1 Chart 2, [illegible] ADHESIVE FILE

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THE ACTION OF ADHESIVES

by Norman A. de Bruyne

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THE ACTION OF ADHESIVES

Fundamentally they work by being liquid and bringing molecules close together. In the newer adhesives this state of affairs is maintained by minimizing stresses within the adhesive itself

by Norman A. de Bruyne

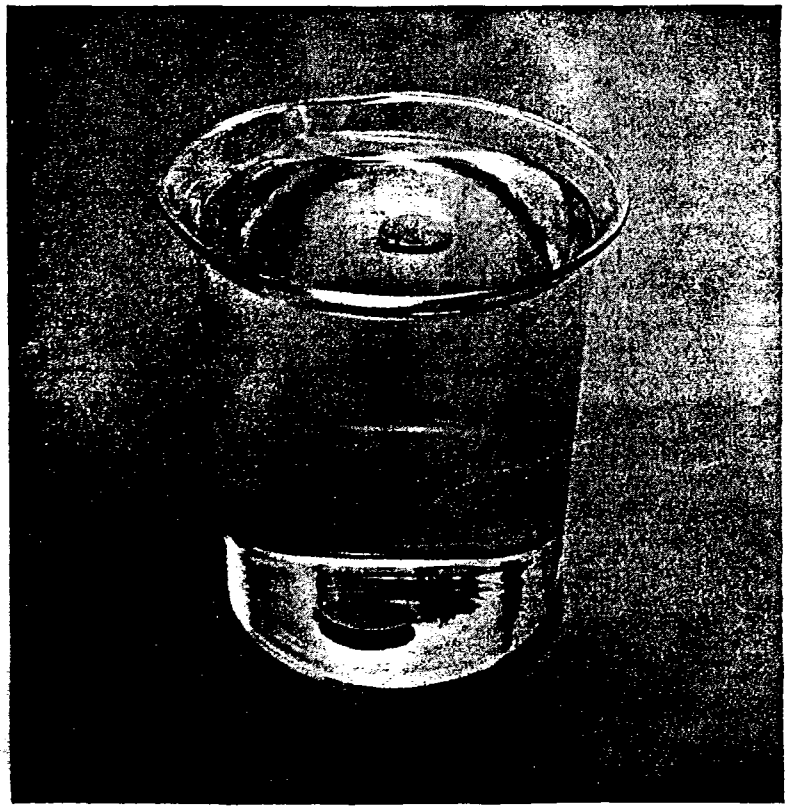
"There are Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions and it is the Business of experimental Philosophy to find them out." So wrote Isaac Newton in his *Opticks* more than 250 years ago. Experimenters—and theoreticians as well—were slow to take up the challenge. They had acquired a thorough knowledge of the forces within the atom, and had even begun to plumb the forces within the nucleus of the atom, well before they could account correctly for the molecular interactions that are responsible for adhesion. Meanwhile the makers of paste and glue had proceeded by trial and error to develop better adhesives.

Finally, in the past 10 years or so, substantial progress has been made in "finding out" Newton's sticky "Agents." H. B. G. Casimir in the Netherlands and E. M. Lifshitz in the U.S.S.R. have explained the attractive force between molecules and predicted its variation with distance of separation. The force turns out to be due to electromagnetic interactions produced by continual fluctuations in the distribution of electrons within the molecules.

Checking the predicted attraction experimentally is extremely difficult—almost at the limit of what is possible. Two bodies must be held at a fixed and measurable distance apart while the attractive force between them is determined. Because the force has an extremely short range, the separation must be minute, on the macroscopic scale. Yet any separation that can be stably maintained is very large on the molecular scale, and so the force of attraction will be tiny. Notwithstanding these problems the molecular attraction between a pair of bodies has recently been measured by B. V. Derjaguin and his colleagues in the U.S.S.R. and by M. J. Sparnaay in the Netherlands. Both experiments confirm the theoretical predictions at "large" separations on the order of a ten-thousandth of a millimeter and more.

At small separations—a few ten-millionths of a millimeter—the theory indicates that the force between molecules will be large. The lesson, so far as adhesion is concerned, is clear. To make two surfaces stick together, bring their molecules very close to each other. If the principle is correct, it should be possible to make solids adhere without using any glue at all. Such is in fact the case. The only trouble is that, on the scale of a few angstrom units (an angstrom unit is one ten-millionth of a millimeter), most solid surfaces are rough and so cannot be brought into really close contact over a substantial area.

The difficulty of bringing solids into



CLOSE CONTACT BETWEEN SOLIDS is difficult to achieve without any intermediating material. As explained in the text, total internal reflection makes it possible to see the

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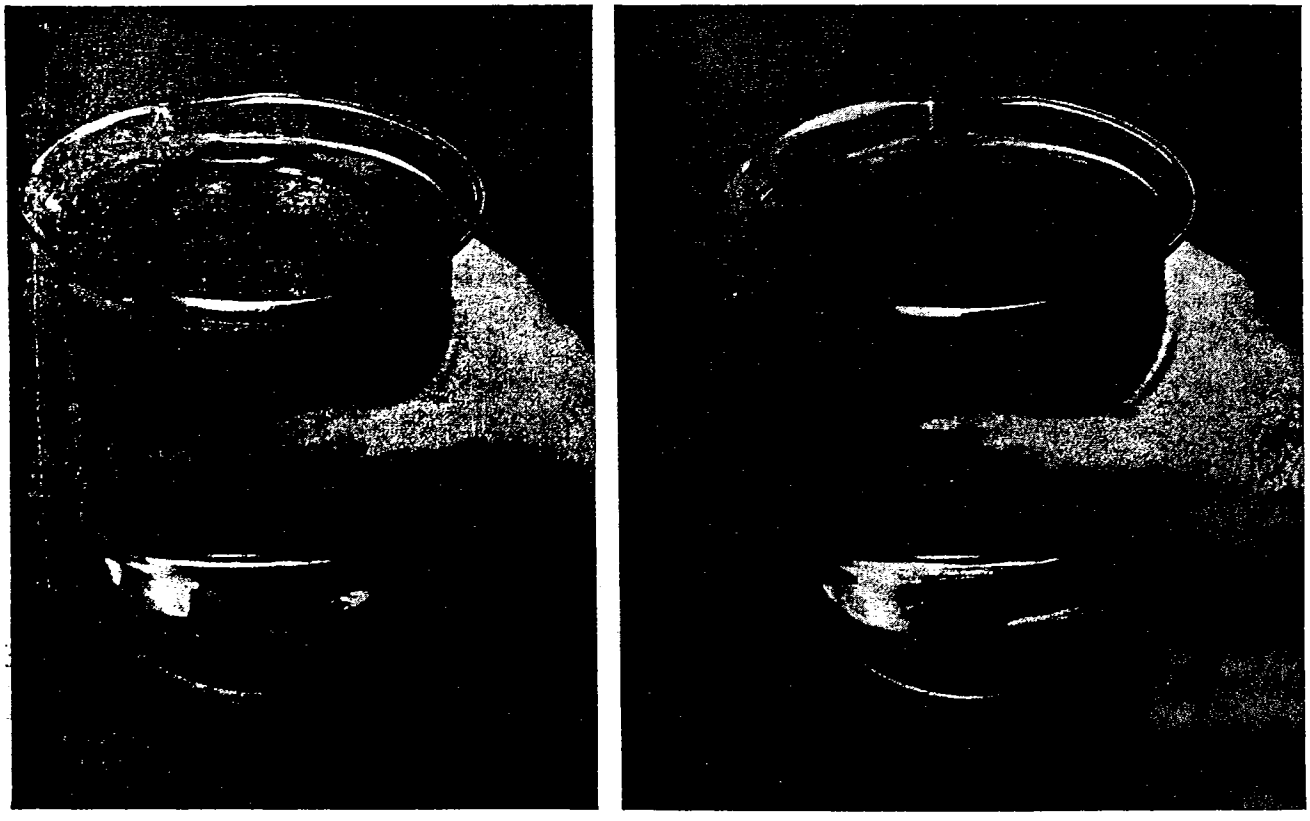
close contact can be demonstrated by means of the phenomenon of total internal reflection. If you look down into a beaker of water, the sides of the beaker have a mirror-like, silvery appearance and reflect objects on the bottom [*see illustration below*]. The reason is that light waves striking the sides at sufficiently oblique angles are totally reflected; they do not pass out of the glass wall into the air, even though the glass is transparent. More accurately, the light travels into the air for a wavelength or two and then turns back into the glass, like a flying fish leaping out of the water for a few feet and then returning.

Now, a flying fish could easily jump high enough to land in a rowboat, its re-entry into the water thereby being frustrated. It could scarcely land on the deck of an ocean liner, however. Similarly, emerging light waves can be captured by an object placed close to the glass surface and their total internal reflection frustrated. In performing the experiment with the beaker of water, first make sure that the outside is quite dry, then press a smooth, polished object against it. You will see nothing; the two surfaces are not close enough to catch the light. Now try your thumb; press hard and you will see a few sweat marks breaking through the silvery surface. A rubber ball pushed against the beaker will also appear as a gray patch. But as soon as the pressure is released, the patch disappears. The elastic energy stored up in the flattened ball is enough to disrupt any bonds that were made on the close approach of the rubber and the glass.

The last experiment suggests that if two clean solids could be deformed plastically when pushed together (so that they have no tendency to regain their original shape), they should adhere. There would then be no stored energy to disrupt the bonds. This can actually be done with soft aluminum, as was discovered some years ago. The surfaces are cleaned with a rotary scratch brush, placed quickly together and given a smart blow with a punch. A good joint results. If the cleaned surfaces are touched with the fingers before they are hit with the punch, there is no adhesion, showing that the joint is not the result of any mechanical interlocking caused by the punch.

If solid surfaces are naturally smooth on an atomic scale, they will adhere spontaneously without having to be forcibly pushed together. Mica can be split so that it is smooth to a few angstrom units over a visible area, and its adhesion is easily demonstrated in another simple experiment. Take a sheet of mica and separate a pair of its layers, starting the cleavage by working the point of a needle into the edge. (Don't use a drop of water to facilitate the separation, as is frequently done: its high dielectric constant considerably reduces the electric forces that hold the layers together.) Stop the splitting before it has gone entirely through the sheet and quickly bring the surfaces together again. They will adhere tightly, although not with quite the strength of the unseparated layers in the sheet because air and moisture are absorbed on any exposed mica surface.

This experiment has been refined by J. S. Courtney-Pratt and Anita I. Bailey at the University of Cambridge. They took a pair of mica sheets silvered on one side, formed them into arches and placed the unsilvered sides in contact with their axes of curvature at right angles. By observing interference fringes at the



reflected image of a penny in a beaker of water (*left*). Fingers of the hand tightly holding the beaker (*middle*) are barely seen from the top because the two surfaces are not close enough to catch the light. When wet, however, the fingers are clearly visible (*right*).

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UNTREATED POLYETHYLENE SURFACE is not wetted by the jet of water seen in this flash photograph; the water is repelled.



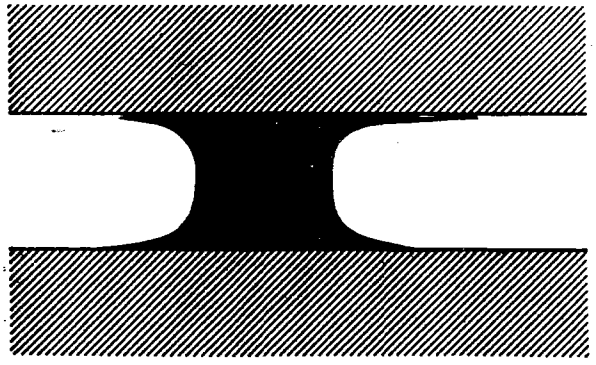
TREATED POLYETHYLENE SURFACE (previously "flamed" with a Bunsen burner) is wetted. Jet of water spreads in a sheet.

point of contact they verified that the area was smooth. Measuring the strength of the tiny joint, they found that it had a shear strength equivalent to 14,000 pounds per square inch—as strong as the mica itself.

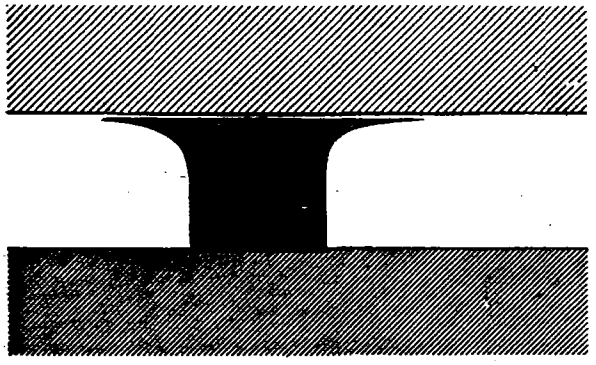
Two pieces of a solid in which the molecules are able to change places (as in glass close to the annealing temperature) or in which the molecules have an appreciable thermal motion (as in rubber and other elastomers) can also be joined by being placed in contact with each other. This, however, is a process more akin to fusion welding than to adhesion by surface forces.

Although solids can be made to stick together without any glue under special circumstances, in practice the extremely small separation necessary for adhesion is almost always achieved by introducing a liquid between the solid surfaces. The function of this liquid, or adhesive, is to adapt itself, in so far as possible, to the irregularities in both surfaces, establishing close contact with each. The effectiveness of a liquid adhesive can again be demonstrated with the beaker of water. A dry finger tip pressed against the glass is barely visible from the top; a wet finger tip completely frustrates total internal reflection and "breaks through" the mirror. After a liquid adhesive has established the necessary contacts it is usually made to solidify.

Not always, however. Some of the most common adhesives in use today are kept permanently liquid in form. These



ATTRACTION resulting from capillarity (or surface tension) of a liquid between two plates that it wets pulls the plates together.



REPULSION results when a liquid between two plates fails to wet one or both of the plates. Bottom plate has not been wetted.

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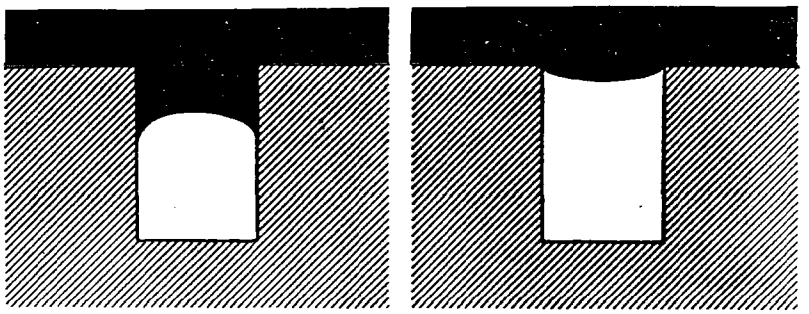
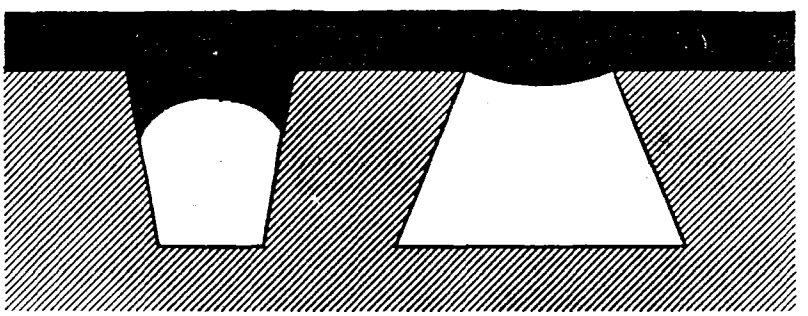
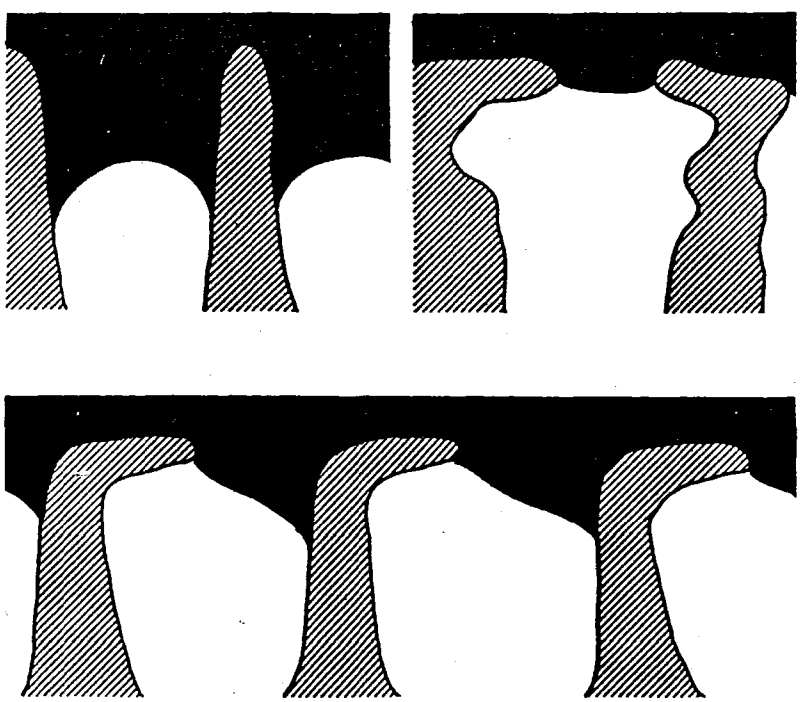


WETTING OR NONWETTING of a solid surface by a glue affects the penetration of the surface and thus the effectiveness of the bond. A glue (*color*) that wets the inside surface of a hole creeps into the hole (*left*), forming a good bond; a nonwetting glue does not (*right*).



"FLOWERPOT" AND "INK BOTTLE" PITS (*left and right respectively*) are depicted in cross section. Glue (*color*) penetrates the flowerpot pit until it is stopped by the pressure of the compressed air trapped in the pit. An ink-bottle pit prevents any effective penetration.



ADHESION OF GLUE AND WOOD is good if the angle between the sides of the wood cells (*hatched areas*) and the surface is roughly 90 degrees (*top left*). Adhesion is poor when this angle is less; i.e., when cells are burred (*top right*) or burred in one direction (*bottom*).

are the pressure-sensitive adhesives. By retaining their mobility they avoid one of the causes of poor adhesion—the locked-in, or residual, stress that is produced by contraction of glue as it solidifies. On the other hand, permanently liquid adhesives are never very strong and they creep under small loads.

Any fluid, even water or air, can act as a pressure-sensitive adhesive. The effect is nicely shown by a pair of flat, smooth objects, such as plate-glass disks, placed one on the other and immersed in water. If the upper plate is lifted, the lower plate will follow. If the lower plate is prevented from moving, a considerable resistance to separation will be experienced until quite suddenly the two surfaces come apart. The resistance to separation is caused by the viscous drag of the water as it creeps in between the surfaces from the edges. The closer the disks are pressed together initially, the longer it will take them to separate under a given force. Hence the name pressure-sensitive adhesives.

Because of their low viscosity and their volatility, simple liquids such as water are not suitable materials for pressure-sensitive adhesives. In practice such adhesives are made from highly viscous materials with complex flow properties. At room temperature they are far too viscous to flow between the surfaces to be joined. This difficulty is overcome by applying them in solution or as a hot melt to a tape backing, to which they adhere firmly. The discovery that one could roll up such a coated tape and then unroll it again was an apparently trivial observation that gave birth to a new industry.

The low mobility of pressure-sensitive adhesives prevents them from getting into good contact with a surface, but they stick tenaciously; when an attempt is made to peel the tape off, it is pulled down onto the surface just before it is torn away. This is because of the stiffness of the tape and probably also because of the movement of the adhesive toward the line of peeling. The effect can be demonstrated by pulling apart two tapes that have been stuck together over a small area. As they come apart, an area of close contact can be seen running ahead of the separation.

The example of the glass plates under water is not typical. Usually objects are glued together in air, and some part of the adhesive is in direct contact with air; the phenomenon of surface tension therefore comes into play. Surface tension is of the nature of a mathematical

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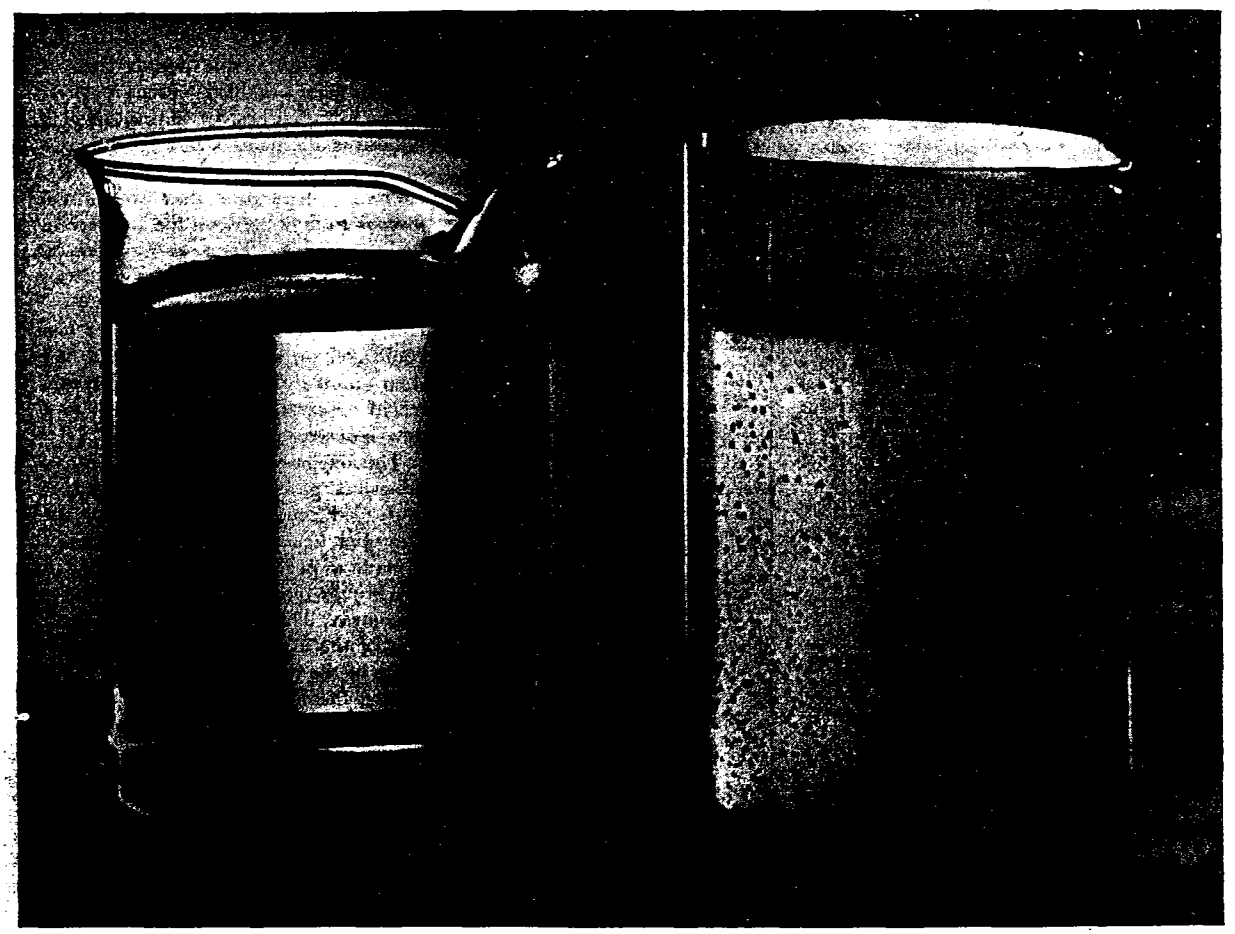
fiction—a convenient way of expressing the fact that each molecule at the surface of a liquid is subject to an unbalanced, inwardly directed force from the molecules inside the liquid. As a result the surface contains as few molecules as possible, tending to contract like a stretched elastic sheet. When a liquid is in contact with both air and a solid, surface tension can produce some interesting situations that are of importance in understanding the behavior of adhesives. Its effects can be decisive, even when the liquid is subsequently solidified. Consider first the effect of surface tension on a liquid of low viscosity between two flat horizontal plates. If the molecules at the interfaces of the liquid and the solid are attracted more strongly by the solid than by the liquid, the liquid wets the surfaces and tends to creep outward along them. Because the curved lateral surface tends to contract under surface tension, it pulls the plates strongly together. For example, a water film one-millionth of a centimeter thick generates a pressure of one ton per square inch. Such gigantic forces are involved even in the simple matter of attaching a postage stamp to an envelope.

On the other hand, surface-tension forces work against adhesion if the liquid does not wet one (or both) of the surfaces. On a nonwetted surface the water molecules are still influenced by their own attraction for one another. As a result the water tends to gather into a hemisphere and the surface will be pushed away [*see illustration below*]. If one attempts to stick a postage stamp to a polyethylene bottle, it soon wrinkles and drops off.

To make a joint strong enough to satisfy an engineer a liquid adhesive must be solidified, and this can be done in various ways. A solid, previously dissolved or dispersed in a liquid, can be allowed to dry out; this is possible only if one or both of the surfaces to be joined are either porous, as are wood and paper, or are themselves soluble in the solvent. To make strong joints between materials such as glass and metal requires a glue free from solvents. One type is a molten solid that refreezes in the joint (this might be called the sealing-wax approach). Another is a liquid in which, after it has been applied to the joint, the molecules can be made to polymerize or to cross-link with each other by the use of catalysts, reactive chemicals or heat

In order to produce a good joint, the adhesive, while still in the liquid state, must wet the surfaces that are to be joined. Just why this should be necessary in a solidifying glue is rather puzzling. The reason is probably that an adhesive cannot penetrate the valleys of a solid surface unless it meets the surface at a small angle, which it does only if it wets the surface.

Penetration depends not only on contact angle but also on the shape of the pits in the surface. If they are "ink bot-



SURFACE-TENSION FORCES work against adhesion when a liquid does not wet the surface it contacts. Glass and polyethylene beakers seen here contain water several hours old. Part of the latter (*right*) has been exposed to chromic acid. Water wets glass and exposed portion of the polyethylene, "creeping" in behind air bubbles formed on the surfaces and enabling them to escape. The unexposed portion of the polyethylene is not wetted: surface tension acts to push nonwetted surface away and bubbles cannot escape.

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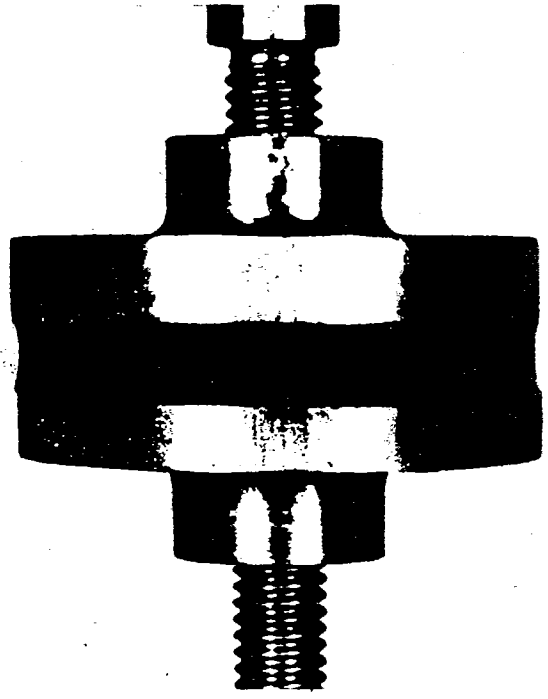
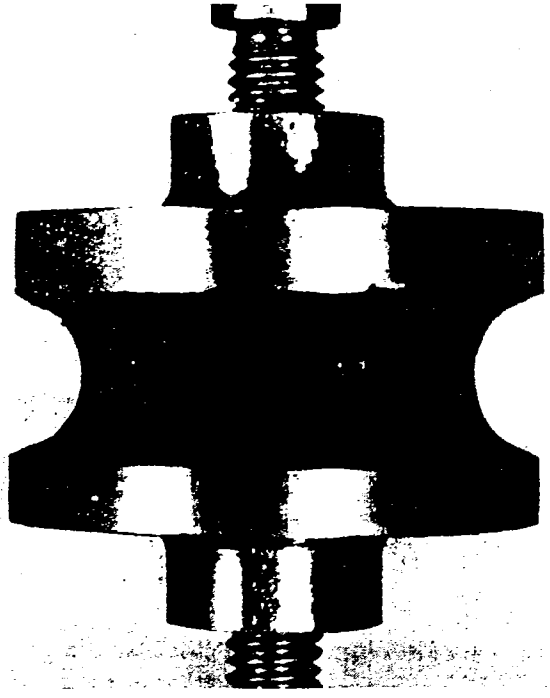
tle" pits—narrower at the top than at the bottom—the adhesive can hardly penetrate [*see second illustration from top on page 118*]. Ink-bottle pits are often produced when the ends of wood cells have been burred over, and a wood surface made up of such cells will produce a joint having practically no resistance to stripping or peeling loads. The only effective remedy is to sand off the burred tops of the cells, as was discovered in England before World War II by C. A. A. Rayner of Aero Research Ltd. After some serious accidents during the war the sanding of all aircraft plywood was made mandatory.

If the pit is shaped like a flowerpot rather than an ink bottle, a liquid adhesive will move down into the depression, compressing the air that previously filled the space. Here the limit of penetration is reached when the force of the surface tension pulling the adhesive into the pit is balanced by the pressure of the trapped air bubble.



UNEVEN DISTRIBUTION OF STRESS in a rubber-to-metal joint under an applied load is reflected in the constriction of the circumference of the rubber portion. The photograph above shows the joint before any load has been applied; that below, the effect of the load.



Good wetting, then, is one of two major requirements for a solidifying glue. The other is that the adhesive must not set up excessive residual stress on solidifying. The process of solidifying always involves some change in volume, which produces a locked-in stress in the joint, tending to weaken it. If the adhesive were free to contract, no stress would be set up as it solidified. But it is not free because it is anchored to the solid surfaces, which keeps the glue in a state of tension and the glued pieces in a state of compression. In a long joint there is inevitably a high shear stress in the interface between the adhesive and the adjacent surfaces at each end of the joint.

In addition to the stress caused by solidification, glued joints are subject to the forces produced by externally applied loads. Differences in the elastic and plastic properties of the adhesive and the pieces it joins usually cause some concentration of stress. A model of the distribution of forces in typical joints under load is provided by large-scale joints cut out of soft plastic sheets [*see illustrations on opposite page*]. The glue itself is represented by a line drawn on the sheet. As the illustrations show, in a lap joint the adhesive is mainly strained at each end, in part by a shearing motion, tending to cause the two portions of the joint to slide over each other, and in part by a tearing force, tending to open up the joint. The result of this lack of uniformity is that while the strength of a lap joint increases with increase in width, it does not rise in proportion to increase in the overlap, and it is influenced by the thickness of both members of the joint. Tension joints also show a nonuniform stress distribution across their area. A scarf joint, in which the two sides are tapered so that they stretch uniformly throughout the length of the joint, is a far stronger arrangement. Uneven concentrations of stress imply that the ultimate breaking strength of a glued joint, even if rupture takes place at the interface, is not in general a measure of the strength of the adhesive bond. For example, lap

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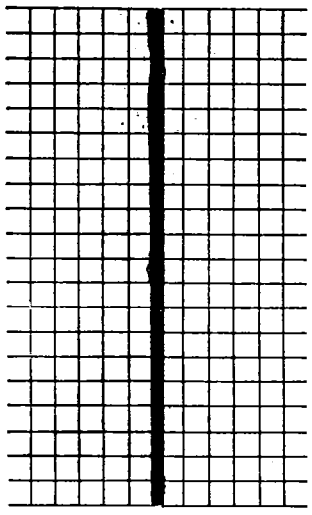
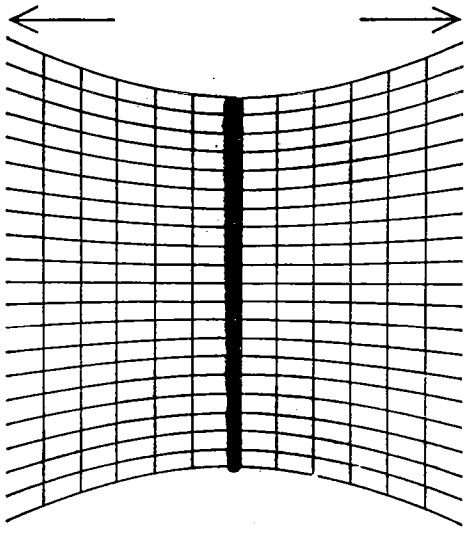
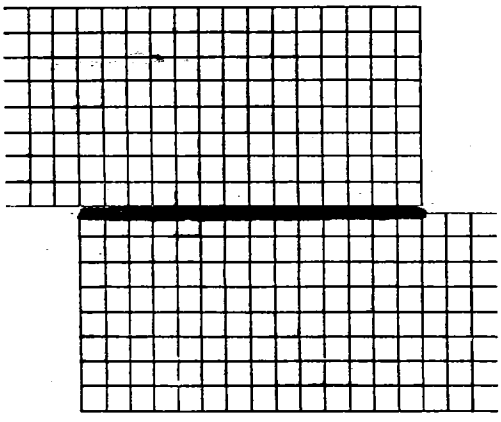
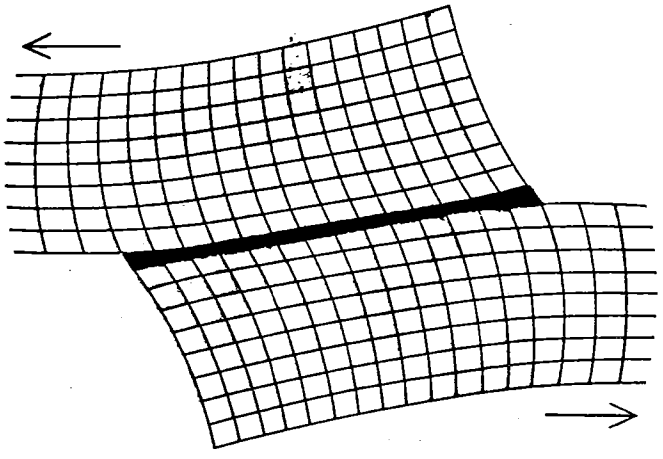


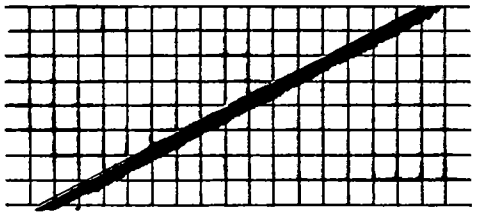


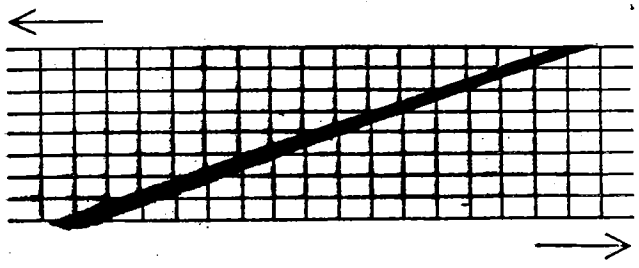
BUTT JOINT is depicted here in two dimensions as it might look before (*left*) and after (*right*) being subjected to an applied load. Arrows indicate the directions of stress; the constriction in the center, the nonuniform distribution of stress across the area of the joint.





LAP-JOINT ADHESIVE (*color*) under an applied load is strained chiefly at both ends. One component of the stress results in a shearing motion, which tends to slide the two portions of the joint over each other; a second component acts to force the joint open.





SCARF JOINT is far stronger than either a butt joint or a lap joint (*see illustrations above*). This is a type of joint in which the two adherent materials are tapered off so that they stretch uniformly throughout the length of the joint when subjected to an applied load.

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joints of copper are usually weaker than those of steel, even though glued with the same material. The disparity is probably due to the greater extensibility of copper rather than to any difference in the intrinsic strength of adhesion.

About five years ago there became available a new class of adhesives with properties far superior to any of the older types for many purposes. These are the epoxy resins. They are formed by mixing together two materials, each composed of small molecules that link together by spontaneous chemical reaction. The resulting long-chain, cross-linked polymer is a strong, hard solid rather like bakelite, containing side groups that promote electrical attraction to other molecules. Before polymerization the liquid mixture has a low viscosity, so that it flows easily between the surfaces to be joined; moreover, it is a good wetting agent and therefore penetrates pits in the surfaces. The process of solidification depends neither on evaporation nor on oxidation; hence it can take place throughout a joint between two large pieces of metal or other nonporous material. No gas is evolved, which means that no bubbles weaken the solidified adhesive. Finally, there is very little shrinkage and therefore a minimum of locked-in stress.

Because epoxy resins polymerize spontaneously, their components must be stored separately and mixed shortly before use. Once applied, they set slower than many other types of glue. This is advantageous in some applications but undesirable in others. The setting time can, however, be shortened with heating.

Epoxy resins provide the engineer with entirely new possibilities of construction. In thin gauges glued metal joints can be far stronger than riveted or spot-welded joints. More important, they have much greater resistance to fatigue. (As a corollary, riveted joints can be reinforced by gluing laminated sections across them.)

The ability to glue metals is a particular boon to the airplane builder, who has acquired a new weapon against fatigue failure and a new freedom in design. He can now thicken a structure by lamination without the expense of machining from the solid. And lamination prevents the rapid propagation of cracks to which one-piece structures are subject. Glued metal parts are to be found in many modern aircraft.

The list of applications is large and still growing. Newton's prevision has been amply confirmed.

NORMAN A. DE BRUYNE ("The Action of Adhesives") is chairman and research director of Techne Limited, an English instrument-manufacturing firm he founded in 1948. De Bruyne was born at Punta Arenas in Chile in 1904. He studied physics at the University of Cambridge, where he took first-class honors in 1923 and was elected to a fellowship at Trinity College for research done at the Cavendish Laboratory under Ernest Rutherford. Having already begun to design, build and fly airplanes embodying structural concepts new at the time, De Bruyne in 1934 founded the firm Aero Research Ltd., acquired in 1947 by the Ciba Corporation. He was awarded the gold medal of the Royal Aeronautical Society in 1937 and later invented honeycomb construction and metal-metal bonding for aircraft structures.

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