

J. L. MOILLIET
EDITOR

WATER-
PROOFING
AND
WATER-
REPELLENCY

WATERPROOFING AND WATER-REPELLENCY

EDITED BY

J. L. MOILLIET

*Research Chemist, Imperial Chemical Industries Limited,
Dyestuffs Division, Blackley, Manchester*



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Preface

The waterproofing of textiles has developed from a traditional art to a highly specialised branch of technology during the past thirty years. This has been achieved by research directed to improving the traditional methods, leading to the present-day waterproofing emulsions, by research directed in its initial stages to obtaining chemical combination of the water-repellent with the fibre, leading to the modern durable water-repellents, and by the development of radically new substances such as the silicones which have greatly increased the range of possible effects. These researches have been supported by work on the techniques of application, not only to the conventional fibres, but also to the newer synthetic fibres, which have posed their own particular problems. These developments constitute the main theme of the present book, which is elaborated in Chapters 3-9, inclusive.

The developments just referred to are nearly all examples of the waterproofing of textiles by making them *water-repellent: i.e.*, by rendering them more difficult to wet by water. Where this is achieved, it is possible to preserve the open structure of textile fabrics more or less completely, so that a waterproofed garment often has much the same porosity, texture, and appearance as the untreated one. The scientific principles behind these effects are based on classical surface chemistry and physics. They have become much better understood in the past twenty years, especially as the effect of fabric structure has been investigated, along with the combined effects of fabric structure and intrinsic water-repellency. This scientific background is summarised in Chapters 1 and 2.

An alternative method of waterproofing fabrics is of course to *coat* them with continuous, water-impermeable films, and for many purposes

this sort of treatment is essential. Like the methods which are based on rendering textiles water-repellent, the coating techniques have evolved from a traditional art into a highly sophisticated technology. This development of modern coated fabrics, which has been made possible by the discovery of synthetic film-forming and fibre-forming "polymers" (in the widest sense of the word) is described in Chapter 10.

Waterproofing treatments, of both the general types referred to above, are of course not limited to textiles. A well-known and extremely valuable example of their use is in the flotation of ores. This subject is fairly self-contained, and it has in any case been so fully treated elsewhere, that we have only touched on it very lightly. Other special waterproofing techniques, however, do not appear to have been described so fully, and since several of these are relatively recent developments, the present book contains accounts of the waterproofing of paper, soils, and building materials, and of the dropwise condensation of steam, in Chapters 11-13. A final chapter deals with waterproofing mechanisms in plants and animals, which owe their remarkable effectiveness largely to the ingenious structures which are found in nature.

Since all the chapters are concerned with one or both of two main themes, and since many of them deal with the same materials, a certain amount of overlapping has been inevitable. The editor has not attempted to eliminate all duplication, partly because it seemed essential to leave the authors as much freedom as possible, but chiefly because the independent approaches to similar subject matter were felt to be highly instructive. A number of cross-references have, however, been inserted to draw attention to related passages in the different chapters.

The editor's thanks are due to the other contributors for their loyal support, and to the various industrial organisations, universities, and other research centres whose permission and encouragement have made this project possible. Permission to reproduce a number of pictures and diagrams is gratefully acknowledged in the text. Finally, very special thanks are due to Professor Adam for his invaluable advice on the scope of the present book.

J. L. MOILLIET

List of Contributors

- N. K. ADAM, Sc.D., F.R.S., Emeritus Professor of Chemistry, University of Southampton, England.
- W. BAIRD, B.Sc., Ph.D., A.R.T.C. (Glasgow), Research Laboratories, Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, England.
- R. L. BASS, B.Sc., A.R.I.C., Midland Silicones Limited, Barry, Glamorgan, Wales.
- J. W. BELL, B.Sc., Ph.D., Department of Textile Technology, University of Leeds, England.
- D. J. CRISP, Ph.D., M.I.Biol., Director of the Marine Science Laboratories, University of Wales, Menai Bridge, Anglesey, Wales.
- W. T. GARTLAND, B.Sc., Group Research, Albert E. Reed and Company Limited, Maidstone, Kent, England.
- E. B. HIGGINS, A.M.C.T., Technical Service Laboratories, Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, England.
- W. N. LISTER, A.M.C.T., F.I.R.I., J. Mandleberg and Company (Holdings) Limited, Pendleton, Salford, England.
- ALAN S. MICHAELS, Sc.D., Professor of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

- J. L. MOILLIET, B.A., Ph.D., Research Laboratories, Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, England.
- C. A. NORRIS, B.Sc., lately Technical Service Laboratories, Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester.
- B. D. J. OSMENT, B.Sc., F.R.I.C., F.I.M., A.M.I.M.M., M. Inst. F., National Engineering Laboratory, Department of Scientific and Industrial Research, East Kilbride, Glasgow, Scotland.
- M. R. PORTER, B.Sc., Ph.D., Midland Silicones Limited, Barry, Glamorgan, Wales.
- F. L. Warburton, M.Sc., A.R.C.S., D.I.C., A. Inst. P., Wool Industries Research Association, Torridon, Headingley, Leeds, England.
- C. S. WHEWELL, B.Sc., Ph.D., F.R.I.C., F.T.I., Professor of Textile Technology, University of Leeds, England.

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CHAPTER I

Principles of Water-Repellency

N. K. ADAM

I. CONDITIONS FOR EQUILIBRIUM OF A LIQUID ON A SOLID: RELATION OF CONTACT ANGLE TO THE ADHESION BETWEEN LIQUID AND SOLID

The term "water-repellent" is a relative one: there is always some attraction between a liquid and any solid with which it is in contact, although this may be slight: no surface actually exerts a repulsive force on a liquid. The practical distinction between a surface that is wetted by water, and one that is not wetted, is that a wettable surface allows water to spread over it in a continuous film, whereas on a non-wetted or water-repellent surface the water stands in separate droplets, covering only a small part of the surface. At the edges of these droplets the water-air surface forms an angle with the solid surface: measured in the water, this is the "contact angle" (Fig. 1). If the contact angle is zero, the surface is

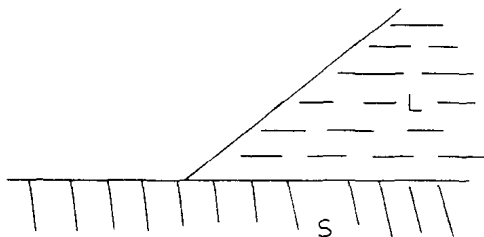


Fig. 1. Contact angle equilibrium.

said to be completely wetted: a large contact angle confers good water-repellency on the surface, and the droplets of water tend to run off in a similar manner to drops of mercury on any surface which is not amalgamated by the mercury.

Thomas Young¹, in 1805, stated the necessary condition for existence of a contact angle, and gave the relation between this angle and the relative values of the adhesion of the liquid to the solid, and its cohesion to itself. If the adhesion of the liquid to the solid is equal to or greater than the cohesion of the liquid, the contact angle is zero and there is complete wetting: if the adhesion between liquid and solid is less than the cohesion of the liquid, there is a finite angle, which is larger, the smaller the adhesion of liquid to solid, relative to the cohesion of the liquid.

Many materials, such as brick and stone-work, also textiles, are porous, containing many fine capillaries. Waterproofing of these requires the maximum possible resistance to penetration of water into the capillaries, and here again a large contact angle with the walls of the capillaries is desirable.

These conditions can be expressed quantitatively as follows. If γ_L , γ_S , γ_{SL} , are the average free energies, for unit area, of the liquid, solid, and solid-liquid surfaces respectively, we can substitute for these free surface energies hypothetical tensions acting parallel to each surface, of equal numerical magnitude to the free energies*. Resolving these tensions parallel to the solid surface

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \Theta \quad (1)$$

By combining with Dupré's equation, which relates the surface free energies to the work required to separate the liquid from the solid, per unit area of contact, eqn. (1) can be transformed into a much more useful equation. Dupré's equation is

$$W_{SL} = \gamma_S + \gamma_L - \gamma_{SL} \quad (2)$$

* A free surface energy, measured in erg/cm², is equivalent to a surface tension parallel to the surface, measured in dyne/cm. Eqn. (1) is most easily obtained by using these tensions and resolving them parallel to the solid surface. It can, however, equally well be obtained by calculating the changes in area of each surface when a small displacement is made of the line of contact between the three surfaces, along the solid surface, multiplying these changes in area by the free surface energies, then putting the sum of the changes in free surface energy equal to zero, in accordance with the principle of virtual work. Proofs of this type are given by Warburton in Chapter 2 of this volume, also in refs. 2-4.

It may be deduced⁵ by considering the free surface energies before and after the separation of a column of unit cross-section in which liquid is in contact with solid, at the plane of contact between liquid and solid. Before separation the free surface energy (Fig. 2a) is γ_{SL} ; after separation

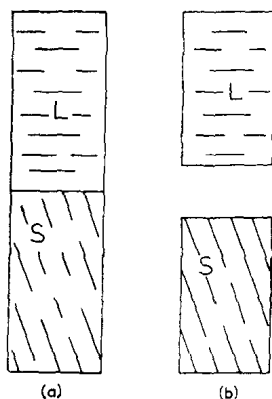


Fig. 2. Separation of liquid from solid.

it is $\gamma_S + \gamma_L$ (Fig. 2b). The work W_{SL} required to effect the separation is the difference between these quantities, giving eqn. (2). W_{SL} is called the “work of adhesion” between liquid and solid.

Combining eqns. (1) and (2)

$$W_{SL} = \gamma_L(1 + \cos \Theta) \quad (3)$$

Either eqn. (1) or eqn. (3) express the condition of equilibrium of a liquid resting on a solid; and both are given, although in words rather than in symbols, in Young's paper¹ of 1805. In recent years, there has been a tendency to call eqn. (1) “Young's equation”. However, there is much more to be said⁶ for attaching Young's name to eqn. (3), which is far more useful, and also less obvious, than eqn. (1). Eqn. (1) contains the two solid surface tensions or free energies γ_S and γ_{SL} , which are extremely difficult, indeed almost impossible, to measure. The right-hand side of eqn. (3) contains only easily measurable quantities, so that it can be used to calculate the adhesion of liquid for solid.

The “work of cohesion” of a liquid, *i.e.* the work required to divide a column of liquid with unit cross-section into two, is $2\gamma_L$. From eqn. (3), if W_{SL} is less than $2\gamma_L$, there is a contact angle: as W_{SL} increases, the angle decreases, becoming zero when $W_{SL} = 2\gamma_L$.

$\cos \Theta$ cannot exceed unity, and when W_{SL} is greater than $2\gamma_L$, the contact angle remains zero. If $W_{SL} = \gamma_L$, the angle would be 90° . A contact angle of 180° would indicate no adhesion between liquid and solid: since there must always be some adhesion between two phases in contact, the angle can never reach 180° , although in certain cases of regularly perforated solids it may reach 160° or perhaps even larger angles.

For a given value of the work of adhesion W_{SL} , the contact angle is shown by eqn. (3) to decrease, if the surface tension of the liquid, γ_L , decreases. Therefore it is important that compositions used to produce water-repellency should not decrease the surface tension of water.

2. EFFECT OF AN ADSORBED FILM OF VAPOUR ON THE CONTACT ANGLE EQUILIBRIUM

The surface tension of the solid, γ_S , depends very much on the state of the solid surface: in particular, if an adsorbed film condensed from the vapour of the liquid is present, γ_S will be substantially lower than the surface tension of a solid without such an adsorbed film of vapour. The difference between the surface tensions of a solid without, and with, such an adsorbed film is the "surface pressure" π_{SV} of the adsorbed film. If γ_{SO} is the surface tension of the solid without this vapour film, and γ_{SV} the tension of the film-covered surface

$$\gamma_{SO} = \gamma_{SV} + \pi_{SV} \quad (4)$$

If W_{SLO} is the work which would be required to detach the liquid from the solid, leaving a vapour-free solid surface, and W_{SLV} the work required to perform the separation but leaving an adsorbed film of vapour, eqn. (2) becomes

$$W_{SLV} = \gamma_{SV} - \gamma_L - \gamma_{SL} \quad (5)$$

$$W_{SLO} = \gamma_{SO} + \gamma_L - \gamma_{SL} \quad (6)$$

$$= W_{SLV} + \pi_{SV} \quad (7)$$

As the region of the solid surface important for contact angle equilibrium is that adjacent to the liquid, there is sure to be an adsorbed film of vapour, probably nearly in equilibrium with the saturated vapour of the liquid, so that π_{SV} should have, nearly, the value appropriate to a solid

surface in equilibrium with saturated vapour. The value of W_{SL} given by measurements of the contact angle is therefore W_{SLV} , not W_{SLO} . W_{SLV} is indeed the important work of adhesion, for it is scarcely possible to imagine removal of liquid from solid without leaving an adsorbed film of vapour behind on the solid surface. W_{SLV} is therefore the quantity directly measured.

To calculate W_{SLO} would be possible in principle⁷. Gibbs's adsorption equation may be written⁸

$$\Gamma = \frac{\partial \pi_{SV}}{RT \partial \ln p} \quad (8)$$

Γ is the amount, in moles/cm², of vapour adsorbed at a pressure p . Integrating eqn. (8)

$$\pi_{SV} = RT \int_0^p \Gamma \, d \ln p \quad (9)$$

By measuring the amount Γ adsorbed at various pressures from zero up to saturation, plotting against $\ln p$, and taking the area under the curve, π_{SV} can be evaluated. The difficulty is likely to be that the amounts adsorbed would be so small as to be very difficult to measure. This difficulty might conceivably be overcome, if anyone really wished to determine W_{SLO} by eqns. (7) and (9), using water radioactively labelled with tritium. But for almost all purposes, W_{SLV} is much the more important quantity, and is directly deduced from contact angle measurements.

The importance of the adsorbed film of vapour on the solid surface, for the contact angle equilibrium, was hinted by Harkins and Dahlstrom⁹, clearly pointed out by Bangham and Razouk¹⁰, and emphasized by others^{7, 11}.

3. MEASUREMENT OF CONTACT ANGLES: HYSTERESIS

The measurement of contact angles is complicated by the fact that true equilibrium, and a single angle, are rarely found. Usually the angle may be anywhere between two extremes, a relatively large "advancing angle" when the liquid is slowly advancing, or just tending to advance, over a dry solid surface; and a smaller "receding angle" obtained when the liquid is receding, or on the point of receding, from a previously wet surface. This difference between the advancing and receding angle is

called the "hysteresis" of the contact angle. Hysteresis is usually larger with water than with organic liquids, and it varies greatly with different solid surfaces. With paraffin wax it is small, rarely exceeding 15° ; but differences between advancing and receding angles as large as 60° have been found with certain varnished surfaces¹². The amount of hysteresis may also vary with the roughness of the solid surface, with the time of immersion of the solid in the liquid; and to a small extent with the rate at which the liquid advances or recedes over the solid.

A satisfactory method for measuring contact angles should therefore include (a) means of controlling the movement of the liquid over the solid, in either direction, and (b) precautions to ensure that the liquid surface has not become contaminated sufficiently for its surface tension to be decreased, since diminished surface tension results in too low values for the contact angle. These conditions are approximated in the "tilting plate" method¹³⁻¹⁵, which is applicable whenever the solid can be obtained as a flat plate, and large quantities of the liquid are available, as is the case with water. The liquid is contained in a glass box with the tops of the sides ground flat and covered with paraffin wax; on these slide paraffined "barriers", preferably heavy strips of plate glass. These barriers can sweep the surface clean from impurities which might depress the surface tension of the water. The solid is held in an adjustable holder, which can be tilted at any angle and can be raised or lowered. To find the contact angle, the plate is tilted until the water surface remains plane and undistorted right up to contact with the plate: the angle between the plate and the water surface is the contact angle. For most purposes this angle can be measured with an accuracy at least equal to the constancy of the contact angle over different parts of the plate, by simply dipping a protractor into the water. The advancing angle is found by gently lowering the plate, the receding angle by raising it. Elaborations of this apparatus have been used by Fowkes and Harkins¹⁶ and Sumner¹⁷, the principal alteration being to have the axis about which the plate is tilted in the water surface. If however the simpler instrument is used in such a way that the last adjustment made to the plate is to raise or lower it, the angle being set (a few trials may be necessary) before causing the liquid to advance or recede, it is not necessary to have the axis of rotation in the surface.

The tilting plate method has the advantage that a considerable area of the surface can be rapidly surveyed for variations in the contact angle.

The contact angle of fibres, yarns, or wires can be measured on a similar principle, they can be held in clips on the points of a pair of spring-bow compasses and subjected to slight tension, then tilted until the water surface remains flat up to contact with the fibre on one side¹⁸.

A very frequently used method is to project a magnified image of the edge of a drop of liquid resting on a flat plate, on to a screen or photographic plate or film, and measure the angle between the plate and a tangent drawn to the liquid surface where it meets the plate. This, sometimes called the "sessile drop" method, can measure angles at one point of the solid surface correct to a degree or so, but it is not very easy to arrange for advancing and receding angles to be measured, and still less easy to ensure that the liquid surface is clean, with the normal surface tension. However, the chance of the surface tension being decreased by contamination is small, with most solid surfaces, provided measurements of the contact angle are made soon after the drop has been placed on the surface.

Alternatively, the profile of a bubble of air in the liquid can be projected and the angle measured on the magnified image.

Measurements of contact angles, from the profile of drops on a horizontal plate, or of bubbles under a plate, without provision for advancing or receding the liquid edge, have been made by many workers, including Bartell and Zuidema¹⁹, Wark and others²⁰, Zisman and his colleagues²¹. In Zisman's laboratory the drop is viewed through a horizontal telescope with two eyepiece cross-wires, one of which is set parallel to the surface of the plate, the other tangentially to the drop surface where it meets the solid, the angle between them being measured. These angles probably approach the advancing angles fairly closely.

Bartell and others²² caused the edge of the drop to advance or recede by admitting or withdrawing liquid from the drop through a tube passing through the flat support of the drop. Beament²³ most ingeniously provided both for continuous renewal of the drop surface by sucking off water through a very fine glass tube placed in the surface; and for advancing and receding edges by introducing water through another fine tube inside the drop. Macdougall and Ockrent²⁴ measured advancing and receding angles by tilting the plate on which the drop rested until the drop began to slide, again projecting a magnified image on a screen.

Most people can estimate an angle to within ten degrees or so by eye; and if only an approximate angle is required this can be found by merely placing a drop on the solid surface, and viewing it in profile against the

light, the solid being gradually tilted so as to observe both advancing and receding angles. Such an estimate is of course rough: but it is far better than saying, as too many people are apt to do, that they have no idea of the contact angle "because they have no apparatus to measure it"!

Another useful method is Bartell's "vertical rod" method²⁵. A vertical rod, fibre, or wire is held in the surface of the liquid, and a magnified image of the junction of the rod with the liquid projected. Quite accurate measurements of the angle formed by the solid with the tangent to the liquid surface at the point of contact are possible.

There are many other ways of measuring contact angles, but none of these are in general use or appear to have any particular advantage over those described above. Slightly better accuracy can apparently be obtained in actual measurement of the angle using the profile of drops or bubbles, than by the tilting plate method: but the tilting plate has the advantage that it is very easy to keep the liquid surface clean and to measure advancing and receding angles, and to survey quickly a large area of the solid surface. For water, which is unusually liable (because of its high surface tension) to contamination, and also shows a large hysteresis of contact angle with many solids, the tilting plate method appears the best.

4. CAUSES OF HYSTERESIS OF THE CONTACT ANGLE

Hysteresis is a very general phenomenon, and is often quite large, when water is the liquid. Considerable ingenuity has been displayed in suggesting causes; but many of these suggestions are applicable only, at most, to a very limited number of cases.

There is probably no single cause of hysteresis. One of the most frequent is undoubtedly that the surface of the solid is penetrated by the liquid to a greater or smaller extent: if there is a contact angle the surface of the dry solid attracts water less strongly than water attracts itself, so that any soaking of water into the solid surface increases its attraction for water, giving by eqn. (3) a decreased contact angle. This cause was suggested long ago, by Edser²⁶ in connexion with mineral surfaces, and by Ablett²⁷, for paraffin wax. None of these solids are readily penetrated by water. At the other extreme of porosity come textile yarns and many fibres; and on many of these the receding angle is very unstable, decreasing rapidly with time of immersion^{28,29}.

It is frequently found that immersion in water for a time causes both advancing and receding angles to decrease. This has been recorded by Adam and others on varnished or enamelled surfaces^{12, 14}, by Yarnold and Mason³⁰ on a rather low-melting (52°C) paraffin wax and by many others. This slow decrease in contact angle is one of the principal causes for deterioration in water-repellency. Many so-called rain-proofed fabrics will shed water as separate drops ("pearling") when first wetted, but after exposure to rain for some time the water forms a nearly continuous film over the surface and eventually penetrates through the pores in the fabric. Indeed the superior waterproofing qualities of some silicone treatments seem to depend on a slow rate of decrease of contact angle on prolonged exposure to water, rather than on an exceptionally high contact angle.

Another probable cause of hysteresis is the presence of a film on the surface of the dry solid, which is removed, either by displacement or by solution after short contact with the liquid. Such a film decreases the attraction of liquid for solid, and therefore causes the angle on the dry solid to be greater than the angle on one which has been wetted. Very small amount of greasy material can radically alter the contact angle: as long ago as 1920 Langmuir³¹ showed that a monomolecular film of oleic acid on a surface whose angle, if clean, was very small, gives a large angle: and much more recently Bartell³² has shown that the advancing angle of water against a chromium-plated surface covered with a monolayer of a long-chain amine remains at about 90° even when about half the monolayer has been dissolved away.

It has been shown mathematically that even if there were no hysteresis of contact angle on a smooth, plane surface, a rough surface of the same constitution would show considerable hysteresis. Shuttleworth and Bailey³ calculated that a liquid surface trying to advance over a series of grooves whose sides are inclined at an angle Ψ to the general direction of the surface will not advance until the liquid forms an angle with this direction at least as large as $\Theta + \Psi$; nor can it recede unless the angle falls to $\Theta - \Psi$. Bartell and Shepard³³ found, on paraffin wax, that the hysteresis increased with increasing steepness of the sides of grooves formed in the wax; and Ray and Bartell³⁴ observed that hysteresis increased with roughness. Roughness alone, however, certainly does not account for all, or probably most cases of hysteresis: some of the largest values for hysteresis recorded were on glossy, varnished surfaces^{12, 14}; and the hysteresis found with a very coarsely rough, perforated grid of