases the wax crystals joined adjacent wires. This irregular coating was improved by heating the grid in an oven to melt the wax crystals. On allowing to cool the wires were found to be uniformly coated with a wax film whose thickness was inappreciable for the present work. All the gratings together with a flat metal surface were coated by the above technique. The values of the contact angles for the plate and the gratings were determined by the plate method of Adam and Jessop.[4] The values for the plate were $\theta_A = 105°$ and $\theta_R = 93°$. The values of $\theta_D$ and $\theta_W$ are given in Table I together with the calculated values.

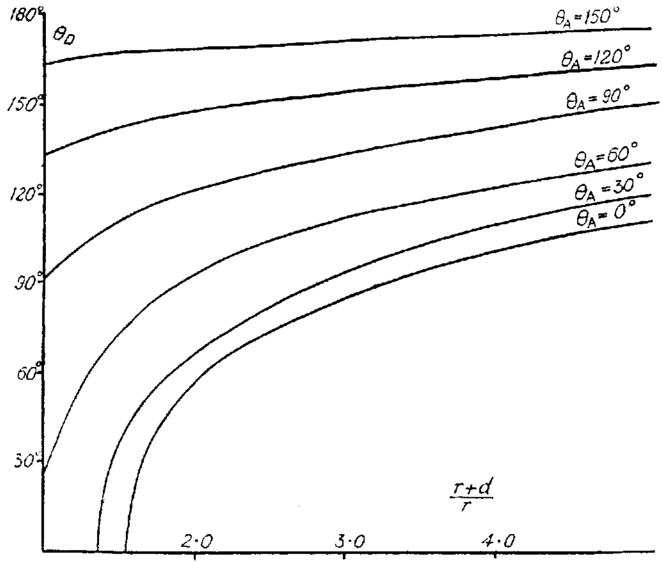


FIG. 3.—Apparent advancing contact angle.

The agreement between the calculated and observed values is good and indicates that the analysis is correct. The values of $\theta_D$ and $\theta_W$ given in Table I were obtained with the grating wires perpendicular to the water surface. It was found, however, that for a given grating the values of $\theta_D$ and $\theta_W$ were independent of the inclination of the wires to the water surface except when the angle of inclination was less than 6° when the

TABLE I.

| | | | | $\theta_D$. | | $\theta_W$. | |
|---|---|---|---|---|---|---|---|
| $2r$. | $2(r + d)$. | $f_1$. | $f_2$. | Calc. | Obs. | Calc. | Obs. |
| 0·007 cm. | 0·025 cm. | 0·366 | 0·730 | 145·5° | 143° | 138·5° | 138° |
| 0·007 ,, | 0·0404 ,, | 0·227 | 0·833 | 153° | 152° | 147·5° | 148° |
| 0·013 ,, | 0·025 ,, | 0·680 | 0·498 | 132·5° | 133° | 122° | 118° |
| 0·013 ,, | 0·0404 ,, | 0·422 | 0·689 | 143° | 143° | 135·5° | 135·5° |

contact angles showed instability due to the water moving discontinuously from wire to wire. The present analysis is inapplicable when the wires are parallel to the surface, since it assumes that for an increase in area $\delta A$ of the porous surface-water interface there is formed an area of solid-water interface, $f_1 \delta A$, and of water-air interface, $f_2 \delta A$, for any infinitesimal value of $\delta A$. This condition is not fulfilled when the wires are parallel to the

[4] Adam and Jessop, *J.C.S.*, 1925, 1865.

surface, but it applies when the wires have a small inclination to it determined by the length and spacing of the wires.

Water repellent textile yarns show the large advancing contact angles predicted for porous surfaces. The fibres in a yarn, particularly in a wool yarn, are not close packed, and it is possible to estimate the average separation of the fibres from the yarn bulk density. Thus, if the fibres are supposed to lie on a hexagonal pattern with their axes a distance $2(r + d)$ apart, the bulk density, $\sigma$, of the yarn is given by

$$\sigma = (\pi/2\sqrt{3})\rho r^2/(r + d)^2 \quad . \quad . \quad . \quad . \quad (8)$$

where $r$ is the radius of the fibres and $\rho$ is their density. The yarns investigated were of bulk density 0·4 g./c.c., and the fibre density was 1·31 g./c.c. According to equation (8), $(r + d)$ is then equal to $1{\cdot}85r$; or the separation of the fibre surfaces is on the average 0·85 times the diameter of the fibres. This fibre separation gives a good impression of the large porosity of wool yarns. The surface of wool fibres has a scale structure, and the measured advancing fibre-water contact angle was 120°, the large value being doubtless due to the rough fibre surface. Fig. 3 gives the apparent

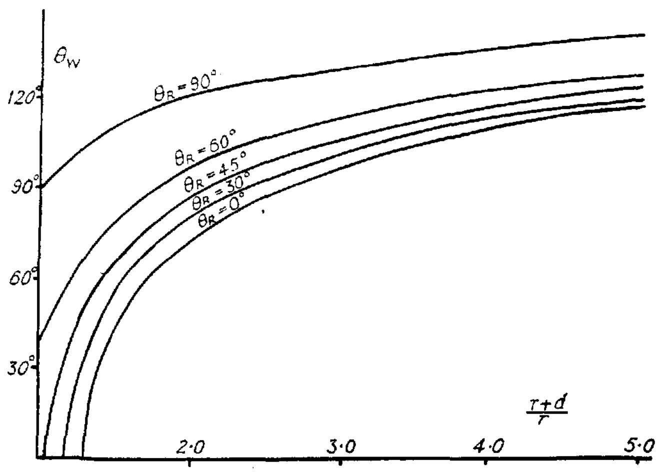


FIG. 4.—Apparent receding contact angle.

advancing contact angle for a grid with $(r + d)/r$ equal to 1·85 and a fibre-water contact angle of 120° as 145°; the measured value was 155°. The agreement is quite good in view of the assumption made to derive $(r + d)/r$, and the uncertainty in the fibre-water contact angle because of the rough fibre surface.

## 5. Apparent Contact Angles and Clothing Structures.

The large apparent advancing and receding contact angles shown by porous surfaces have much significance for the movement of water drops on these surfaces. Thus, if a drop of water is placed on the wire grid used for the experiments described in Section 3, the large apparent advancing and receding angles are immediately obvious and the drop moves much as drops of mercury move on a glass surface; even uncoated wires with the low advancing angle of 55° and a receding one of 25° show great mobility for the drop. The mobility of the drop is clearly significant for the behaviour of clothing surfaces in rain, for a structure that gives large apparent advancing and receding contact angles and a mobile drop will ensure that the rain drops will roll off the surface without wetting it to any extent. Indeed, the wire grid used in these experiments would prove an excellent rain resistant structure provided that the rain drops did not penetrate the grid on impact.

The effect of the roughness and porosity of natural structures on their water-repellency has been qualitatively discussed by Woog.[5] It is, however, profitable to discuss the rain resistance of natural and artificial structures by use of the apparent contact angles. So far as animals are concerned, these structures are usually formed from grids made from roughly circular fibres, and Figs. 3 and 4 show the variation of the apparent contact angles for these grids with the ratio of the spacing of the fibres $(r + d)$, to their radius, $r$. Large apparent contact angles are obtained when $(r + d)/r$ is large. If, however, $(r + d)$ is large, rain drops will pass through the structure at impact; this is avoided in clothing by using fibres of small radius, so that the ratio $(r + d)/r$ may be large without the presence of large pores.

A second requirement for rain resistance is that the ratio $(r + d)/r$ must be maintained at a large value: if the surface is covered with fibres that are free to move under the tension at an air-liquid surface, they are pulled together by rain drops, $(r + d)/r$ becomes small, and the apparent contact angles decrease; the drops adhere to the surface which then becomes wet. Most artificial clothing suffers from this defect, for all textile structures have a surface cover of fibres with free ends, and these are readily pulled into the surface of the fabric by rain. Animal furs also have fibres that are free to move at their outer ends, and in rain they are pulled together at the tips by the surface tension of water; $(r + d)/r$ is decreased, and the tips wet out in tufts giving the characteristic appearance of an animal's fur in rain. But near the skin the fibres are held apart, and wetting does not take place.

The duck is generally regarded as having attained perfection in water-repellency, and it is usually taken for granted that the duck uses an oil or similar coating with larger contact angles than any known to man. In actual fact, the duck obtains its water-repellency from the structure of its feathers.

Thomson [6] gives a general description of the structure of feathers, and it is surprising how closely it conforms with the theoretical requirements for water-repellency. The main stem or rachis of the feather carries barbs on either side; the barbs are visible to the unaided eye, and give the feather its characteristic appearance. Each barb supports fine fibres, known as barbules, on either side of it. The barbules on one side of the barb carry hooks and those on the other side appear to be notched; Thomson [6] describes them as long scrolls. The two different types of barbules from neighbouring barbs overlap and the hooks from one set engage the notches of the other so that the whole is held firmly as a framework of fibres with no free ends. The framework of barbules is a very open one: the barbules of the breast feather of a duck are roughly 8$\mu$ in diameter, and the ratio of $(r + d)/r$ for one layer of parallel barbules is roughly 5.

The advancing contact angle for the stem of the duck's feather appears to be around 90° to 100°, with a receding angle of approximately 60°. Figs. 3 and 4 give the corresponding apparent advancing and receding contact angles as 150° and 130° respectively. Measurement of the angles for the outer surface of the feather shows that these values are roughly correct. The inner surface of the feather gives smaller angles because the comparatively large continuous surfaces of the barbs are exposed on the inside; in fact, if a duck's feather is dipped into water and then withdrawn, the difference between the contact angles at the outer and inner surfaces is easily seen, and gives an excellent demonstration of the importance of

[5] *Arch. Phys. Biol. et Chim. Phys. Corps Organ*, 1942, **16**, (53), 15-16 (*cf. Biological Abstracts, A*, 1944, **18**, 2067).

[6] Thomson, *Biology of Birds*, Sidgwick and Jackson, 1923, p. 17.

surface structure for water repellency. If the structure of the feather is destroyed, it can be wetted out, much as a water-repellent textile wets out, by repeatedly immersing and withdrawing it from water.

There is little apparent difference between a hen's and a duck's feathers except that the duck maintains them in better condition. But many hen's feathers which have been examined show a continuous film of some material between the barbules, and this would, of course, destroy the feather's water-repellency. A complete discussion of the water-repellency of feathers would, however, require a detailed examination of the individual feather structures. At present, it is sufficient to note that water rolls off a duck's back because of the structure of its feathers rather than because of any exceptional proofing agent, and that man's attempts to make clothing with the water-repellency of a duck should be directed to perfecting an appropriate cloth structure rather than as at present, to searching for an improved water-repellent agent. This problem is discussed in a paper to be published elsewhere.

## Summary.

The analysis of apparent contact angles for rough surfaces is extended to porous surfaces, particularly those encountered in natural and artificial clothing. Formulæ are derived for the apparent contact angles, and experimental data confirming the formulæ are given.

Water-repellent clothing structures are discussed by means of this analysis, and it is shown that the water-repellency of the duck is due to the structure of its feathers rather than to any exceptional proofing agent.

We are indebted to Mr. B. H. Wilsdon, Director of Research, for discussion of the work, to Professor N. K. Adam, F.R.S., for helpful criticism, and to the Council of the Wool Industries Research Association for permission to publish this account.