

Adhesion Between Viscoelastic and Hard Materials

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1. Introduction

There is a very extensive literature on the subject of adhesion, but very few publications are of the more fundamental type and contribute to our real understanding of the phenomenon. Perhaps the easiest way to survey the literature on this subject is to consider the various tests used for measuring adhesion.

In the first place we have the so-called "peeling test," one of the most promising and also one of the best investigated tests. In this experiment, a layer of glue or resin adhering to a hard substrate is torn off, and the force necessary for the performance of this operation is measured. In purely technical experiments, where testing of the materials is the purpose, no further interpretation of the results is tried and the numbers obtained in the test are used directly for the characterization of the junction. Other people have pointed out that it is not so much the force necessary for the release which is decisive for the test, as the stress at the edge of the tear where the process of release occurs. Various investigators have tried to calculate this stress distribution; it is a matter of considerable difficulty.¹

In other experiments the adhesive layer is released from the substrate by means of ultrasonic waves (cavitation), or by ultracentrifuging.^{2,3} However, it is a mistake to believe that in these cases the resin or glue layer should be removed instantaneously and completely from its substrate and that the calculated forces could be interpreted as something like the adhesive forces per square inch. In reality we have here also a process of tearing, starting from a weak spot, and the experiment is not essentially different from the peeling test except for a stress distribution which is even more complicated.

2. Some Theoretical Considerations

The following investigations are based on the peeling test, but we have applied this test in a way different from the ordinary one. When a strip of a

high polymeric material is partially attached to the underside of a horizontally mounted glass plate and the free end, hanging down, is loaded (Fig. 1), the strip is released from the glass plate at a constant rate, provided that the temperature is above the transition point of the polymer. Figure 2 gives a picture of what happens if such a film strip is loaded with various weights. On the abscissa is plotted the time, on the ordinate the rate of the load (solid line) and the rate of release of the edge of the strip (dotted line). At the moment $t = 0$ the strip is loaded with 8.2 g. and, immediately after the moment of loading, the velocity of the weight is high and so is the rate of release, but after a few minutes both velocities become constant and a steady state is reached. These phenomena are repeated if after 1000 sec. the load is increased to 11.9 g. and after 2000 sec. to 15.6 g. It will be clear that there is no point in performing the peeling test in the traditional way in this case, that is at a temperature above the transition point of the polymer. For it appears that the rate of release is strongly dependent on the load, that is to say: the force for stripping off the film is indeterminate. However, we can measure the rate of release as a function of the load and of the temperature.

The following schematic considerations will make clear why the process above the transition point proceeds in quite a different manner from the process below that point. Suppose that between the resin layer and the glass plate there are a finite number of discrete contact places, each consisting of a junction between an atom of the resin layer and an atom of the glass plate. For the sake of simplicity we assume that the points of contact form a quadratic lattice, the distance between the points being λ . What are the forces to which such a contact-making atom of the resin layer is subjected? First we have, of course, the molecular forces which are always working between two or more atoms. These forces are repulsive when the distance of the atoms decreases below the equilibrium value; they are attractive for distances above this value

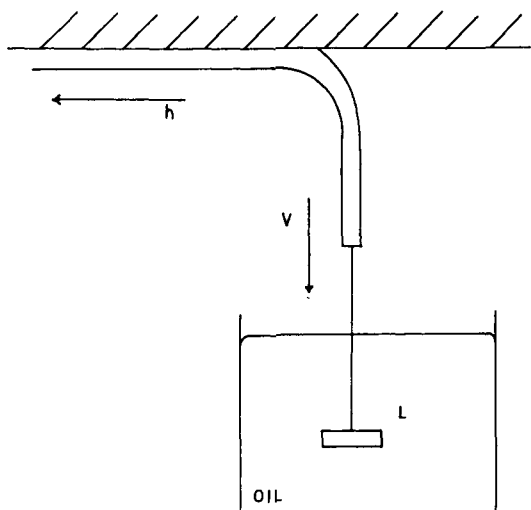


Fig. 1. Sketch of the peeling test.

and approach zero when the distance increases to infinity. The potential energy due to these forces can be represented by the line ABCD in Figure 3.

The abscissa in this figure is the distance between an atom and the glass surface, the ordinate is the potential energy of the atom. Now we suppose that in addition to this molecular field there is also another one, originating from the elastic stress; the potential energy due to this elastic force field is represented by the line EFGH. With the molecular forces alone, and without an elastic force field, the touching atom should be in the first well, without the molecular forces and with the elastic forces alone, the molecule should be in the second well. With both force fields together there are also two wells, but separated by a barrier. The potential energy as a function of the distance is represented by the broken line in Figure 3. There are now two equilibrium positions for the touching atom, one quite close to the glass surface and the other much further away. We call the depth of the molecular potential well u , and that of the elastic potential well ϵ . Then the height of the barrier for a movement of the atom in the direction of release is $u - n\epsilon$ and for a movement in the direc-

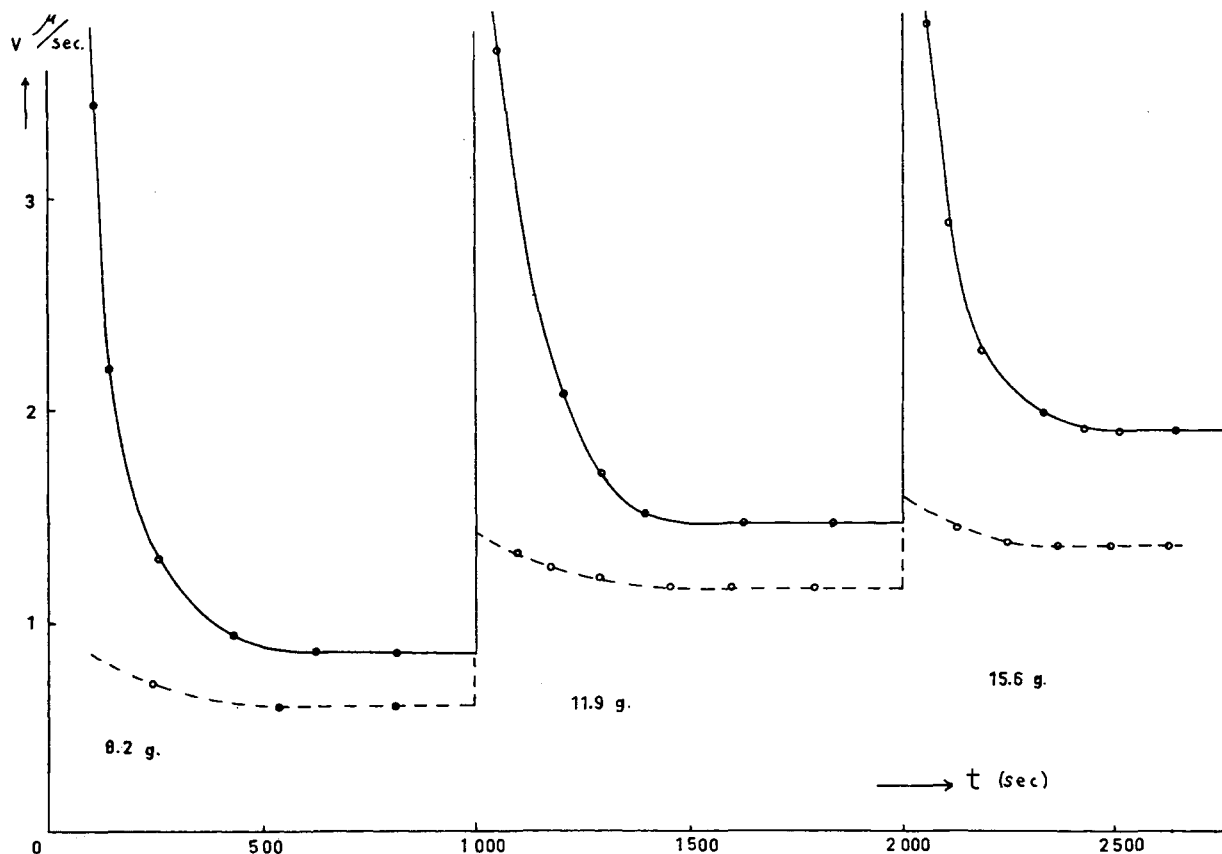


Fig. 2. Changes of the rate of release of the strip immediately after loading. A few minutes after an increase of the load, a steady state is reached: (—) rate of the load; (---) velocity of release of the frontier.

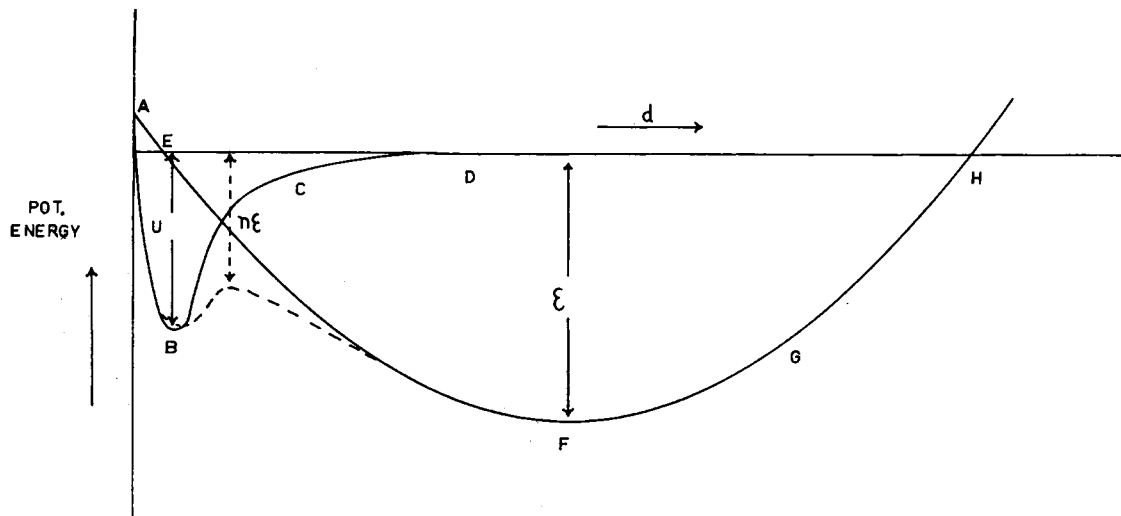


Fig. 3. The balance between the energy of adhesion u and the stored elastic energy ϵ . The abscissa d is the distance from the point of contact to the glass surface. The potential wells are separated by a barrier of height $(\epsilon - n\epsilon)$.

tion of adhesion $\epsilon - n\epsilon$, n being a number between 0 and 1. As an effect of thermal energy the touching atoms will jump backwards and forwards, and the release of the resin strip from the glass plate (i.e., the proceeding adhesion) is the result of two opposite reactions; it is a rate process, greatly dependent on temperature.

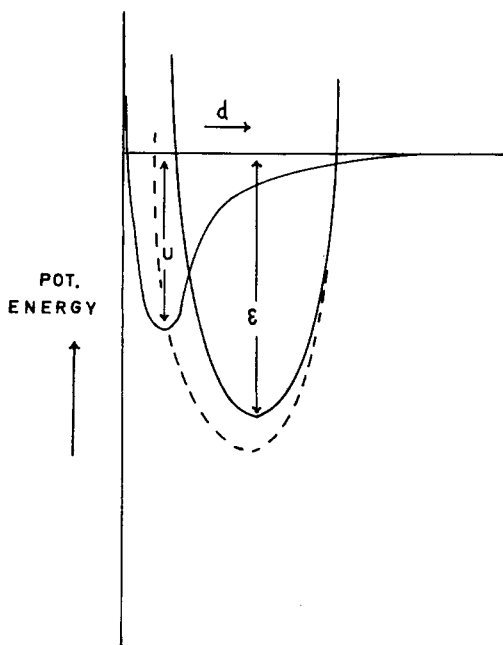


Fig. 4. As for Fig. 3, but the slope of the elastic energy well is much steeper and there is no longer a barrier.

The possibility of the coexistence of two potential wells separated by a barrier is due to the different character of the elastic and the molecular forces. In Figure 3, we have taken it for granted that the temperature was above the transition point of the resin. Then the elastic forces are weak functions of the deformation as compared with the molecular forces. This means that the potential well for the latter is a very steep one, but the slope of the elastic well is small. In Figure 4, on the contrary, we have supposed that the elastic forces are not composed out of weak entropy springs, but are comparable with the molecular forces, and thus the temperature is below the transition point. In this case, both potential wells are nearly equally steep, and the superposition of both wells does not result in the building of a potential barrier. Below a certain limit of the elastic stress all touching points will be in the position of adhesion, and above this limit all will be released. There is no longer a rate process with a balance of energies, but there is a balance of forces. Either the stress is so small that nothing happens at all, or the release of the resin layer is so rapid that the process is comparable with the propagation of a tear in the case of brittle fracture, which goes on with a velocity approximating that of sound propagation. It is not by chance that most investigators were mainly engaged on this second case, since most of the adhesives used in practice are materials which after drying change into the hard solid state. However, the first case is experimentally much better accessible.

Now what is the rate of release? If we call the number of thermal excitations per unit of time N , then the number having an energy so high that transition of the atom in the direction of release can occur, is $N \exp - \{u - n\epsilon\}/kT$, T being the absolute temperature and k Boltzmann's constant. The number moving into the direction of adhesion, is $N \exp - \{\epsilon - n\}/kT$. The total number of wells, both of type 1 and of type 2, that are involved if the process is always the same equals the number of points of contact at the front of the process of release. Every time a row of atoms jumps from wells of type 1 into wells of type 2, the front of the adhesion is going back over a distance λ . If we call the rate of release ξ , we find:

$$\xi = \lambda N [(\exp - \{u - n\epsilon\}/kT) - (\exp - \{\epsilon - n\}/kT)] \quad (1)$$

This equation can also be written:

$$\xi = 2\lambda N [\sinh(\epsilon - u)/2kT] [\exp - \{u + (1 - 2n)\epsilon\}/2kT] \quad (2)$$

Thus the front of adhesion stops if $\epsilon = u$, it goes backwards (direction of release) if $\epsilon > u$, and forwards (direction of sticking) if $\epsilon < u$.

What do we know about ϵ ? The calculation of the stress distribution in a film strip attached and loaded as indicated in Figure 1 is a matter of considerable difficulty, mainly because of the boundary conditions which are partly given as prescribed deformations and partly as prescribed stresses. Moreover, it is generally supposed in the traditional theory of elasticity that the elastic behavior of the material follows a linear law and that the time dependency of the elasticity may be neglected. Neither of these two suppositions, however, is allowed. Just at the place of the front the material is much deformed and does not follow Hooke's law. Also we must take into consideration that the process of release is a steady one and has its own internal time scale which must be compared with the rate of energy dissipation. Fortunately it is not necessary to calculate the whole stress distribution if we wish only to know the value of ϵ . If the release of the film strip is infinitely slow, then $\epsilon = u$. For a finite rate of release, the excess energy ($\epsilon - u$) is released by the decrease of the potential energy of the load L . If the front of the adhesion shifts over a distance dh , the energy liberated or consumed (dependent on the sign of dh) is: $bdh\lambda^{-2}(\epsilon - u)$, b being the width of the film strip and λ^{-2} being the number of the points of

contact per unit area. In the same time the load is lowered or raised over a distance dv and the change in potential energy is Ldv . Thus we have:

$$\epsilon - u = L(1/b)(dv/dh) \lambda^2 = \zeta \lambda^2 \quad (3)$$

where we define λ as

$$\lambda = (L/b)(dv/dh)$$

We will remark here that the quantity ϵ cannot be interpreted as an elastic energy per unit of volume. As a first approximation we can write:

$$dv = dh[1 + (JL/b\delta)] \quad (4)$$

J being the compliance of the material and δ the thickness of the strip. Substituting eq. (4) in eq. (3), we get:

$$\begin{aligned} [(\epsilon - u)/\lambda^2]bdh(1/dt) &= Ldv(1/dt) \\ &\sim Ldh/dt + J(L/b\delta)^2b\delta dh/dt \end{aligned}$$

That is to say, ϵ is proportional to neither L nor to L^2 ; in a rather complicated way ϵ is related to the thickness and the width of the strip. As the process of release is not an equilibrium but a steady state involving a continuous stream of energy, not the stored elastic energy per unit of volume, but the energy supplied to the frontier per unit of time is of importance.

Elimination of ϵ from eqs. (2) and (3) and use of the approximation $\sinh(\epsilon - u)/2kt \sim (\epsilon - u)/2kT$ and of the logarithmic form, gives:

$$\begin{aligned} kT \ln \xi/\zeta &= (n - 1)u + (n - 1/2) \lambda^2 \zeta \\ &+ kT \ln(\lambda^3 N/2kT) \quad (5) \end{aligned}$$

Differentiation with respect to temperature, ζ being kept constant, gives:

$$\begin{aligned} kT^2 [(\delta \ln \xi/\zeta)/\delta T]_{\zeta = \text{const.}} \\ = (1 - n)u + (1/2 - n) \lambda^2 \zeta - kT \quad (6) \end{aligned}$$

This is an equation giving the relation between the experimentally accessible quantities T, ζ , and ξ and the molecular ones u, λ , and n .

3. Experimental

To check the validity of eqs. (5) and (6) it is necessary to do peeling tests under appropriate conditions, i.e., temperature and relative humidity must be kept constant. This was attained by use of an air stream and a system of thermostats. The relative humidity of the air was important because alkyd resins were used, and these dry by oxidation when they are exposed to air and then

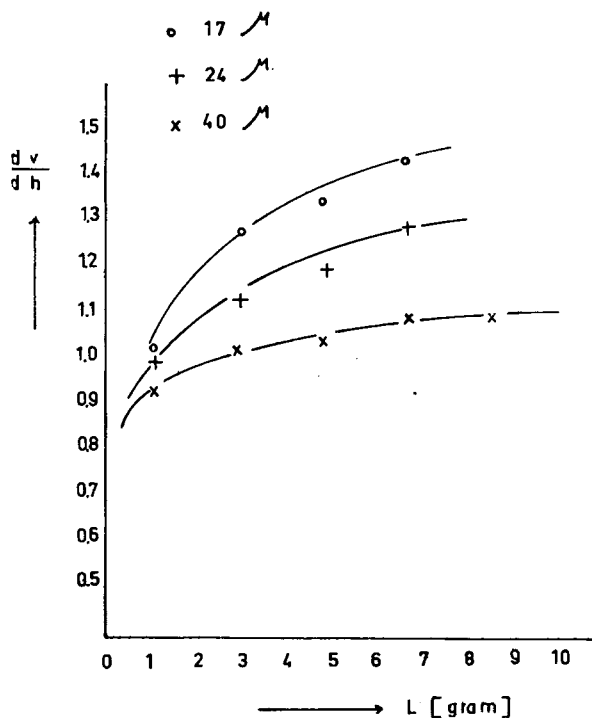


Fig. 5. The quantity dv/dh as a function of the load for film strips of various thickness.

contain many hydrophilic groups. Therefore they are sensitive to changes in humidity. On the one hand this was a drawback, but on the other hand, there was the possibility of changing the mechanical properties in a known way, without changing the temperature at the same time. By previous investigation (which will be published elsewhere), it was proved that the water content of this resin did not vary if the temperature was decreased or increased as long as the relative humidity was kept constant.

The two slow velocities dh/dt and dv/dt were measured with microscopes. The load L was hung in a cup filled with Apiezon oil in order to eliminate swinging and oscillation.

All the properties of what we call the "adhesion" are situated in the border layer between the hard and the soft material. The ordinary mechanical properties, modulus, damping, etc. are composed of contributions of the whole three-dimensional volume of the sample. Small dust particles, however, can destroy the whole effect of adhesion measurements. So it will be clear these measurements are very sensitive to impurities of all kinds, but especially to contamination of the surface of the plate.

The samples which were used were composed of

glass covered with a layer of alkyd resin about 20 microns in thickness. For cleaning, the glass plates were immersed in concentrated sulfuric acid for 24 hr., then rinsed with tap water and distilled water and dried in vacuum. The resin was well diluted with methyl isobutyl ketone and centrifuged till the liquid was perfectly clear. The glass plates were put on a mercury surface and the required quantity of resin carefully dropped on the glass surfaces. After evaporation of the solvent in a dust-free nitrogen stream, drying occurred by exposure to air.

If the quantity ξ really refers to the conditions in the boundary layer where the process of release occurs, then ξ as a function of ζ must be independent of the thickness of the film strip layer. This was the first thing to be checked; it was done by means of three samples of identical material, but with different thickness of the resin layer, viz. 17, 25, and 40 microns. In Figure 5 the quantity dv/dh for each of these strips is plotted against the load L . Stress is the highest in the thinnest strip, and three different curves are obtained. In Figure 6 ξ is plotted as a function of ζ for these three layers; the points can be fitted perfectly well on a single line.

Equations (5) and (6) were tested by measuring the quantities ξ and ζ for four different temperatures at the same relative humidity of 50%. In

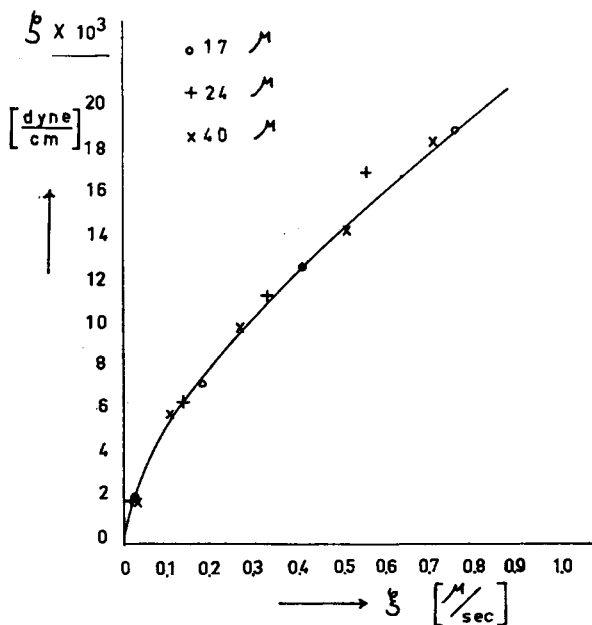


Fig. 6. ξ as a function of ζ for the same strips as in Fig. 4. The quantity ξ/ζ is independent of the layer thickness, and therefore really a quantity related to the state of the interface.

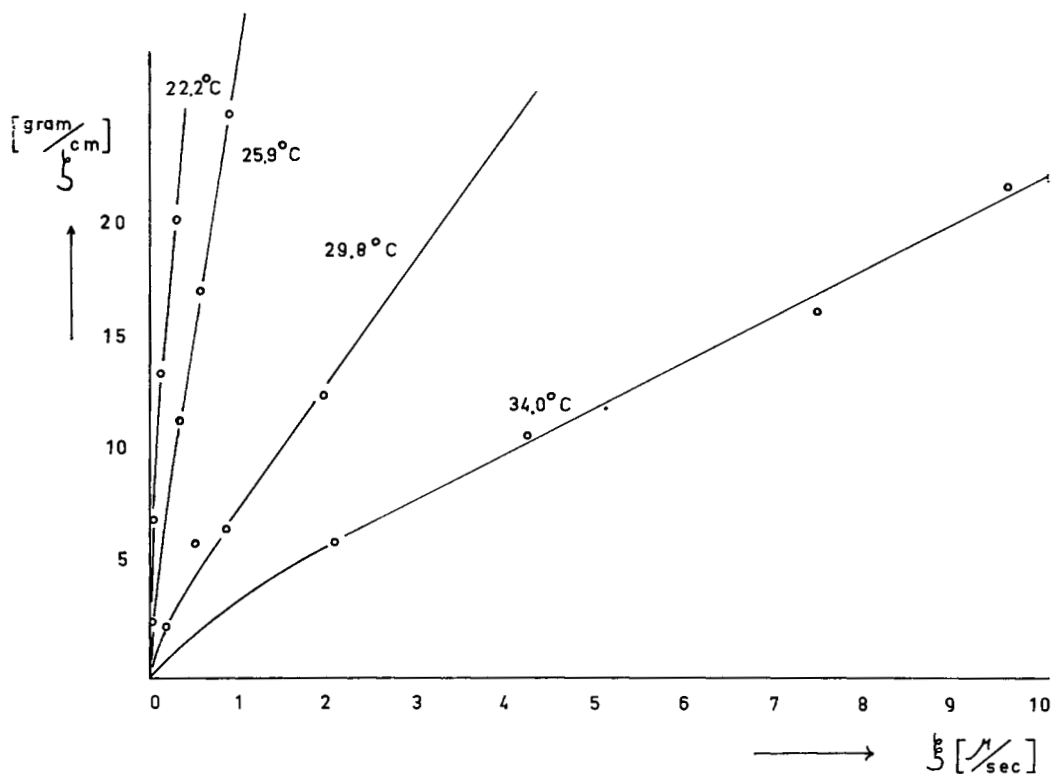


Fig. 7. ξ as a function of ζ for various temperatures.

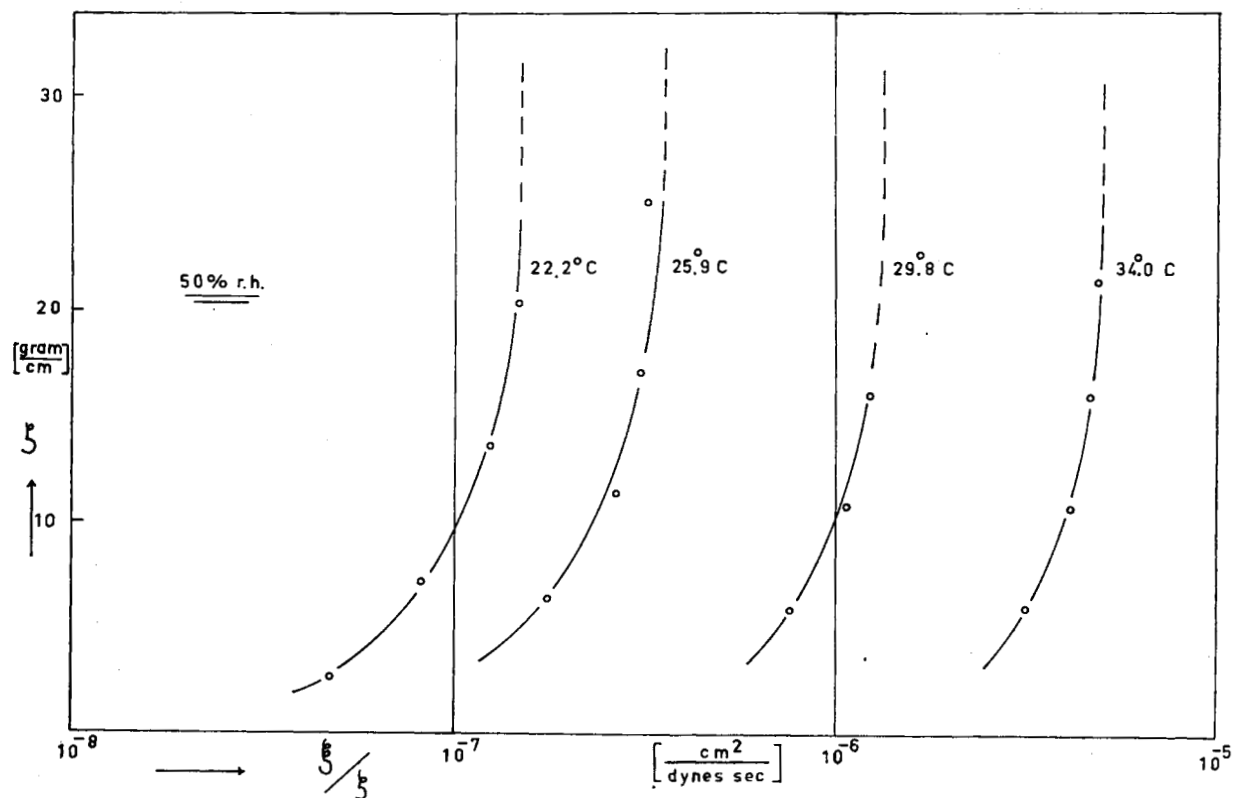


Fig. 8. The quantity $\log \xi/\zeta$ as a function of ζ for various temperatures.

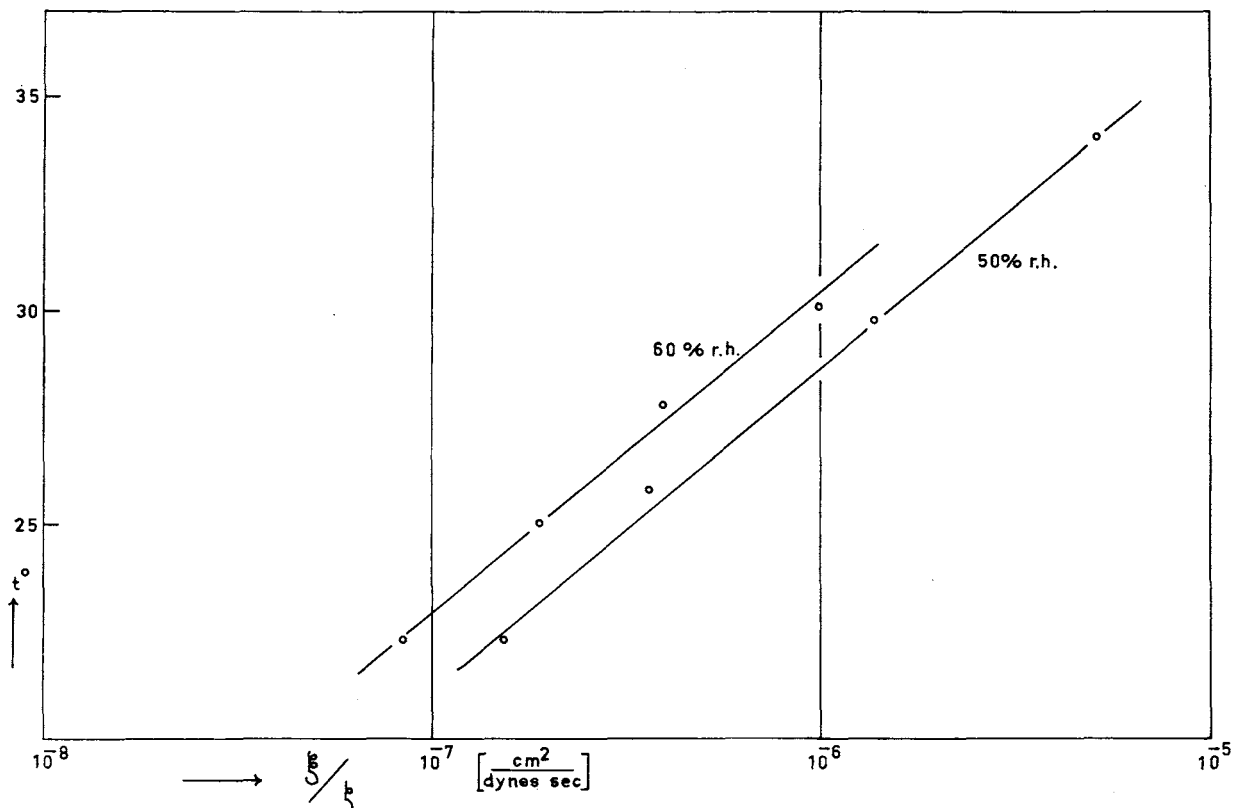


Fig. 9. The value of $\log \xi/\zeta$ as a function of temperature. The slope of the line gives the energy of adhesion. Two experiments done at 50 and 60% R.H. give the same slope, which means that the energy of adhesion is independent of the mechanical properties of the resin; at 60% R.H. the resin is more swollen and much softer than at 50% R.H.

Figure 7, ξ is plotted as a function of ζ under these conditions. It appears that this function is linear for not too small values of ζ , which means that the exponential factor in eq. (2) is independent of ζ and thus also of ϵ , which makes it very probable that:

$$n \sim 1/2 \quad (7)$$

and

$$\delta n / \delta \zeta \sim 0$$

In Figure 8 the logarithm of the ratio ξ/ζ is plotted against ζ for each temperature. It also appears from this plot that with increasing ζ the logarithm of the ratio ξ/ζ becomes constant. Supposing that eq. (7) holds for a value of ζ of about 22×10^{-3} dynes/cm., the quantity $\log \xi/\zeta$ is plotted in Figure 9 against temperature. A straight line is obtained, which means that the energy of activation is independent of temperature. We find the value of u to be about 100 kcal./mole, which seems to be on the high side. However, we are not able

to calculate the adhesion energy per square centimeter, that is, the quantity $u \lambda^{-2}$, since we do not know the value of λ .

In the experiments described above, temperature and humidity were changed in such a way that the water content of the resin remained the same and the change in mechanical properties was wholly and exclusively an effect of the temperature. However, we can also keep the temperature constant and change the relative humidity. Then the water content of the film shows an increase or decrease. That is to say, the film swells or shrinks and the mechanical properties change considerably in such a way that the inflection point of the creep curve shifts about a half decade for each 5°C. variation of the temperature. However, the equilibrium value of the creep reached after an infinite time remains unchanged. This experiment, having a well-defined time scale, is of course, very sensitive to shifts of the creep curve. The higher the temperature, the softer the material, and the more rapid is the rate of release. The adhesion energy u , how-

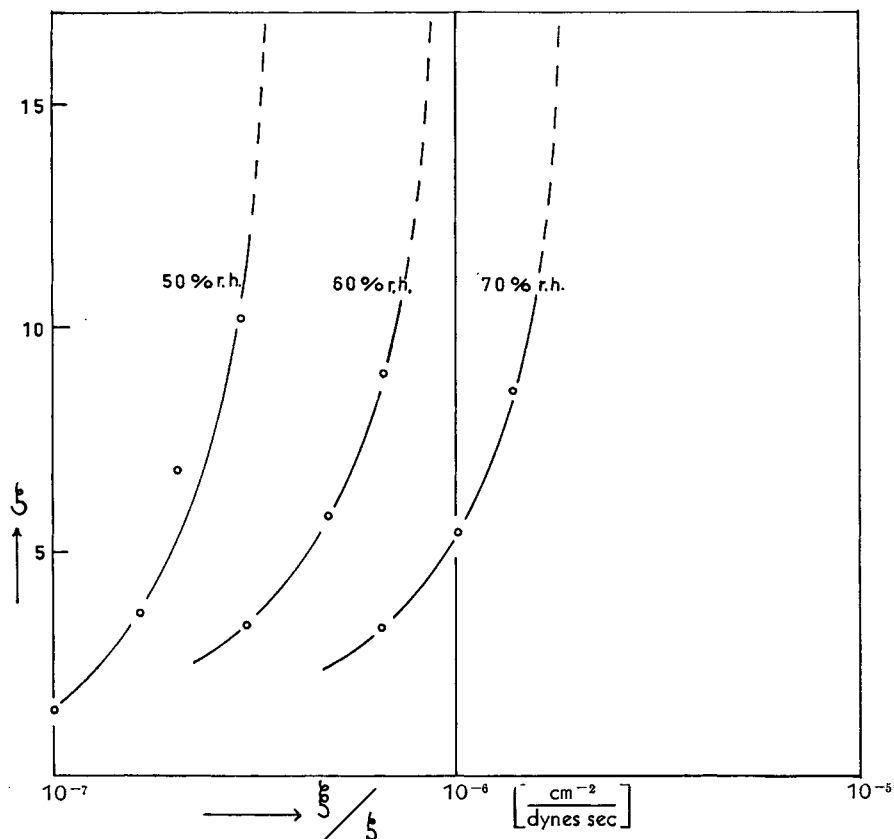


Fig. 10. The quantity $\log \xi/\zeta$ as a function of ζ for the same temperature, but for different degrees of relative humidity. The softer the resin, the higher is the stored elastic energy and the more rapid the rate of release of the strip at the same load.

ever, being a molecular quantity, must be independent of the special mechanical properties of the material. To check this claim, measurements at various degrees of relative humidity were made. In Figure 10 the value of $\log \xi/\zeta$ is plotted against ζ for three relative humidities and at the same temperature. For identical values of ζ the rate of release increases as the relative humidity increases. The second well in Figure 2 does not change in depth, but it does in shape.

At 60% R.H., four sets of measurements were made, at 22.2., 24.9, 27.8, and 34.0°C. In Figure 9 $\log \xi/\zeta$ is plotted against temperature, and it appears that there exists a line parallel to the one measured at 50% R.H. This fact demonstrates the independence of the energy of activation from the mechanical properties.

Ordinary glass is, under normal conditions, covered with a layer of water, the thickness of which is estimated to be about 500 molecules.⁴ Heating the glass to a temperature somewhat below the softening point will destroy this water layer.⁴

Therefore it seemed very interesting to compare the real energy of adhesion of the same resin on an ordinary glass plate and on one from which the water layer was removed. A glass plate treated in the same way as described above, but thereafter heated to 500°C. was covered with the resin immediately after cooling. The result of this experiment is shown in Figure 11, where $\log \xi/\zeta$ is plotted versus the temperature. There appears to be nearly no difference between these two cases. However, one must keep in mind that the resin was strongly permeable to water vapor, and so it is very questionable whether the removed water layer is not re-established, when the covered glass plate is exposed to an atmosphere containing water vapor.

In the same way a comparison was made between the adhesion on glass and on stainless steel. Therefore a stainless steel plate was carefully polished till the surface was a faultless mirror, and then cleaned by boiling the plate for several hours in the solvent used for the thinning of the resin.

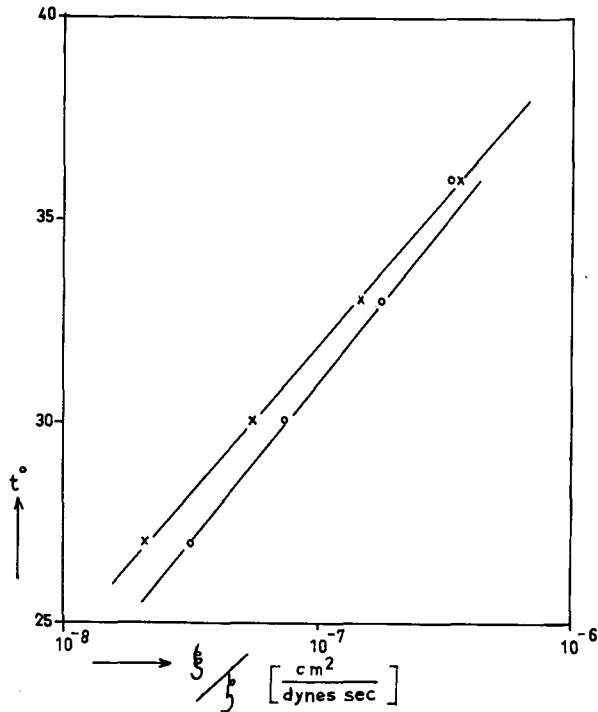


Fig. 11. A comparison of the energy of adhesion of the same resin on glass under normal conditions, and on glass after removal of the water layers from the glass surface by heating to 500°C.

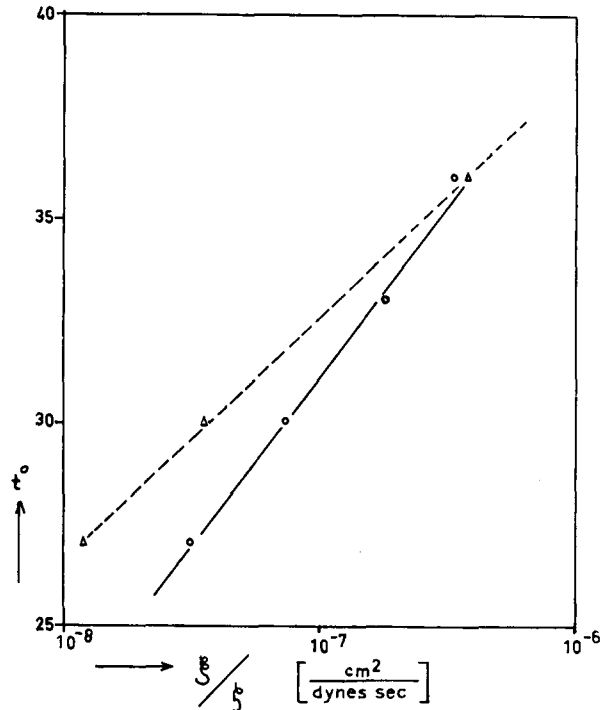


Fig. 13. Influence of time and temperature of the curing of the resin on the energy of adhesion: (O) resin cured for 24 hr. at 60°C.; (Δ) cured for 24 hr. at 60°C. and an additional 5 hr. at 90°C.

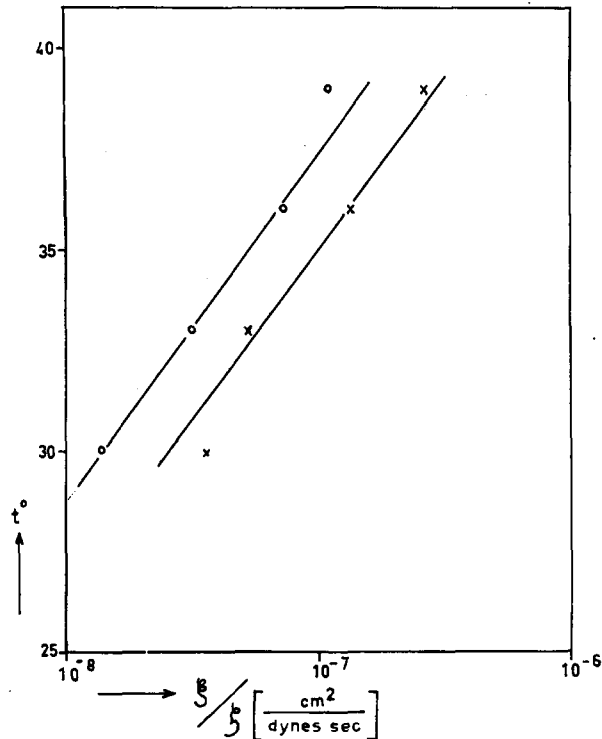


Fig. 12. A comparison of the energy of adhesion of the same resin on glass and on stainless steel: (O) on steel; (\times) on glass.

The covering with the resin was carried out in the same way as with the glass plates. Figure 12 gives the results. The slope of both lines is the same, and therefore there is no appreciable difference in energy of adhesion between the combinations steel-resin and glass-resin.

Of course, the depth of the adhesion potential well does not (for a small part) depend only on the chemical nature of the two adhering materials, but also on the number of atoms contributing to the adhesion of a contact place. According to the simplest theory, the depth of the well is proportional to this number. We can expect that time and temperature of the curing of the resin will influence this quantity. Therefore, a comparison was made between the adhesion energy of a resin cured for 24 hr. at 60°C. and one that was additionally cured for 5 hr. at 90°C. The slope of the plot of $\log \xi/\eta$ versus temperature for this second case was somewhat smaller, as is seen from Figure 13. It seems therefore from this investigation that the number of atoms contributing to the adhesion is of greater importance than the chemical nature of the atoms.

Summarizing the results of our investigation we

can conclude that the notion of adhesion in the popular sense of the word is a very complicated one. When we think of adhesion, we have in our minds an idea about a certain experiment. We try to strip the resin layer from its back, and we estimate the force necessary for the performing of this operation. Now it is clear that this force depends on several conditions, one of which is the energy of adhesion, defined as above, but it is certainly not one of the most important factors. The very great differences in "adhesion" in various practical cases for various combinations of materials is for the major part a consequence of the mechanical properties of the materials and the geometry of the stress distribution proper to the special test which is made for this purpose.

The author wishes here to express his thanks to his collaborator Mr. J. Albers, whose experimental skill has made possible this investigation.

References

1. Spies, G. J., *Aircraft Eng.*, **25**, 64 (1953); J. J. Bikerman, *J. Appl. Phys.*, **28**, 1484 (1957); D. H. Kaelble, *Trans. Soc. Rheol.*, **3**, 161 (1959); Y. Inoue and Y. Kobatake, *Appl. Sci. Research*, **A8**, 321 (1958).
2. Mozes, M., *Ind. Eng. Chem.*, **41**, 2334 (1949).
3. Malloy, A. M., W. Soller, and A. G. Roberto, *Paint, Oil Chem. Rev.*, **116**, 18, 14 (1953).
4. Debye, P., and L. K. H. van Beek, *J. Chem. Phys.*, **6**, 1595 (1959).

Synopsis

The steady peeling off process of a resin layer from a hard substrate can be considered as a rate process, being greatly dependent on temperature. Formulae relating the rate of release, the temperature, and the load with the energy of adhesion and the number of contact points between resin layer and substrate are derived. In the experimental part the energy of adhesion is measured according to these formulae for a number of different combinations of the same resin with glass, glass after removal of the water layers ordinarily adsorbed on a glass surface, and stainless steel. In all these cases there is but very little difference between

the real energies of adhesion. Of more importance are time and temperature of the curing of the resin.

Résumé

Dans l'essai de pelure une couche de résine peut être détachée de sa base avec une vitesse uniforme, si la température pendant l'exécution de l'essai est plus élevée que le point de transition de la résine. Dans ce cas, on peut considérer le procédé du détachement comme un "rate process" dans le sens attaché à ce mot par Eyring et on peut définir une énergie d'adhésion, qui est en balance avec une énergie élastique. Par conséquent, la vitesse de détachement est beaucoup plus sensible à la température. De la variation avec la température on peut déduire l'énergie d'adhésion. Ces mesures sont faits pour les combinaisons d'une même résine avec du verre ordinaire comme base, avec le même verre mais après l'élimination des couches d'eau qui adhèrent au verre sous des conditions normales, et avec de l'acier inoxydable. Il s'établit que la différence d'énergie d'adhésion dans ces cas est faible. Par contre, le temps de durcissement de la résine dans le four a une certaine influence.

Zusammenfassung

Im Abschälversuch wird ein Filmstreifen von irgendeinem Harz von seinem Untergrund losgerissen. Das Losreißen geht mit gleichförmiger Geschwindigkeit vor sich, wenn die Belastung konstant ist und die Temperatur bei der das Experiment durchgeführt wird höher ist als die Übergangstemperatur des Harzes. In diesem Fall kann man das Prozess des Losreißen als einen "rate process" im Sinne Eyrings betrachten und man kann eine Adhäsionsenergie welche im Gleichgewicht ist mit der elastischen Energie definieren. Die Geschwindigkeit des Losreißen ist deshalb stark temperaturabhängig und aus dieser Abhängigkeit kann die Adhäsionsenergie bestimmt werden. Das ist experimental für einen bestimmten Harz in Kombination mit gewöhnlichem Glass, mit Glass nach Entfernung der unter normalen Bedingungen fast immer anwesenden Wasserschicht, und mit rostfreiem Stahl durchgeführt. Es zeigt sich, dass die Unterschiede in der Adhäsionsenergie für diese Fälle sehr gering sind. Im Gegensatz mit dieser schwachen Sensibilität für die chemische Beschaffenheit des Oberflächen steht ein stärkerer Einfluss von Dauer und Temperatur des Trocknungsprozesses des Harzes.

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