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STUDIES IN THE NATURE OF
ADHESIVE TACK

A thesis submitted for the degree of Doctor of
Philosophy in The City University, London

by

Robert Bates, B.Sc.,

July, 1974.

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[REDACTED]

R. Bates

July, 1974.

A B S T R A C T

The term tack was defined and the concept of tack energy was discussed. A method of measuring tack energy was devised, the principle of which is based on the parallel plate theory of Stefan (1874). The method was used to study the variables involved in tack energy measurement using an adhesive composition which was compounded from poly (isobutyl vinyl ether).

The solvent used to prepare the adhesive strongly influences the tack energy of the dry adhesive composition.

The results showed that tack energy is strongly time and temperature dependant and additionally the nature of the substrate surface had a direct influence on the observed tack energy.

A procedure was devised which reduced the number of variables involved in tack energy measurement, including surface effects, to a single common variable. This variable was the logarithm of the speed of testing. The relationship of this variable to the rate of testing was discussed and for viscoelastic materials the procedure has been widely used in adhesive science to superimpose time and temperature effects.

A theoretical justification for treating surface energy effects in this way was derived, based on free volume and activation energy considerations in the bulk and surface phases respectively.

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INTRODUCTION

Tack is the complex combination of properties commonly described as 'stickiness'. It is a feature of a diverse range of materials for example, syrup, tar, printing ink and natural rubber. A closer examination indicates that tack is associated with a surface and the ability of that surface to cling spontaneously to other similar or dissimilar surfaces. Here, we are concerned to define the essential features more precisely and to study how these are related to other properties of the material.

Since tack is associated with a surface and the ability of that surface to cling to other surfaces, it follows that tack is an adhesion phenomenon and the force of attraction which enables a tacky surface to adhere to another surface is termed an adhesive bond.

In this context therefore, adhesion and adhesive bond are taken to mean the same thing - the force of attraction between two surfaces, and the two substances which are joined together by the adhesive bond form a single unit termed the adhesive assembly.

Tack has wide technological importance and application in several entirely different contexts but without exception it involves the formation of an adhesive assembly in which the adhesive is in the viscoelastic state. The term 'viscoelastic state' of matter is that state in which the material behaves partially as a viscous fluid and partially as an elastic solid. The characteristic feature of this is that the application of a stress results in a deformation which is dependant on the time of application.

Workers in the field of adhesion science have defined tack as the ability of an adhesive to form rapidly and spontaneously an adhesive bond under specified conditions of time of contact, temperature and pressure (ASTM D.1878-61T). An adhesive exhibits 'good tack' if the time of contact and pressure is small. The extent of adhesive bond formation is generally assessed by mechanically destroying the adhesive assembly and measuring the force necessary for destruction of the assembly. Often, but not always, this procedure separates the two materials at the point (termed the interface) where the adhesive bond is formed.

In one type of tack the adhesive is deposited from solution onto the surface of two materials which are to be joined (substrates), and the solvent removed by evaporation. After drying the two surfaces are placed together under suitably chosen conditions of pressure and an adhesive bond is formed rapidly between the two surfaces of the dry adhesive. The ability of the adhesive surfaces to do this is generally restricted to the time interval immediately after the removal of solvent, or at most, up to a few hours after this. Note that during this time interval, the adhesive surfaces show a tendency to bond to themselves only. This type of adhesive is termed a 'contact' adhesive since an adhesive bond is formed on contact. This type of tack is not the subject of the present investigation.

A second type of tack is exhibited between two blocks of rubber under certain conditions. In this case the rubber is both the adhesive and the substrate and the phenomenon is termed 'building tack' and it is exploited in the manufacture of rubber tyres. Again the feature of the tack is that under conditions of low pressure and short contact time a measurable bond is formed.

Both these kinds of adhesive behaviour have been identified as a mutual interdiffusion on the molecular scale across the interface between the two surfaces and Russian workers have called the phenomena 'autohesion' since it occurs between substances which are chemically identical.

A third type of tack is of great importance in the printing industry and is observed principally in materials of low cohesive strength, eg. ink, that is materials which are unable to sustain applied stresses. It is applied to the substrate and on removal of the applicator, cohesive failure occurs so that a portion of the material is retained on the substrate. The force required to cause cohesive failure is termed 'printing tack'. A wide variety of substrates may be used and printing tack is again a feature of short contact time and low contact pressures.

A related phenomenon is observed in hot melt adhesives. In this type of adhesive, heat is applied such that the adhesive becomes molten and is applied in the molten state to the substrate. The tack in this instance is related to the ability to wet out onto the substrate prior to cooling and solidification of the adhesive. This type of tack is not the subject of the present work.

A fourth type of tack is again of considerable commercial importance, in this instance in the labelling and adhesive tape industry. Certain materials are capable of forming an adhesive bond to a wide variety of substrates in which they are not soluble. Again, the principal feature is the short contact time and low contact pressures necessary to form the adhesive bond. It differs from printing tack in that generally speaking the substrates may be separated, the principal feature being interfacial failure between adhesive and substrate rather than cohesive failure within the adhesive. Since, as will be explained later, the magnitude of the force required to

break the bond is proportional to the pressure applied during bonding, the adhesives are termed 'pressure sensitive' adhesives. This type of tack is the subject of the present investigation.

A definition of tack could be as follows:

The ability of a material to form a measurable adhesive bond with another substance with which it is not mutually compatible or soluble, within a very short interval of time after initial contact.

The weakness of this definition lies in the interpretation of the word 'measurable' and the phrase 'within a very short interval of time'. The usual meaning of the word 'measurable' in this context refers to the destruction of the adhesive assembly formed and good tack is inferred to be an easily measured force, i.e. a force of magnitude of tens or hundreds of grams force. Poor tack is taken to mean a low magnitude of force. The interval of time referred to is of variable magnitude according to the chosen method of measurement of tack, but the essence of tack is that it should be of short duration, preferably less than ten seconds. During this short interval, it is certain that the full potential bond strength has not developed, i.e. the adhesive is not at equilibrium with the substrate.

One of the aims of this work is to elucidate the basic mechanism involved in tack, and to arrive at a more satisfactory definition.

Measurement of adhesive bond strengths is at the moment only possible by destroying the adhesive assembly formed. This is therefore an indirect measure of bond strength

since deductions about the bonding process are only made by observing the debonding process and clearly this is only possible if the bonding/debonding processes are identically reversible. The literature indicates that in very many cases this is not so; for instance, the configuration during debonding and the mechanical properties of the substrate have a significantly different role to play than during bonding. A second difficulty is that the imprecise knowledge of the nature of tack has resulted in many differing methods of measurement which in most cases cannot be usefully compared or correlated. This work uses a method of measuring tack which is more amenable to theoretical analysis than some procedures used hitherto and the effect of mechanical properties of the substrate is eliminated as the probe used to test tack can be regarded as infinitely rigid.

The effect of the geometry of the test will be briefly discussed, as will be the relevance of the short interval of time after initial contact and before debonding. This period of time is termed the 'dwell time'.

As mentioned in the opening paragraph, tack involves an adhesive in the viscoelastic state. The measurement of debonding force is not satisfactory since the energy dissipated during the test is the parameter most characteristic of a viscoelastic process. Tack tests reported in the literature hitherto, have measured force only. This work measures tack energy, i.e. energy dissipated viscoelastically during tack measurement and is therefore more amenable to theoretical interpretation. The energy criterion of viscoelastic measurements arises from the fact that, when subject to stress, materials in the viscoelastic state store elastic energy. Entanglements of the polymer chains in the viscoelastic substance, in

the time scale of the stress process do not have chance to slide past each other in viscous flow to relieve the stress and enable the material to store energy. During the time scale of tack measurement elastic energy is stored and viscous energy is dissipated and it is these processes which determine the response of the material. As the process operates over finite time, force measurements cannot adequately represent these processes; hence the significance of measuring energy.

Coupled with this in recent literature is the energy criterion for adhesive debonding (Gent (1971)). This is concerned with the adhesion of viscoelastic materials to rigid substrates of which the tack test method used in this work is a special case. This criterion stipulates that regardless of test specimen geometry, there is a characteristic failure energy per unit area of interface which is a function of the rate of debonding. In other words, the total failure energy (that is energy dissipated on adhesive debonding) has two components: the reversible work of adsorption and the irreversible work of deformation of the adhesive in effecting debonding.

This thesis is therefore particularly concerned with the measurement of tack energy and its implications with regard to characteristic failure energy hypothesis although it must be stated that in the procedure used in this work the effective rate of interfacial separation is not measured.

CHAPTER 2

REVIEW OF CURRENT KNOWLEDGE

2.1 INTRODUCTION

From the consideration indicated in Chapter 1, it is apparent that the term 'tack' covers a diverse range of phenomena but the underlying feature of all types is the formation of an adhesive bond between the adhesive surface and the substrate at some stage before the measurement of tack. The nature of the adhesive bond is in itself complex and several theories have been put forward, each based on certain special cases of bond formation. No one single theory can explain every type of adhesion encountered.

2.2 Current Theories of Adhesion

2.2.1. The Diffusion Theory of Adhesion

The Diffusion Theory of adhesion is associated with the work of S.S. Voyutskii and his School in Russia and concerns particularly the adhesion of two surfaces of polymeric materials. When it is the adhesion of two identical materials the process is called 'autohesion'. Vassenin (1969) indicated that two criteria are necessary for this type of adhesion. Firstly, a thermodynamic criterion which states that the adhesive and substrate must be mutually soluble to a finite extent. Secondly, a kinetic criterion that the macromolecules involved or the segments of these macromolecules must be mobile, that is they must possess translational as well as rotational degrees of freedom. The first criterion is

considered to be the more important since without mutual solubility, adhesive bond formation by a diffusion process could not occur. Nevertheless Vasenin (1969) has indicated that even with limited solubility, bond formation can take place.

The proposed mechanism of bond formation is as follows:

On contacting the two polymers, provided that the criteria mentioned above are satisfied, a process of interpenetration of molecular chains or chain segments occurs. The segments which have diffused across the interface are retained in the adhesive (or substrate) by means of intermolecular forces and the resulting joint strength, F , is proportional to the number of molecular chains intersecting the phase boundary and their depth of penetration.

The constant of proportionality is estimated (approximately) from group interactions, distance, dipole moments, etc. Vasenin (1969) estimated the number of molecular chains intersecting the phase boundary as $(\frac{2N}{\rho})^{2/3}$ where ρ = density, M = molecular weight and N = Avogadro's number. He estimated the depth of penetration of the chains using Fick's second law of diffusion, the final result being a function of contact time.

Experimental work confirmed the dependance on $M^{-2/3}$ and contact time. This is at best indirect qualitative proof. That diffusion can and does occur cannot be denied, but further to postulate that it is the prime mechanism and cause of adhesion is very difficult to establish experimentally. However, this theory is applicable in the case of building 'tack'.

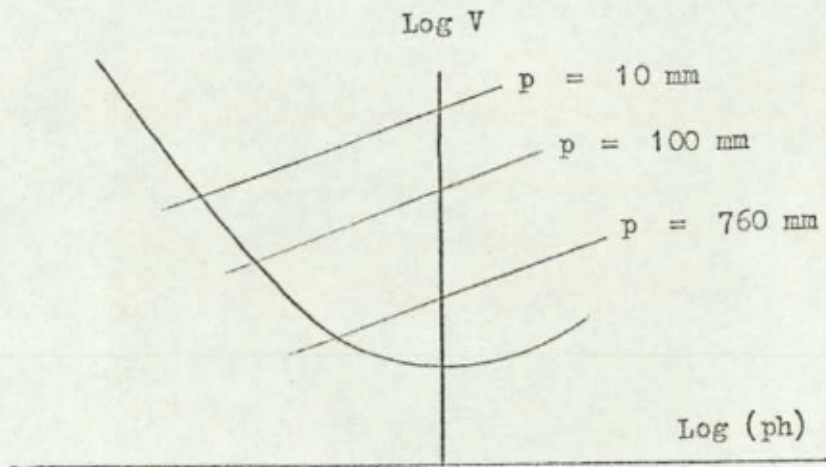
2.2.2 The Electrostatic Theory of Adhesion

Like the Diffusion Theory of Adhesion, this theory originates in the Soviet Union. Deryagin (1969) has

argued that when two substances form a sharp continuous interface, forces occur across the interface which may be molecular, valency, or electrostatic. The electrostatic force originates from the formation of a double electrical layer at the interface which arises from the difference in work functions of the two materials in contact. The evidence quoted for the existence of this electrostatic component of force is as follows:

1. The work of adhesional film detachment (10^5 - 10^6 ergs/cm²) is several orders of magnitude greater than that required to break molecular or valency forces and of the correct order for forcing apart the sides of the double layer to discharge.
2. A potential difference may be measured across the interface and is of the correct order of magnitude.
3. Rapid peeling of adhesive from substrate in a darkroom gives rise to a luminous electrical discharge.
4. Siloxane modification of the surfaces changes the sign of the double layer, yielding a minimum in adhesion at that point.

The force required is a function of charge size and voltage difference and the Paschen curves indicate discharge potential as a function of pressure p and distance h



Isobars may be constructed at constant gas pressure and the point of intersection of the isobars with the Paschen curve yields the discharge potential and Deryagin assumed that the energy of the condenser (a function of charge and voltage) was the work of adhesion. Deryagin has claimed a universal applicability but this is doubtful where charge dissipation occurs. This theory is of particular application in photo copying machines and the removal of charged particles from gaseous effluents.

2.2.3 The Mechanical Theory of Adhesion

This is similar to the diffusion theory in postulating that joint formation is due to the flow of an adhesive into pores, fissures or cracks in the substrate surface by a microrheological process. In other words, the adhesive is mechanically keyed into the substrate. The theory is applicable to a greater or lesser extent in cases where some penetration of adhesive into the structure of the substrate occurs, eg. in fabric or leather.

2.2.4 The Adsorption Theory of Adhesion

The adsorption theory has wide applicability whilst not a universal theory and has its foundations in the quantum

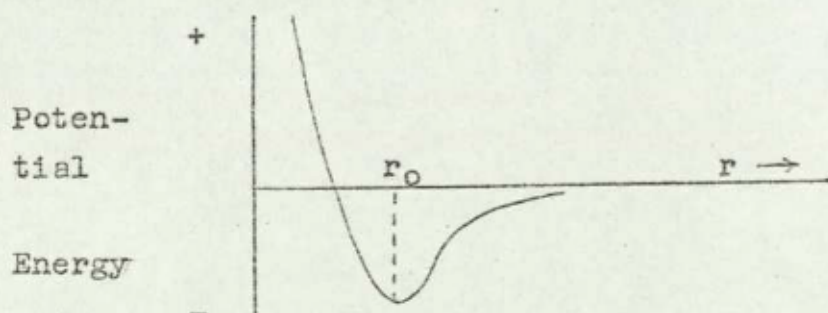
theory of the chemical bond. Covalent bonds uniting atoms in a chemical compound are highly directional primary forces responsible for chemical bonding and require 9 - 25 KJ mole⁻¹ for their rupture and are operative over a distance of 0.1 - 0.2 nm. Ionic and metallic bonds are similar in range and energy to covalent forces but are only weakly directional.

In addition to these primary sources of attraction, whereby molecules associate with members of their own, or other species, there exist also forces which are called variously 'secondary forces' or Van der Waals forces and are considered to be the origin of the adhesive bond in the adsorption theory of adhesion. Their energy is of the order 0.5 - 1.0 KJ mole⁻¹ and their range of activity about 0.3nm.

The potential energy between two isolated atoms separated by a distance r , is given by the Lennard-Jones potential function:-

$$\text{Potential Energy} = -\frac{A}{r^6} + \frac{B}{r^{12}} \dots (1)$$

The term A/r^6 is the attractive force contribution between the two atoms and B/r^{12} the repulsive force. This equation is adequately represented by the curve:



r_0 represents the separation distance of minimum potential energy.

The constant A is the Van der Waals force contribution to the potential energy and may be expressed as the sum of three components as follows:

$$A = X + Y + Z \quad \dots\dots\dots (2)$$

from the London Theory (London 1937), X termed the dispersion force component, represents the force between the two atoms in the case where they are neutral and symmetrical. At any instant in time the electrons in atom a may be regarded as having a definite configuration which is asymmetric so that molecule a has at that instant a particular dipole moment. This instantaneous dipole in molecule a, induces a dipole in molecule b. The interaction between these two dipoles results in a force of attraction between the two molecules which, because of its electromagnetic origin is termed the dispersion force. This force is then the instantaneous force of attraction averaged over all instantaneous configurations of the electrons in molecule a. The instantaneous dipole moment arises from the fact that the electron cloud of an atom can be considered to be an oscillator. Since whenever the electron cloud is asymmetrically distributed, the attraction of the nucleus provides a restoring force which is proportional to the displacement. If the natural frequency of oscillation is ν_0 then Quantum Mechanics shows that the energy of a simple harmonic oscillator in the n^{th} quantum level is

$$\text{Energy} = h\nu_0 \left(n + \frac{1}{2} \right) \quad \dots\dots\dots (3)$$

where h is Planck's constant and n an integer

The instantaneous dipole is proportional to the polarizability α which is proportional to $\nu_0^{-1/2}$. The instantaneous dipole in atom a is attracted to the dipole in atom b, but because of the strong angular dependance and the fact that the fluctuations in a and b are not

synchronized, the average attraction is small. A much greater attraction is that between the instantaneous dipole in a and the induced dipole in b since these fluctuate synchronously.

London showed that $h\nu_0 \approx I$ the ionisation energy of the atom and between atoms a and b

$$X = \frac{3}{2} \left[\frac{I_a I_b}{I_a + I_b} \right] \alpha_a \alpha_b \dots\dots\dots (4)$$

ν_0 is experimentally determined by the dispersion of refractive index with frequency for the substance in question: hence the name 'dispersion force'. This force is by far the most predominant contribution to the Van der Waals forces.

The second term Y is the Keesom dipole term and is expressed by equation (5)

$$Y = \frac{2}{3kT} (\mu_a^2 \mu_b^2) \dots\dots\dots (5)$$

where μ_a and μ_b are permanent dipole moments in atom a and b respectively, k is Boltzmann's constant and T is the absolute temperature. The Keesom term arises from the interaction of permanent dipoles in the atoms concerned.

Finally, the third term Z (Debye term) is the result of the interaction of a permanent dipole and an induced dipole and is given by

$$Z = \alpha_a \mu_b^2 + \alpha_b \mu_a^2 \dots\dots\dots (6)$$

The relevance of the discussion is that bringing a substrate into contact with an adhesive will result in attractive forces between these two materials of the type indicated above. Since most adhesives used in tack work are neutral, non-polar materials, the interaction of adhesive with substrate will be predominantly by the dispersion

force component of the Van der Waals forces.

With regard to the debonding process, the surface free energy, γ , may be defined as the energy required to separate the two surfaces of unit area out of range of these Van der Waals forces. It is possible (Fowkes 1967) to calculate the interfacial interaction energy per unit area resulting from the dispersion force interactions between bulk adhesive and vacuum by integrating the term $-\frac{K}{r^6}$ of one atom with all the volume elements in the bulk phase. This gives the surface energy h_N which can be related to the surface free energy, γ , by incorporating a term due to the entropy of the surface. This entropy term arises from the packing and orientation in the surface being less than in the bulk:-

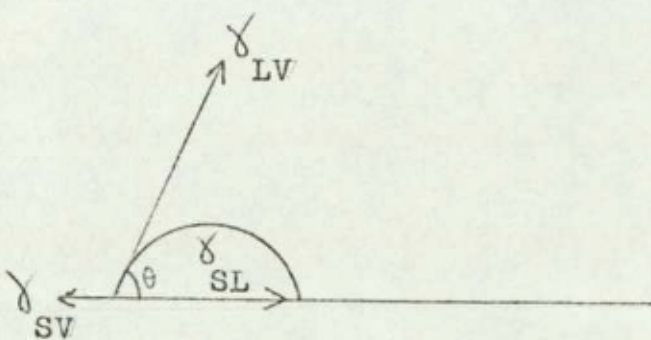
$$h_N = \gamma - T \left[\frac{d\gamma}{dT} - \frac{dh_N}{dT} \right] \dots\dots\dots (7)$$

eg. for octane $h_N = 25 \text{ KJm}^{-2}$ and $\gamma = 21.8 \text{ KJm}^{-2}$.

The interfacial free energy γ_{12} between adhesive and substrate is given as

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1 \gamma_2} \dots\dots\dots (8)$$

In the case of liquids, the surface free energy is simply the surface tension so that γ_{12} in equation (8) is the interfacial surface tension. If however, we consider the case of a solid, there is no direct way of deducing what the surface free energy is. Let the surface free energy of a liquid in equilibrium with its own vapour be γ_{LV} and for a solid in contact with the liquid vapour γ_{SV} . Then we can define the interfacial free energy between liquid and solid, γ_{SL} , in terms of the contact angle θ the liquid makes with the solid:



$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos \theta \quad \dots\dots\dots (9)$$

This equation was derived by Young (1805). As the contact angle tends to zero $\gamma_{SL} \rightarrow \gamma_{SV}$ until the liquid spreads spontaneously over the solid in a very thin uniform film. The significance of this is that the adhesion between liquid and solid is at its optimum when $\theta \rightarrow 0$.

Dupré (1869) showed that the reversible work of adhesion W_A between liquid and solid is given by equation (10)

$$W_A = \gamma_S + \gamma_{LV} - \gamma_{SL} \quad \dots\dots\dots (10)$$

where γ_S refers to the surface free energy of the solid in vacuum. The work W_A required to remove the droplet of liquid from the solid leaving a monolayer of equilibrium - adsorbed liquid is

$$W_A^* = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad \dots\dots\dots (11)$$

Using equation (9)

$$W_A^* = \gamma_{LV} (1 + \cos \theta) \quad \dots\dots\dots (12)$$

From these three last equations, Bangham and Razouk (1937) derived equation (13)

$$W_A = (\gamma_S - \gamma_{SV}) + \gamma_{LV} (1 + \cos \theta) \quad \dots\dots\dots (13)$$

Spreading of liquids on solids is therefore a function of surface energies since if $\gamma_S - (\gamma_{LV} + \gamma_{SL}) > 0$ then spreading (wetting) occurs and if $\gamma_S - (\gamma_{LV} + \gamma_{SL}) < 0$ then non-wetting occurs (Cooper & Nuttall, 1915). If we define

$$\gamma_S - (\gamma_{LV} + \gamma_{SL}) = S \quad \text{then}$$

$$S = - \frac{\partial G}{\partial A} \quad \dots\dots\dots (14)$$

where G is the free energy of the system and A the surface area.

Zisman measured $\cos \theta$ on a series of low energy solid surfaces using a range of organic liquids of differing surface tension. Empirically he showed that a graph of $\cos \theta$ against the surface tensions of the liquids yielded a straight line of intercept γ_c on the $\cos \theta = 1$ axis, when a homologous series of liquids was used. He defined γ_c as 'the critical surface tension of wetting' and it was found to be a characteristic of the nature of the solid surface.

Fowkes (1967) derived equation (8) and argued that if two substances interacted they did so almost entirely by dispersion force interactions unless both substances possessed permanent dipoles. This implies the relegation of dipoles induced by other dipoles to a minimum role and the absence of interactions between metallic valencies and organic molecules. However, the concept is reasonably well supported by observation

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2 (\gamma_1^d \gamma_2^d)^{\frac{1}{2}} \quad \dots\dots\dots (15)$$

where γ_1^d and γ_2^d denote the dispersion component of

surface free energy. Taking subscript 1 as LV and 2 as S then using equation (9)

$$\gamma_{LV} \cos \theta = -\gamma_{LS} + 2\sqrt{\gamma_L^d \gamma_S^d} \dots\dots\dots (16)$$

If in equation (13) $(\gamma_S - \gamma_{SV})$ is taken as zero then

$$W_A = 2\sqrt{\gamma_S^d \gamma_L^d} - \gamma_L \dots\dots\dots (17)$$

Andrews and Kinloch (1973) have conclusively shown that the thermodynamic work of adhesion has an important bearing on the observed bond strength. This has been shown by other workers (eg. Kaelble 1969) and hence in dealing with the tack of an adhesive it is important to consider the surface energy characteristics of both the adhesive and the adherend.

2.3 Methods of measuring Tack

2.3.1 Measurement of Tack by the Probe Technique

Most attempts at measuring tack take their origin from the age-old subjective thumb or finger test in which tack was assessed simply by pressing one's thumb on the 'tacky' substance and then removing it. A subjective judgement was then made as to the force required. Obviously in its simple form the pressure and time of contact were unknown and variable as were the debonding parameters such as speed of withdrawal, angle of withdrawal etc.

A theoretical paper by Stefan (1874) outlined a framework which is relevant to this thumb test. Consider two parallel discs of radius a immersed in a liquid of viscosity η , then the force F necessary to move the plates from a separation distance h_1 to a separation distance h_2 ,

was shown to be a function of time t as follows:

$$Ft = \frac{3}{4} \pi \eta a^4 \left(\frac{1}{h_2} - \frac{1}{h_1} \right) \dots\dots\dots (18)$$

It is possible to consider the case of two parallel plates separated by a fluid but not immersed in the fluid by taking the fluid surface tension, γ , into account. The expression in this case is

$$\frac{4\eta}{h^3} \frac{dh}{dt} = \frac{Fn^3 (2a)^2}{V^3} - \frac{2\gamma h(2a)^2}{V^2} \dots\dots\dots (19)$$

where V is the volume of liquid between the two parallel plates.

This situation is directly analogous to the debonding step in the thumb tack test. In fact this force expression is associated with the tack of printing ink and many instruments have been designed to measure the force. The viscosity, η , in the above equations is a constant in the case of a Newtonian liquid since the ratio of stress to strain rate is constant in this instance. In the case of viscoelastic substances encountered in pressure sensitive adhesives, η is strongly rate dependant and in a very complex manner since tack measurement extends into a region where strains are of the order of several times the original dimensions of the material involved. In this region not only is stress time dependant but strain is extended well above the limits of reversible deformation. In this instance mathematical expression of the relationship of stress, strain and time is formidably complex and at the present time of little practical value.

The bonding step in tack is analogous to the Stefan parallel plate expression. In this case instead of an

extensive force required to separate the plates from adhesive, there is a compressive force. This compressive force causes or increases wetting of the substrate by the adhesive. By the term 'wetting' is meant the flow on a microrheological scale by which an adhesive comes into sufficiently close contact with a substrate for the Van der Waals forces to become operative. This definition is that of Huntsberger (1967) who also considers the state of wetting to be the number of molecular contacts achieved between the two materials relative to the maximum possible. Wetting in the probe tack test is mechanically induced flow during the compressive bonding step that is the driving force is the applied pressure and also the time during which this pressure is operative.

As mentioned above, the ease of flow into substrate and conformation of the adhesive to the probe surface will be governed by the adhesive viscosity during the bonding stage. Early ideas on tack (Josefowitz and Mark 1942) emphasised this viscosity effect particularly during the debonding stage. Josefowitz and Mark pointed out that perfectly elastic solids such as glass or steel do not exhibit tack and liquids such as water fail to resist the force of separation due to their low viscosity. After comparing the tacky behaviour of a series of liquids of viscosity $10^2 - 10^4$ poise, they concluded that the viscosity has an important bearing on the result obtained.

Scott (1944) considering the autotack of rubber pointed out that two important factors are involved. Firstly to obtain sufficient contact. This is greatly influenced by surface roughness. The second factor is a rapid mutual interdiffusion of the molecules from each side of the interface.

Busse Lambert and Verdery (1946) pointed out the importance of the rheology of the material since deformation during the bonding stage (at least at the interface) must occur in order to produce close contact. The amount of molecular contact achieved depends on initial surface roughness, applied bonding force (including external applied force and the molecular forces at the interface) and the extent of deformation on a macro and microscale. They also showed that the force of separation is a function of real bonded area, molecular forces, the ultimate tensile strength, the rate of stress application and finally the distribution of the applied stresses and the resulting elongation. They pointed out that in the tack test the material is stressed to its 'tensile strength' and that the separating force produces a stress gradient in the samples. This means the force observed depends strongly on the ultimate elongation and that the viscoelastic properties of the rubber result in differing observed tack behaviour. They repeated the point made by Josefowitz and Mark (1942) that 'liquids such as water are non-tacky because the tensile strength or viscosity is too low to resist separation'. The remainder of the paper was concerned with the practical determination of tack. A peel method was used to determine the influence of applied rate and temperature on the tack of a pressure sensitive adhesive tape bonded to glass. It was demonstrated that the method measured a property of the tape assembly as a whole, rather than a fundamental property of the material. Another method involved a machine for measuring the autohesion of rubber which was improved by Lambert and McDonald (1948) by incorporating automatic functions.

The same tack meter was used by Schildknecht (1948) to determine the tack of various poly (isobutyl vinyl ethers)

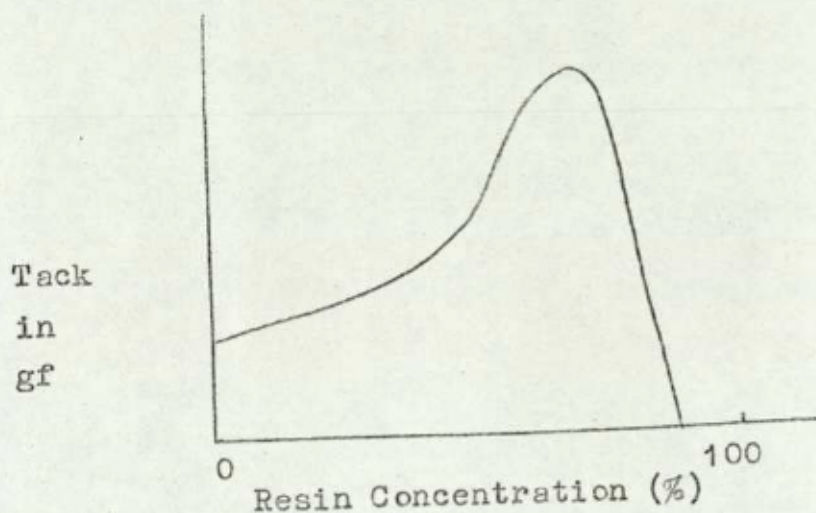
to a polished chromium plate. Three types of tack were defined - 'instant tack', '5 second contact' and '10 second tack'. Most polymers tested showed an increase of tack force with time of contact.

Hatfield and Rathmann (1956) used a probe test to examine a Rate Theory of Adhesion. The theory was based largely on Eyring's Theory of Rate Processes. A hyperbolic sin dependence of debonding force with reciprocal time was the principle conclusion. This does not relate completely to the tack test since it concerned the debonding stage assuming that optimum bonding had been achieved prior to debonding. They used a poly (methyl methacrylate) probe and a poly isobutylene adhesive.

Wetzel (1957) and Hock (1957) were the first to refine the tack test, and they developed a powerful method for the accurate measurement of pressure sensitive tack. Their method became the basis of an A.S.T.M. method and consisted of an Instron tensile testing machine used in conjunction with an electronic recording apparatus. A cylindrical brass probe with a flat contacting surface was housed on a suitable low friction housing permitting an accurately known pressure to be exerted on the adhesive on contacting the probe with the adhesive. The adhesive was coated in a thin uniform layer onto a glass plate. The time of contact (dwell time) was accurately controlled by employing automatic functions.

Using constant dwell time, probe withdrawal speed, adhesive film thickness and temperature, Wetzel studied the variation of tack force with concentration in mixes of natural rubber and various tackifying resins.

Generally the tack curve/concentration curve had the following form:



The peak generally occurred within the range 50-75% resin concentration. Wetzel pointed out that the adhesive should be removed cleanly from the probe and that cohesive failure in the adhesive bulk should not occur. However, he then stated that the observed tack force is a function of the surface properties only. This overlooks the fact that the contact pressure of 860 psi applied during bonding must have a drastic deformative effect on a soft material in the visco-elastic state such as resin/rubber mixes.

Wetzel demonstrated that the peak position depended on the softening point of the resin. Generally the higher the resin softening point, the lower the concentration of resin at which the maximum is observed. Electron microscopy showed that the surface changed in appearance with resin concentration in a way which paralleled the tack force. This was interpreted in terms of the formation of a two phase surface structure. At lower resin concentrations, the resin is present as a solid solution in the rubber. Wetzel proposed that as the resin content was increased and the peak in tack force reached, a situation developed where microscopic particles of

resin surrounded by a continuous phase of rubber saturated with resin was present. The continuous phase had a much lower viscosity than the particles (disperse phase). During contact of the probe with the adhesive, the low viscosity phase deforms, allowing the disperse phase to conform to the probe surface and promoting increased wetting and hence increased observed bond strength. Above the concentration at which the tack peak occurred, Wetzel postulated phase inversion (i.e. rubber particles suspended in a continuous resin phase) resulting in very much increased viscosity to the point where wetting could not occur, and tack force decreased rapidly to zero. The weakness of the argument is that these two phases cannot be isolated and characterised and also that a phase inversion effect does not occur in many materials which, whilst being tacky, are chemically and physically homogeneous.

The great value of Wetzel's work was firmly to establish a sound method of determining tack force.

Dahlquist (1959) examined Wetzel's argument in detail. Using Stefan's equation he pointed out the linear dependance of force or time on viscosity and that with materials which were elastic in nature rather than viscous, the elastic component governs the time dependance of flow. He went on to consider the extension of a single strand of adhesive and showed that the maximum load observed would be determined by the elastic modulus of the adhesive. On expanding Wetzel's probe test results, he assumed values of tensile modulus for various compositions, and using the area of contact, calculated the force required for maximum load. The curve obtained showed similar trends to the tack/resin content curve.

He therefore concluded that tack is dependant only on the adhesive modulus as opposed to the explanation offered by Wetzel.

This criticism is not entirely justified for two reasons. Firstly he assumed a time invariant value of tensile modulus. This is unrealistic since in all viscoelastic materials, modulus is time dependant. Secondly, Dahlquist admits that the dependance of the observed force with the nature of the probe material is not explained by his arguments. Dahlquist went on to consider results obtained using constant applied debonding force. The dependance of the time to failure on this force and the close agreement between his theoretical calculations and the experimental observations was interpreted as confirmation of the dependance of tack on modulus.

Weidner and Crocker (1960) in a review of adhesion, included a sympathetic review of Hatfield and Rathman's Rate Theory of adhesion mentioned above, and a section on rheology and tack was included. Weidner and Crocker pointed out the dual nature of the viscoelastic state and they defined tack as the ability to conform to and wet a surface and to resist subsequent loading stress. They also emphasised that tack is a vague term unless the conditions of observation are specified. The usage of the term was discussed. In considering Wetzel's work, they examined possible reasons for the variation of tack peak with resin softening point. They argued that it was not a solubility effect and postulated that it may be a polarity effect or concerned with an increase in the short term relaxation time of the rubber without a corresponding decrease in the long term modulus.

Rivlin (1944) and Voet (1950) had considered the effect of energy rather than force in connection with printing ink tack, but Wake (1961) was one of the first to apply the argument to the tack of viscoelastic materials. In these materials, long filaments can be formed on application of a pulling force, which retract when adhesion fails due to the response of the elastic component to the applied. He considered the extension of a single filament (as did Dahlquist) and assumed that the work done was equal to the elastically stored energy in the filament. The total deformation due to viscous flow was then related to filament geometry, applied stress, relaxation time and elapsed time. He used an expression given by Treloar to relate stored elastic energy to extension ratio, and pointed out that at rapid extension rates, the stored elastic energy is proportional to the square of the extension ratio. Only when the time taken for the extension is much greater than the relaxation time of the filament can the elastic component be ignored.

Real polymers have a very large number of relaxation times, but a maximum relaxation time τ_m may be defined (Tobolsky 1960a), hence only when the debonding time is greater than τ_m can the elastic component be ignored.

Hammond (1963) developed and tested a probe tack meter which employed a mechanical recording device and large diameter cylindrical probes. A wide range of speeds, temperatures, contact pressures and contact times were within the capabilities of the machine used. A disadvantage of the method was that only a small section of the adhesive surface area could be scanned and that replicate determinations were performed on the same area of adhesive.

With very soft adhesives, it is possible to envisage that deformation would effect reproducibility. A further

disadvantage was that the actual time of contact was not precisely determined. Also, Hammond found that using flexible materials as supports for the adhesive strongly influenced the results. This was the conclusion reached by Busse, Lambert and Verdery (1946) and hence the results of this test are not a function of the adhesive properties alone.

Experimental data was listed which indicated the variation of tack force with contact time, separation rate, contact pressure, temperature and probe surface roughness. The following general conclusions were reached:

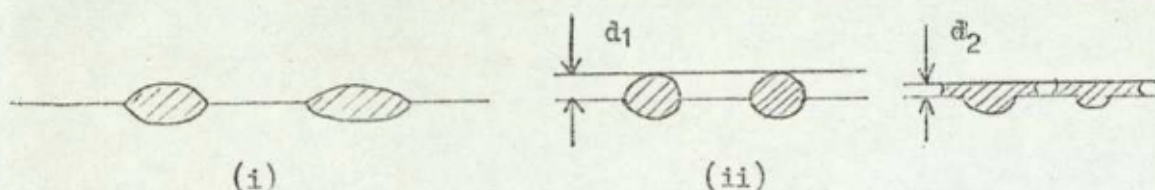
- a) Increased contact pressure gives increased tack force.
- b) Increased contact time, gives increased tack force.
- c) Increased separation rate gives increased tack force.
- d) Increased temperature gives decreased tack force.
- e) Increased surface roughness gives decreased tack force.

The effect of film thickness did not yield useful results since the trend of results varied with backing material. Probe surface free energy variations had been investigated but Hammond did not include the results on the grounds of concurrent differences in probe surface roughness with probe type.

In a further paper, Wetzel (1964) replied to the criticisms of Dahlquist and of Wiedner and Crocker and extended the work to cover synthetic elastomers such as SBR, polyisoprene and polychloroprene. A section on the tack behaviour during heat ageing was also included. A speculative argument was put forward concerning the nature of the two phase system. He postulated that the disperse (low viscosity)

phase was in the shape of biconcave lenses on the surface of the continuous phase, see Diagram 1. (i). On contacting a low energy probe with the surface, these lenses formed micro Stefan discs, the separation distance being d_1 , see Diagram 1. (ii). On contacting a high energy probe with the same surface, the separation decreased to a value d_2 , smaller than d_1 , due to increasing wetting out of the probe.

Diagram 1



The Stefan equation indicates that as d_1 decreases in value then the force of separation increases and hence the result proposed by Wetzel is that a higher tack force is observed with high energy probes.

Wake (1965) and Salomon (1965) reiterated the concept of tack energy being of more significance than tack force. Salomon described tack as the ratio of elastically stored energy to the dynamic loss factor at the rate of test. This definition is inadequate since it makes no reference to the bonding step involved in tack. He described tack as a transient phenomenon dependant on the network structure of the adhesive.

Parry and Ritchie (1966) extended the work of Wetzel on rubbers and resins using identical experimental conditions. In this case however they used emulsions of resin esters and natural rubber latex, and compared these mixes with their solvent based equivalents. As Wetzel did, they assumed that the force of probe separation was in no way connected to the cohesive properties of the adhesive.

In all cases examined, the observed tack force was lower for an emulsion based composition than for the corresponding solvent based system. Further, the tack force varied with the type and concentration of surfactant. The ageing characteristics of emulsion based systems were very similar to those of solvent based adhesives.

Kambe and Kamagata (1969) in an important paper which has a direct bearing on the present work, used mixtures of polyisobutylene and rosin and derivatives in a study of tack. A probe tack device had been used on a tensile testing machine and this device closely resembled the probe assembly used by Hammond. An estimate of adhesive viscosity was obtained using a shear creep method, the derived value being used to assess the cohesive properties of each adhesive.

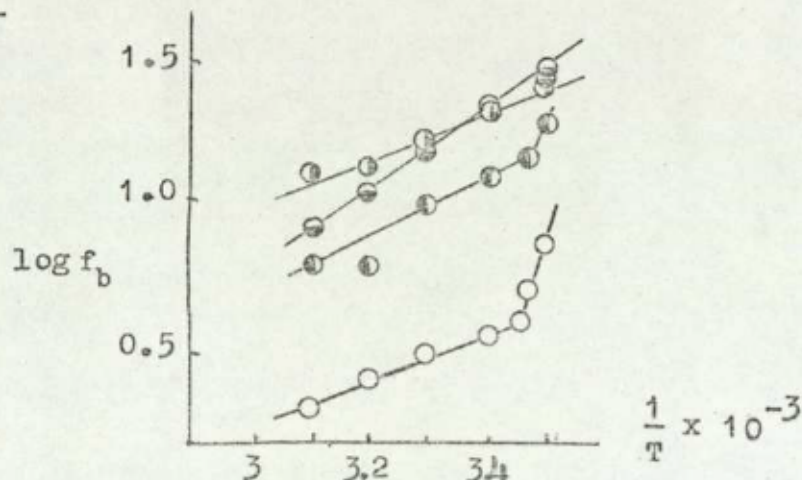
The variations of breaking force with dwell time contact pressure and rate of probe withdrawal were examined. The authors then used the ratio of force at a particular resin concentration to that at zero resin concentration to express their results. The force at break was shown to be inversely proportional to the square root of the time to break. A short section was devoted to the consideration of the adhesive energy E_a which was stated to be a product of force and time. This is dimensionally incorrect for an energy.

$\log_{10} E_a$ was linearly dependant on the $\log_{10}$ (speed of test) and of negative slope. This slope varied with adhesive composition. A further strange procedure was adopted; a plot of $\log_{10}$ (force) against reciprocal temperature yielded straight lines from which activation energies were calculated. Further, as shown in Diagram 2, some lines exhibited marked discontinuities depending on

the speed of test.

Two activation energies were calculated in the cases of discontinuous lines. They stated that the force f_b to break decreases with absolute temperature. This is not so; their results show that the force to break increases with reciprocal temperature.

Diagram 2



Probes of varying surface free energy were used and the observed tack force varied with the probe value as follows, for a rate of probe withdrawal of 20 mm/min.:

Brass > polyethylene > polymethyl methacrylate > P.T.F.E.

but the order was as follows for a rate of 1 mm/min.:

P.T.F.E. > poly methyl methacrylate > Brass

From these results they concluded that at higher rate, failure is at the adhesive/probe interface and at the lower rate cohesively within the adhesive.

De Welt (1970) used the probe technique to study the influence of resin structure and molecular weight distribution on the tack of natural rubber/resin mixes. After discussing the work of Wetzell with rosin esters, the effect of α and β pinene copolymers was considered. He emphasised mutual solubility and suggested that this may be a prerequisite for tackification. The α polymer has a much

narrower molecular weight distribution than the β polymer of identical softening point. The average molecular weight is lower for the α polymer than for the β polymer and according to De Welt has greater solvent power (and hence tackification). The result is that the tack force peak occurs at a lower value of concentration for the α than for the β - an effect usually associated with higher softening point.

De Welt then developed a grid system of solubility assessment which used the hydrogen bonding index ζ and solubility parameter δ . Solvents of known ζ and δ were used to dissolve resin and rubber. From the solubility characteristics the ζ and δ value of the resin and rubber were deduced. Where ζ and δ contours of resin and rubber were superimposable, tackification of the rubber by the resin is possible. The α and β pinene resin solubility contours were very similar to those of natural rubber.

Kamagata, Saito and Toyama (1970) reviewed several methods of tack testing some of which were quantitative, others of which were entirely qualitative. The 'polyken' probe tack tester was used and it was observed that for resin/rubber mixes, the peak in tack force occurred at a higher resin concentration than the peak for the rolling ball tack - presumably due to differences in the rate of making and breaking the adhesive assembly.

Dahlquist (1969) noted a similar dependence of the tack force peak with rate of test. At 5 cm sec^{-1} probe speed, the peak occurred in the range 40 - 50% resin. At 0.02 cm sec^{-1} probe speed, the peak occurred at 65 - 80% resin. In the same paper, he discussed the phenomenon of tack and its measurement, indicating the difficulty of interpreting results in terms of fundamental properties of matter. He pointed out that the adhesive's time dependant compliance

and its ability to wet the adherend are extremely important factors in the bonding step. An adhesive having good 'quick stick' tack will have a greater short time compliance than one having poor 'quick stick'. Dahlquist indicated that the bonding process is not experimentally accessible, whereas in the debonding process more information may be derived by virtue of the fact that the time dependant mechanical properties involved can be measured. He then compared the modulus temperature characteristics with tack force/temperature characteristics. At low temperatures, he showed that the bonding process was the controlling factor. At higher temperatures, this dominance was much reduced. He showed that the tack force - separation rate behaviour showed very similar behaviour to the modulus-frequency characteristics confirming that adhesive modulus strongly influences tack behaviour.

Wetzel had assumed that the adhesive modulus increased monotonically with increasing resin concentration up to the point where the compliance was too low to permit conformation of the adhesive to the probe and subsequent wetting. Hence the drop in tack force above a certain concentration. Dahlquist used dynamic methods to determine the modulus of various rubber/resin mixes and found that the modulus did in fact behave in a very similar way to the observed tack force.

Toyama Ito and Moriguchi (1970a) used tack studies to determine the influence of surface properties on adhesion, using the polyken tack tester together with three types of pressure sensitive adhesive:

- a). Natural rubber - rosin ester.
- b). A copolymer of ethyl acrylate and 2-ethyl hexyl acrylate
- c). Poly ethyl vinyl ether.

Probes of various composition were used and their γ_c values determined using the sessile drop technique and aqueous solutions of di propylene glycol. The effect of contact time and rate of separation in the tack test were examined. Activation energies for viscosity and tack were calculated and compared. They concluded that tack measurement is related to the debonding process (not the bonding process). This view conflicts with that of Dahlquist.

The tack force was found to be variable with probe γ_c and a maximum in tack force was observed at the γ_c of the adhesive. Theoretically, this can be justified as the point where the interfacial surface free energy is at a minimum and hence the work of adhesion is a maximum. However, they over-looked a point which Hammond (1963) was careful to make. Uniform and identical surface roughness of probe materials of differing compositions is very difficult to achieve, and the effect of increasing surface roughness is to decrease the observed tack force. Toyama does not indicate surface roughness data and hence the results do not conclusively point to a surface energy effect.

In a subsequent paper, Toyama Ito and Moriguchi (1970b) demonstrated by a radio active tracer technique that apparent adhesive failure may in fact be cohesive failure in the surface region of the adhesive. This cohesive failure occurred at the point where the γ_c of the adhesive was equal to the γ_c of the probe and his interpretation of this was that the real area of contact was proportional to the γ_c of the probe material and that cohesive failure occurred at these points. This is not consistent with the experimental results since as the real area of contact tends to the apparent area of contact (increasing probe γ_c) a constant maximum tack force and

extent of cohesive failure would be approached. In fact a maximum is observed at a certain value of probe γ_c and any further increase in probe γ_c causes a decrease in tack force and in the extent of cohesive failure.

Kamagata, Kosaka, Hino and Toyama (1971) attempted to combine the work of Wetzel and Dahlquist using natural rubber and a rosin ester. They studied surface effects by contact angle measurements and electron microscopy and bulk effects using a torsion pendulum, viscosity measurement tensile testing and relaxation techniques. Torsion pendulum data and electron microscopy indicated the two phase nature of the adhesive system. Viscosity was found to be a minimum where the tack force was a maximum at temperatures up to 60°C. Activation energies were calculated from the viscosity data, and were in the range 3 - 5 K Joules mole⁻¹. They calculated "Young's modulus" from the tensile test data and found this to be a minimum where the tack peak occurred. This is unexpected as Dahlquist (1969) had found it to be a maximum. Relaxation techniques indicated a gradual loss in rubber properties with increasing resin content. Tack measurements showed the familiar peak in tack force at about 60 - 80% resin content. The authors noted that up to 60% resin content, the tack force was independent of dwell time.

Sherriff, Knibbs and Langley (1973) used a probe technique to measure the tack of various natural rubber/resin mixes. By using probes of varying critical surface tension, γ_c , they showed that for a wide range of resin concentration the tack force was higher for probes of high γ_c than for probes with low γ_c and the tack force resin concentration curves gave peak values at a certain resin concentration independent of probe composition.

The γ_c of the adhesives increased linearly with increasing resin concentration to approximately 36 ergs/cm² for pure resin. Variations in probe withdrawal speeds showed that tack force increases with increasing speed in only a certain restricted region near the tack force peak. At higher and lower resin concentrations this did not apparently occur. The position of the peak altered with probe withdrawal speed.

Without exception they showed that an increase in dwell time gave an increase in the observed tack force at every value of resin concentration.

By using a Weissenberg rheogoniometer they showed that at long times the storage modulus G^1 decreases and the addition of resin further reduces the values of G^1 observed. This corresponds to the dwell time in the probe tack test, hence the addition of resin promotes faster and more intimate wetting of the substrate and the resulting increased bond area will lead to higher observed bond strengths. At short times corresponding to the debonding stage, G^1 of the resin containing mixes increased above that of the rubber alone, hence a high value of tack force is observed as resin concentration increases.

However, the effect of adding resin is also to increase the glass transition temperature (T_g) of the adhesive mass until at a certain concentration, T_g is above room temperature. At this point the adhesive is unable to wet the adherend and a dramatic loss in bond strength is observed.

Sherriff argues that these effects occur independantly of any compatibility effects hence Wetzel's view that incompatibility is a prerequisite to tack is not correct.

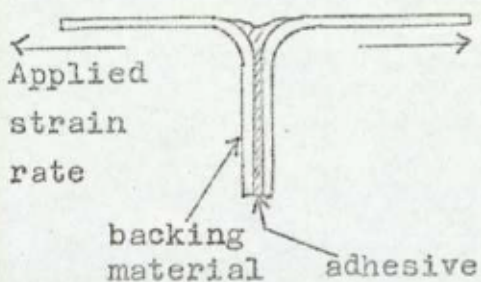
2.3.2 Peel Techniques - measurement and theory

The peel technique is widely used in adhesion science to yield information on the response of adhesive assemblies to a constant applied rate of testing. A flexible backing material is coated with a thin film of adhesive and the adhesive coated side laminate is then brought into contact with either a similarly coated laminate or alternatively a rigid or semi-rigid substrate.

The adhesive assembly formed is then tested at constant rate of testing and the force required is taken as a measure of peel strength. The following diagram indicates a few of the possible configurations.

Diagram (a)

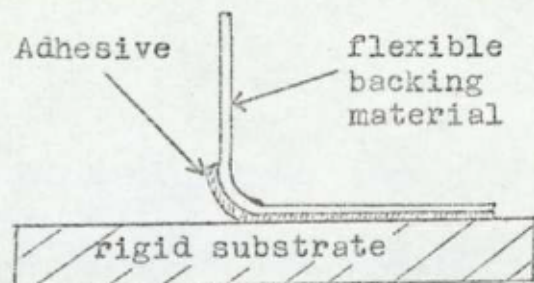
"T peel" configuration



(angle of peel = 180°)

Diagram (b)

90° peel configuration



The method was applied to tack tests by Busse Lambert & Verdery (1946), who concluded that the results obtained were characteristic of the peel assembly as a whole rather than of the adhesive mass alone. Since the flexibility of the substrate is involved, this test is not a fundamental measure of tack. Despite this, the method has been widely used.

Chang (1957) specified that a tape coated with adhesive be laid on a glass plate such that the weight of the tape alone was the contact pressure. The peel force was then a measure of tack. Again, the tape is involved in the process since it is deformed by bending, but the advantage of the method is the very low contact pressures.

Bull (1968) designed a tack testing apparatus in which the adherends were rigid. A rotating drum was covered with an adhesive tape, adhesive side upwards. A freely rotatable wheel was placed in contact with the adhesive under light pressure. The drums were rotated at fixed speed and the horizontal force necessary to retain the axis of the wheel in a stationary position was measured as the tack force. Using this method, it was not possible to retain constant dwell time whilst varying the rate of test. Also, the profile of the wheel had an important bearing on the results obtained.

An advantage of the method was that a large area of adhesive could be scanned so that any local surface variations were effectively averaged out. An important source of error was the way in which the adhesive tape was applied to the drum. This means that the effect of the substrate had not been effectively removed.

2.3.3 Measurement of tack by rolling ball or cylinder

The principle of the method is that a flat plane is inclined to a certain angle and a film of adhesive placed on the lower portion of the plane. A sphere or cylinder of metal is released from the top of the inclined plane and allowed to roll down the plane for a certain distance before coming into contact with the adhesive film. The distance travelled on the adhesive before coming to rest is taken as a measure of tack. It is usually assumed that whilst in motion on the adhesive, the velocity of the ball is constant and that motion is instantaneously arrested. The distance travelled on the adhesive is not easily measured and hence a large number of tests are necessary in order to obtain a good estimate of the mean.

Dow (1954) and Condon (1959) suggested that this type of method be used for tack measurement. The rolling ball

method is in fact a low angle peel in which a non constant rate of test is employed.

Simon (1971) attempted to differentiate 'dynamic' and 'static' tack. He defined dynamic tack as the resistance to sliding of an article over an adhesive surface. This definition confuses tack with friction. He defined static tack as the force necessary to withdraw an adherent after lightly contacting the adhesive with the adherend. This test is not static. He used the rolling ball test method and derived an equation for tack which had the units of velocity and found the tack of polyisobutylene to be 7.2732 cm/sec.

Kamagata Saito and Toyama (1970) recently demonstrated by a photographic method, that the velocity of the rolling ball on the adhesive is not constant but decreases linearly with time. They also showed that on a plane surface the ball may slide rather than roll and they devised an S shaped track which eliminated this problem.

2.4 Relationship between Applied Stress and Strain in a Viscoelastic Material

The literature on tack has indicated that the modulus of the adhesive has a bearing on the observed tack. In the simplest case, i.e. in which deformation is completely reversible, the ratio of the applied stress to the induced strain is a constant and is termed the modulus. Boltzmann (1876) using the assumption that observed strain is proportional to the applied stress stated that the total effect of applying several stresses is the same as applying a single stress which is the sum of applying each one separately. Mathematically, if an ideally elastic material of modulus E is subjected to series of small tensile strains $\epsilon_0, \epsilon_1, \epsilon_2, \dots, \epsilon_n$ at times $t = 0, t_1, t_2, \dots, t_n$ then after the total elapsed time

$$\begin{aligned}\sigma &= E\epsilon_0 + E(\epsilon_1 - \epsilon_0) + E(\epsilon_2 - \epsilon_1) \dots\dots\dots (20) \\ &= E\epsilon_n\end{aligned}$$

where σ is the stress and $\epsilon_n = \epsilon_0 + (\epsilon_1 - \epsilon_0) \dots\dots (\epsilon_{n-1} - \epsilon_{n-2})$

In viscoelastic materials however, E is not a constant but varies with time. This does not affect the principle for small reversible deformations.

Let E_t denote the modulus at any time t then

$$\sigma_t = E_{t_0} \epsilon_0 + E_{(t_0-t_1)} (\epsilon_1 - \epsilon_0) + \dots\dots\dots E_{(t_n-t_{n-1})} (\epsilon_n - \epsilon_{n-1})$$

This is a formal expression of the Boltzmann principle.

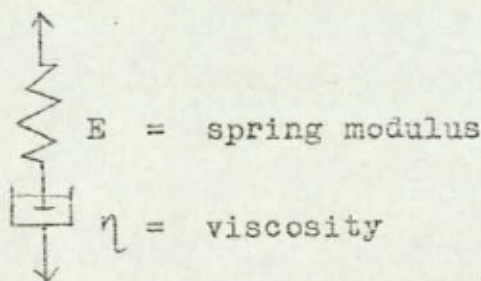
If instead of applying incremental strains, a continuously increasing strain is induced, then the sum may be replaced by an integral:

$$\sigma = \int_0^t E_{(t-\theta)} \frac{d\epsilon_\theta}{d\theta} d\theta \dots\dots\dots (21)$$

where θ is the current time $0 < \theta < t$ and $d\epsilon_\theta/d\theta$ is the extension rate at time θ . Note that the curve of σ_t/ϵ_0 versus t should be independant of the actual value of strain.

The above reasoning may further be applied to materials which are not perfectly elastic but which are viscoelastic. Maxwell proposed a simple model to describe the strain response of a viscoelastic solid which incorporated a perfectly elastic spring and a dashpot of newtonian viscosity, η in series.

Diagram 3



The equation of the model is the sum of the strain rates

in each element

$$\frac{d\epsilon}{dt} = \frac{\sigma}{\eta} + \frac{1}{E} \cdot \frac{d\sigma}{dt} \quad \dots\dots\dots (22)$$

In the situation when a constant strain ϵ_0 is applied to the model, $d\epsilon/dt = 0$ hence

$$\sigma_t = \epsilon_0 E \exp\left(-\frac{tE}{\eta}\right) \quad \dots\dots\dots (23)$$

η/E may be defined as the relaxation time of the model, that is the time required for the stress to be dissipated by the dashpot.

Equation 23 may be rewritten as

$$E_t = \frac{\sigma_t}{\epsilon_0} = E \exp\left(-\frac{t}{\tau}\right) \quad \dots\dots\dots (24)$$

If a series of n elements are coupled together and each element has a unique relaxation time τ_i then using Boltzmann's principle, the observed modulus is the sum of each individual modulus

$$E_t = \sum_{i=1}^n E_i \exp\left(-\frac{t}{\tau_i}\right) \quad \dots\dots\dots (25)$$

Finally, for an infinite number of elements

$$E_t = \int_0^{\infty} E_{\tau} \exp\left(-\frac{t}{\tau}\right) d\tau \quad \dots\dots\dots (26)$$

where E_{τ} is the modulus of the element of relaxation time τ .

It is experimentally more convenient to use a logarithmic time scale by defining $\frac{d\tau}{\tau} = d\ln\tau$ hence

$$E_t = \int_{-\infty}^{+\infty} E_{\tau} \tau \exp\left(-\frac{t}{\tau}\right) d\ln\tau \quad \dots\dots\dots (27)$$

Defining $H = \tau E_{\tau}$ then the equation becomes

$$E_t = \int_{-\infty}^{+\infty} H \exp\left(-\frac{t}{\tau}\right) d\ln\tau \quad \dots\dots\dots (28)$$

H is termed the relaxation spectrum and is a characteristic of the material under consideration. Adhesive testing procedures often employ constant strain rate and the response of a series of Maxwell elements to a constant applied strain rate is deduced by an analogous procedure. In this case $\sigma_0 = 0$ and $\epsilon = At$ where $A = d\epsilon/dt$.

$$\sigma_t = A \int_{-\infty}^{+\infty} H \left(1 - \exp(-t/\tau) \right) d\ln \tau \quad \dots\dots\dots (29)$$

This equation is of interest since the debonding procedure used in adhesive testing is predominantly that of measuring the stress (or force) in an adhesive assembly at a constant applied strain rate. It also serves to illustrate why adhesive testing is so closely related to the modulus characteristics of adhesives.

To evaluate fully the modulus characteristics of any viscoelastic material requires the measurement of the strain and stress over many decades of time, in fact on a logarithmic time scale from $-\infty$ to $+\infty$. In a practical sense this is at first sight seemingly impossible. However Tobolsky and Ferry, working independently found that by measuring modulus properties with the experimentally convenient time scale but at many different temperatures, an empirical procedure could be devised which in effect measured modulus properties well into the regions of time which were experimentally inaccessible. This technique involved plotting all the results on identical ordinate and abscissa scales but to 'shift' the curves obtained horizontally until a single continuous curve was obtained. This purely empirical procedure implies that time and temperature are superimposable, i.e. that a variation in time is equivalent to a variation in temperature and vice versa.

These workers found that the amount of shift required was a function of the test temperature T and the glass transition temperature of the material T_g . Let the shift factor at temperature T be represented by a_T then

$$\log_{10} a_T = \frac{-C_1 (T - T_g)}{C_2 + T - T_g} \dots\dots\dots (30)$$

C_1 and C_2 were found to be constants which were the same for a wide range of viscoelastic polymers of widely differing chemical composition. Equation (30) is known as the W.L.F. equation after Williams Landel and Ferry (1955) who first indicated a theoretical justification of the equation. Doolittle (1951) had proposed that the viscosity of a material η is a function of the free volume, F , in the material. The free volume is the difference between the actual volume of a material V_T at temperature T and the volume occupied by the close packed mass of the material V_{Tg} which is assumed to be a minimum and a constant at and below the glass transition temperature, T_g , expressed as a fraction of V_T .

$$F = \frac{V_T - V_{Tg}}{V_T} \dots\dots\dots (31)$$

The Doolittle equation is

$$\eta = A \exp (B/F) \dots\dots\dots (32)$$

where A and B are constants.

Williams Landel and Ferry (1955) recognised the inadequacy of the activation energy concept viscosity in the case of polymeric liquids. Dilatometric experiments had shown that the glass transition temperature is characterised by a distinct change in slope of the volume-temperature curve. In other words, there is a discontinuity in the coefficient

of thermal expansion α . This arises from a reduction in molecular mobility as the temperature approaches T_g and William Landel and Ferry (1955) suggested that molecular mobility is a function primarily of the free volume remaining. This concept does not entirely contradict the activation energy theory of viscosity which states that the temperature dependence of viscosity is determined by an energy barrier for flow (which is in turn related to intermolecular forces) since this energy barrier could be related to the free volume available. However, the energy barrier theory leads to an equation of Arrhenius form which is not compatible with many viscosity measurements.

Ferry (1950) took the Doolittle equation and related the viscosity η_T at temperature T with the viscosity η_{Tg} at temperature T_g

$$\ln \eta_T = \ln A + \frac{B}{f_T} \dots\dots\dots (33)$$

$$\ln \eta_{Tg} = \ln A + \frac{B}{f_{Tg}} \dots\dots\dots (34)$$

whence $\ln \frac{\eta_T}{\eta_{Tg}} = B \left(\frac{1}{f_T} - \frac{1}{f_{Tg}} \right) \dots\dots\dots (35)$

where f is the volume fraction of free volume (V_f/V)

Ferry (1950) then assumed that $f_T = f_{Tg} + \alpha (T - Tg)$ hence

$$2.303 \ln \frac{\eta_T}{\eta_{Tg}} = \log_{10} a_T = - \frac{(B/2.303 f_g)(T-Tg)}{(f_g/\alpha) + (T-Tg)} \dots\dots\dots (36)$$

which is identical in form to the empirical equation.

The application of this type of approach to peel adhesion can be seen in the work of Kaelbe (1971) who defined the

peeling rate $P_{(Tr)}$ at temperature T and rate r in terms of the peeling rate $P_{(T_0 \text{ rat}_T)}$ at a standard temperature T_0

$$r = \text{Rate of test} = \frac{\text{Peeling Speed}}{\text{Adesive Film Thickness}} \dots\dots\dots (37)$$

$$P_{Tr} = \frac{T}{T_0} \cdot \frac{d}{d_0} \cdot P_{T_0 \text{ rat}_T} \dots\dots\dots (38)$$

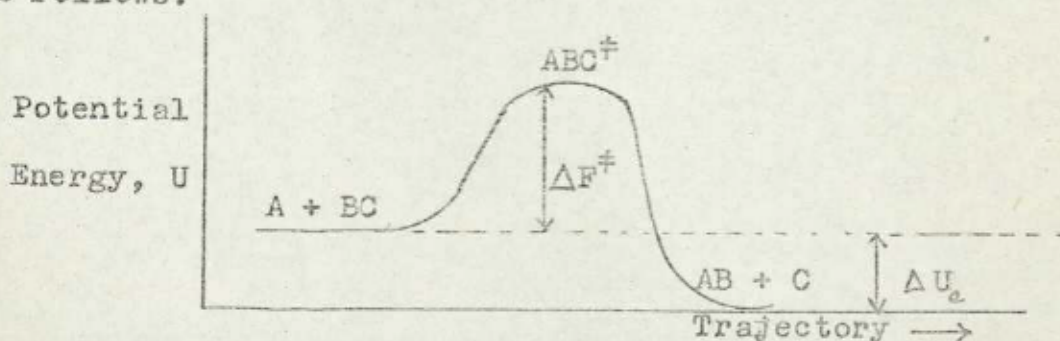
where a_T is a shift factor used in an identical fashion to the shift factor of the W.L.F. equation. From this, a master curve of peeling force plotted against $\log_{10}$ rate can be constructed.

Outline of Basic Reaction Rate Theory

As will be explained later, this thesis uses the Absolute Reaction Rate Theory to describe the bond formation between adhesive and substrate (termed the bonding step) in terms of bulk and interfacial effects.

Eyring (1941) used a two stage analysis to predict reaction rates in the gas phase : a quantum mechanical calculation of the ground state electronic energy surface (potential surface) for the reaction followed by a statistical mechanical calculation of the reaction rate.

The trajectory of a particle along the potential surface during reaction was described as an activation energy process in which this activation energy $\Delta F^\ddagger$ raised the potential energy of the particle sufficiently for reaction to take place. Diagrammatically, this may be represented as follows:



The activated complex $ABC^\ddagger$ was assumed to be a stable molecule in equilibrium with reactants A and BC. Eyring went on to show that the rate of reaction was the rate of decomposition to products of $ABC^\ddagger$:

$$\text{Reaction Rate} = C_0 \frac{kT}{h} \exp \frac{-\Delta F^\ddagger}{RT} \dots\dots\dots (39)$$

where k = Boltzmann's constant
 h = Planck's constant
 C_0 = concentration of activated complex
 R = Universal Gas Constant
 T = Absolute temperature.

Theoretically it is possible to calculate this rate from fundamental properties of the gaseous molecule, hence the term 'Absolute' Reaction Rate.

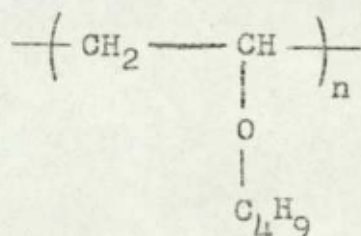
The theory was applied by Eyring to many processes both in the gaseous and liquid states to explain the observed experimental facts with a certain degree of success. This thesis utilises the application of the theory to viscous flow processes.

C H A P T E R 3

EXPERIMENTAL METHODS USED TO STUDY TACK

The experimental work was carried out using a single adhesive composition. The composition was a blend of three types of poly (isobutyl vinyl ether) differing in molecular weight only. This polymer whose structure is indicated diagrammatically below is commercially available and is used in industry in the manufacture of pressure sensitive adhesives.

Diagram Structure of Poly (isobutyl vinyl ether)



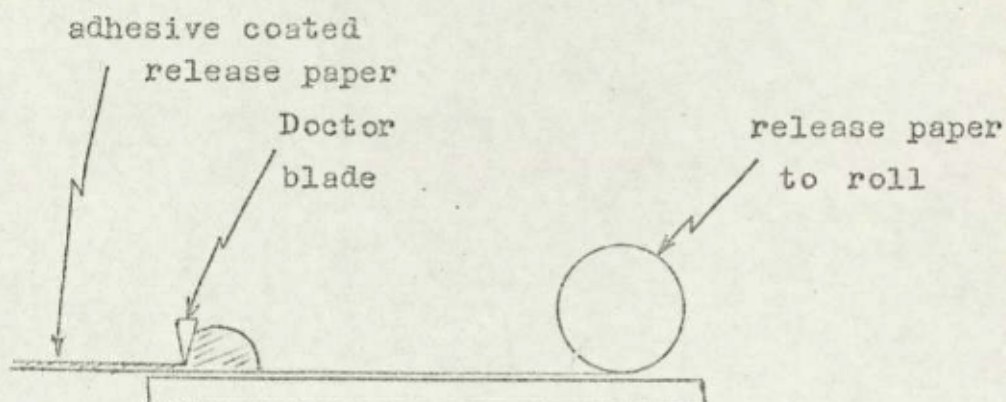
Experience has shown that a satisfactory blend of properties is obtained by using three different molecular weights in the following proportions by weight:

Poly (isobutyl vinyl ether)	(M = 30,000)	33.0g
Poly (isobutyl vinyl ether)	(M = 60,000)	16.8g
Poly (isobutyl vinyl ether)	(M = 125,000)	12.3g

The polymers were commercially available from B.A.S.F. (UK) Ltd., Cheadle Hulme. The blend was obtained by dissolving the three components in toluene, unless otherwise stated. After the components had completely dissolved, the adhesive was isolated in the form of a thin film by using

a doctor blade technique indicated in the following diagram:

Diagram 4



A roll of silicone coated release paper (type 001517 supplied by Sterling Coated Materials Ltd. of width 180 mm was coated with a thin uniform film of adhesive solution using the doctor blade which had been adjusted to yield a known constant thickness of adhesive solution. The desired thickness of wet adhesive film was in the range of 0.1 to 1.00 mm.

The solvent was evaporated from the adhesive in a dust free atmosphere for 24 hours, then further dried for 72 hours at 5 mm mercury pressure at 20°C. A portion of the dried adhesive film was then laminated to a clean glass plate of dimensions 152 mm x 100 mm x 4 mm whilst still attached to the release paper, taking extreme care to avoid the inclusion of air bubbles between the glass plate and the adhesive film. The release paper was then removed from the adhesive film and discarded. This yielded a glass plate covered on one face by a continuous adhesive film of uniform thickness and composition, which was then stored in a dust free environment until used.

A portion of the remaining adhesive/release paper laminate was then laminated to a second piece of clean release paper such that the adhesive formed an inter-layer between the two pieces of release paper. A circular disc of accurately known area was cut from the laminate using a metal punch. The weight of this disc was measured to 0.1 mg and then the adhesive was removed and the weight of the two paper discs was measured to 0.1 mg. From these measurements, the weight of a known area of adhesive film of uniform thickness was deduced to 0.1 mg. This figure was re-expressed as grams weight per square metre of adhesive film and was usually in the range of 40-150 g/m².

From the density of the adhesive (0.806 g/ml) the thickness of the adhesive film was derived and was usually in the range 0.5 - 1.5 mm.

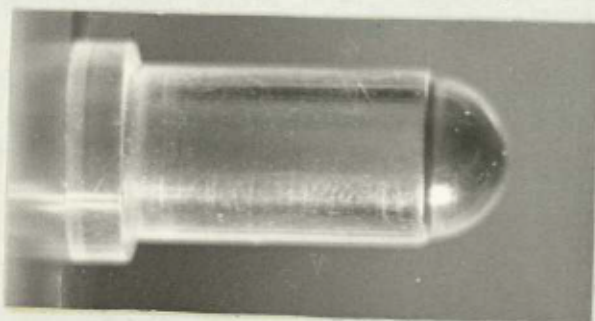
3.1

Measurement of Tack by the Probe Technique

The principle of the Probe method was outlined by Hammond (1963) and by Wetzel (1964) and was indicated in Chapter 2. A probe of known dimensions was brought into contact with the adhesive film supported on a glass plate, under known conditions of pressure and time. After a pre-set, finite time, the probe was withdrawn and the force required to cause adhesive failure between probe and adhesive was measured.

The geometry of the probe used in the work described here is indicated below:

Diagram 5.



It consisted of a solid cylinder of material 10 mm in diameter and total length 25 mm. At one end, the cylinder was shaped to a hemisphere of radius of curvature 4.5 mm. At the other end was a circular collar thickness 3 mm and radius 6.25 mm which was an integral part of the probe.

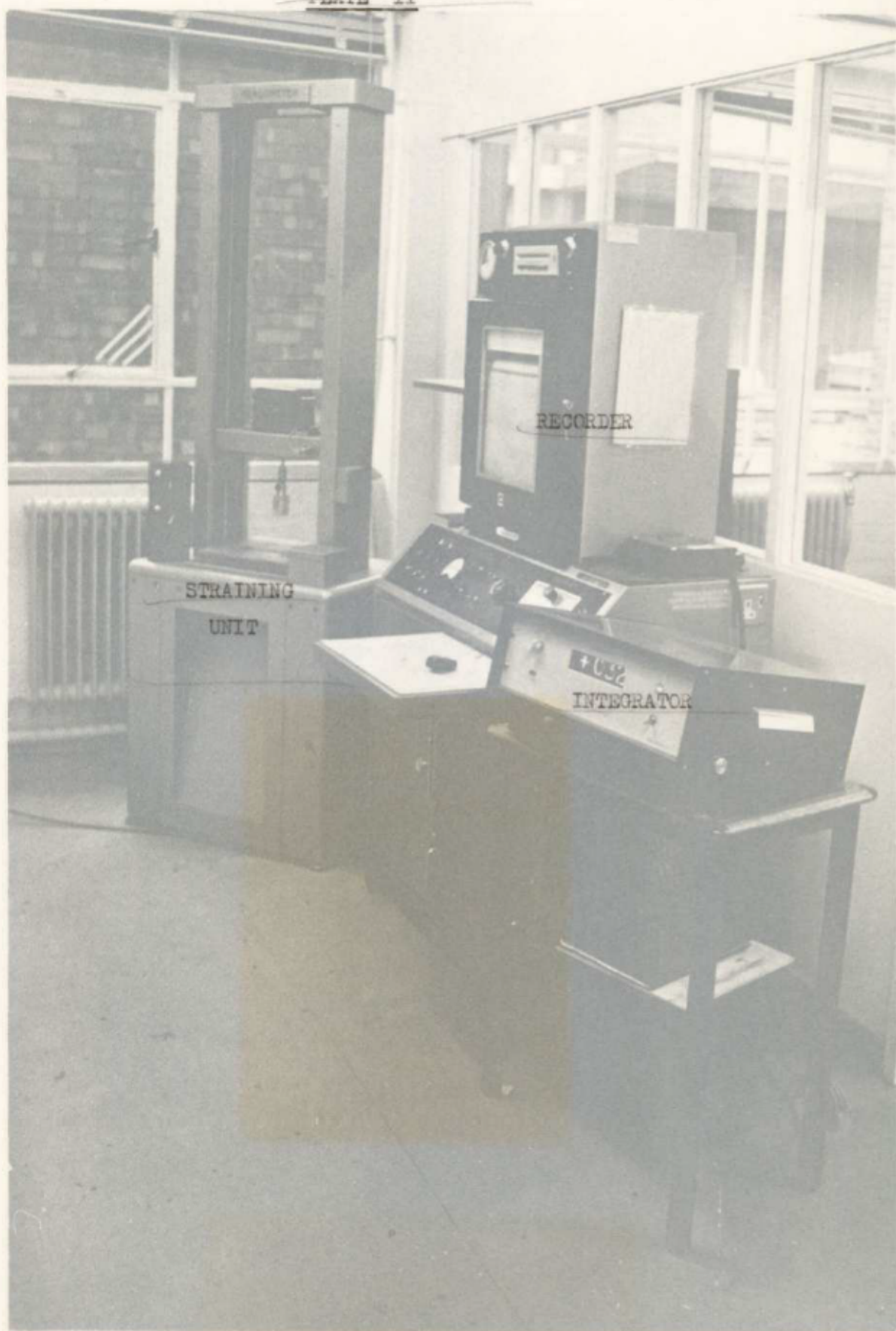
The probe was attached to a tensile testing machine load-detecting cell by means of a holder. This was a cradle holding the probe in the vertical plane with minimal friction losses between probe and probe holder. The tip of the hemispherical section of the probe was the portion which came into contact with the adhesive film. The arrangement is indicated in Plate I and the general view of the tensile testing machine is indicated in Plate II.

Plate I



The tensile testing machine was a Tensometer Type E series N10 (Monsanto Tensometer Ltd., Swindon) and the adhesive film on the glass plate was supported horizontally on a steel table which rested on the base housing of the

PLATE II





Tensometer. This steel table was accurately levelled by its levelling screws. The load detecting cell (to which probe and probe holder were attached) was positioned on the mobile crosshead of the Tensometer, which moved in the vertical plane at any pre-selected velocity such that the probe could be brought into contact with and removed from the adhesive film as required for tack force determination.

By suitable arrangement of limit switches, the downward travel of the crosshead was automatically arrested as soon as the probe came into contact with the adhesive film. The compressive force on the film was then the weight of the probe alone. The upper limit switch was used to restrict the upward movement of the crosshead from the contact position to 3 mm. In practice, this was beyond the point at which adhesive failure occurred.

The load detecting cell to which the probe and probe holder were attached was a transducer which measured electronically the deflection of a steel beam under the action of the debonding force. The deflection was converted to an electrical signal which was then relayed to an electronic pen recorder (Speedomax G, Leeds and Northrup Ltd., Birmingham) which was an integral part of the Tensometer Type E. In the recorder, the electrical signal was amplified and followed by a motor driven pen recorder on chart paper as a deflection in the x direction proportional to the force. Concurrent with this deflection, the chart paper moved uniformly in the y direction, such that movement was linearly proportional to the time or distance of crosshead movement. The results of the tests were therefore recorded as the variation of force with time or distance of crosshead movement. Generally, the observed force was in the range 20 - 80g, and consequently the recorder was set for

a full scale deflection in the y direction of 100 g force.

The theoretical considerations discussed earlier indicated that the energy of tack was to be measured and this was done using a digital x-y integrator in conjunction with the recorder. The instantaneous force and the corresponding chart movement were fed into the integrator by means of a digitizer. This digitizer converted the product of force and distance into electronic pulses which were counted and displayed visually by Nixie display tubes. The displayed counts were recorded manually on the chart paper.

The calculation of energy from the displayed number of counts was as follows:

$$\text{Total energy} = \frac{C \times 1.27 \times 0.98}{20000 \times X} \text{ Joules} \quad \text{..... (40)}$$

where X = chart magnification factor
= $\frac{\text{speed of chart movement}}{\text{speed of crosshead movement}}$
C = number of observed counts.

The principle of operation of the integrator was to break down the area under the force-distance curve into a number of rectangles. The area of each rectangle was computed and the individual areas summed to give the total area. This area was only absolute when the increments of force and distance were reduced to an infinitely small value. The integrator was designed to give an accuracy of the display within 1% of the total area.

3.2 Procedure for measuring the tack energy of an adhesive

The adhesive supported on a glass plate was placed on the steel table described in section 3.1 on the base of the

Tensometer housing, adhesive side upwards. By operating the controls of the Tensometer the probe /probe holder which were attached to the load cell were brought vertically downwards at a constant selected speed until the tip of the hemisphere of the probe was in contact with the adhesive. At the instant of contact a stop watch was started and the downward movement of the probe was simultaneously arrested by the automatic operation of the lower limit switch. After a predetermined time interval, termed the 'dwell time', the crosshead was moved in the reverse direction at constant speed until the probe had separated from the adhesive film. The force and energy were recorded. This procedure was repeated five times using a different portion of the adhesive film for each determination. The average energy reading was then determined and was taken as the tack energy of the adhesive under the imposed conditions. Several parameters were independently varied : dwell time, temperature, speed of probe withdrawal, adhesive film thickness, applied probe load, probe composition and the environment of storage of the adhesive prior to test.

For variation of temperature, the adhesive probe and probe holder were enclosed in a constant temperature circulating oven (Sondes Place Research Institute, Dorking, Surrey), the temperature being controlled to $\pm 2^{\circ}\text{C}$ and a conditioning time of thirty minutes was allowed at each temperature such that the adhesive was in thermal equilibrium with its environment.

3.3 Estimation of Errors involved in the described method.

An estimation of the variability involved in the described technique was obtained by reference to the coefficient of variation and how this varied with the imposed test

conditions. The standard deviation (SD) in a group of random data is a measure of the scatter of the data around the arithmetic mean of the data. If there are n results and each result is expressed as x_i

where $i = 1, 2, 3 \dots n$ then

$$SD = \frac{\left(x_i^2 - \frac{(x_i)^2}{n} \right)^{1/2}}{n - 1} \dots \dots \dots (41)$$

The coefficient of variation is the ratio of the standard deviation to the arithmetic mean of the data expressed as a percentage.

$$C.O.V. = \frac{SD}{mean} \times 100 \dots \dots \dots (42)$$

Using the same adhesive, the parameters in the tack test were varied over a wide range and an estimation of the coefficient of variation used to assess the variability of the data in order to assess the useful working range of the machine. A low value of C.O.V. implied a narrow distribution of the data around the mean of the data and hence statistically, a more acceptable result, assuming that the results follow a normal distribution about the mean.

Table I refers to tack energy determinations on the poly isobutyl vinyl ether using a polytetrafluoroethylene (P.T.F.E.) probe, loaded to 4.1 g weight using a dwell time of 10 seconds and variable probe withdrawal speeds. Table II refers to the same conditions except that the probe material was poly methyl methacrylate (perspex). In both cases, the adhesive film thickness was 1.45 mm.

TABLE I

Reproducibility of tack energy results at varying
probe withdrawal speeds (PTFE probe)

Probe Speed (mm/ min)	Tack Energy (μ Joules)	Average	S.D	COV %
145.0	234.6, 227.4, 205.7, 148.0, 209.3	205.0	34.1	16.7
116.0	207.9, 207.9, 144.4, 184.8, 167.5	182.5	27.3	15.0
87.0	168.9, 164.5, 138.5, 166.7, 201.3	168.0	27.1	16.1
58.0	167.4, 144.4, 135.7, 183.3, 148.7	155.9	20.5	13.1
29.0	163.8 159.5, 152.3 145.1, 152.3	154.6	8.0	5.2
14.5	153.8 171.4 167.1 168.9	165.3	7.5	4.6
7.25	120.7, 118.0, 129.8, 125.6, 119.6	122.6	7.3	5.9

TABLE II

Reproducibility of Tack energy results at varying
probe withdrawal speeds (perspex probe)

Probe Speed (mm/ min)	Tack Energy (μ Joules)	Average	S.D.	COV %
145.0	591.7, 56.28, 598.9, 534, 472.6	552.2	54.3	9.8
116.0	412.9, 404.2, 485.1, 366.7, 672.8	523.2	131.6	25.0
87.0	526.2, 502.4, 435.3, 491.6, 448.3	481.6	39.1	8.1
58.0	473.6, 451.9, 438.9, 446.2, 440.4	450.2	14.9	3.3
29.0	331.4 337.0, 363.1, 348.7, 311.2	338.3	22.2	6.6
14.5	305.4, 310.8, 242.2, 280.1, 237.6	275.0	31.5	11.5
7.25	193.6, 180.5, 174.6, 184.9, 180.9	182.9	8.2	4.4

In Table I it is apparent that at high probe speeds the results show more scatter than at low probe speeds. It was probable that at high probe speeds, the duration of the tack determination was of the order of one second or less and approaching the one second response time of the recorder.

To verify this, the chart records were examined and the duration of each determination deduced from the extent of chart movement during the tack determination. This was also done for the data obtained in Table II, and the results are indicated in Tables III and IV.

TABLE III

Duration of Tack energy determination with varying probe withdrawal speeds (refers to data in Table I)

Speed of Probe (mm/min)	145.0	116.0	87.0	58.0	29.0	14.5	7.25
Chart movement during test (mm)	1.75	1.90	2.10	3.0	6.0	13.0	15.0
Chart movement in 1 sec. (mm)	4.16	4.16	4.16	4.16	4.16	4.16	4.16

TABLE IV

Duration of Tack energy determination with varying probe withdrawal speeds (refers to data in Table II)

Speed of Probe (mm/min)	145.0	116.0	87.0	58.0	29.0	14.5	7.25
Chart movement during test (mm)	3.0	3.5	4.25	6.0	11.5	10.0	19.0
Chart movement in 1 sec. (mm)	4.16	4.16	4.16	4.16	4.16	4.16	4.16

In both Tables III and IV, certain determinations were less than the one second response time of the recorder in duration and consequently inaccurate, since the results have a negative bias and do not follow the normal distribution around the true mean.

Excluding the results obtained below the one second response time, the average C.O.V. in Tables I and II is 6.2%. This figure therefore defines the average level of reproducibility attainable by the method. Using a constant probe speed, dwell time, probe load and composition, the variation of C.O.V. with adhesive film thickness was determined.

TABLE V.

Reproducibility of tack energy results at various values of Adhesive Film Thickness (Probe load 4.1g, Dwell time 10 secs., Probe Speed 58 mm/min)

Film Thickness (mm)	Tack Energy (μ J)	Average	SD	C.O.V. %
1.79	440.6, 453.6, 561.6, 553.0, 368.6	504.0	83.0	16.5
1.64	441.7, 487.9, 551.4, 368.8, 412.6	446.0	70.8	15.8
1.19	342.1, 363.8, 359.4, 389.8, 330.6	358.0	25.5	7.1
1.06	271.4, 290.0, 287.3, 233.9, 280.0	276.0	13.3	4.8
	281.4, 267.1, 265.6, 281.5, 301.7			
0.76	196.3, 140.0, 207.9, 210.8, 186.2	187.5	15.1	8.1
	184.8, 155.9, 171.8, 216.5, 181.9			
0.53	114.0, 92.4, 99.6, 140.0, 102.4	112.5	9.4	8.3
	122.6, 103.8, 128.4, 134.1, 93.7			

At the two highest levels of film thickness, the coefficient of variation is in excess of 10% whereas it is in the range 4 - 8% for the remaining film thicknesses. There is no obvious explanation for this, but in all tack determinations, film thickness did not exceed 1.5 mm.

TABLE VI indicates the variation of C.O.V. with dwell time using a perspex probe, 2.5g probe bond, a probe speed of 58 mm/min and an adhesive film thickness of 1.50 mm.

TABLE VI

Reproducibility of tack energy results
at various Dwell Times

Dwell Time (Secs)	Tack Energy (μ Joules)	Average	SD	C.O.V. %
2	212.0, 219.2, 190.4, 216.3, 167.3	201.0	22.3	11.1
5	256.7, 213.5, 262.5, 263.9, 216.3	242.6	21.7	8.9
10	284.1, 298.6, 302.9, 315.9, 330.3	306.4	19.9	6.5
20	367.8, 402.4, 408.2, 379.3, 425.5	396.6	24.8	6.25

At short dwell times, the C.O.V. is larger than at long dwell times. The origin of this effect is at least partly due to the fact that the dwell time was controlled manually. At short dwell times any slight error would have a larger effect on the observed energy than at long dwell times since the tack energy is changing most rapidly during the initial time interval just after contact.

Another point however is that at short dwell times the value of tack energy is small and may even be sufficiently small in duration to pass below the one second response time of the recorder. Table VII indicates clearly that at dwell

times less than five seconds the duration of the tack test is less than one second.

TABLE VII

Duration of Tack Energy Measurements with
Dwell Time (refers to data in Table VI)

Dwell Time (secs)	2	5	10	20
Chart Movement (mm)	4.0	4.5	5.0	5.5
Chart Movement in one second (mm)	4.16	4.16	4.16	4.16

The results obtained at two seconds are consequently incorrect since the sample mean is less than the true mean.

TABLE VIII indicates the reproducibility of the tack energy results with temperature using a perspex probe weight 4.41g, an adhesive film thickness of 1.39 mm, 10 seconds dwell time and a probe withdrawal speed of 58 mm/min.

TABLE VIII

Reproducibility of Tack Energy results
at various temperatures

Temperature (°C)	Tack Energy (µJoules)	Average	SD	C.O.V. %
12-15	347.6, 301.4, 263.9, 288.5, 338.9	308.4	36.0	11.7
18-20	441.4, 451.4, 477.4, 452.9, 448.6	454.8	15.5	3.4
24	390.9, 354.5, 396.6, 403.8, 403.8,	390.4	21.0	5.4
31	331.7, 354.8, 326.0, 354.8, 356.3,	345.1	13.0	3.8
36	377.9, 300.0, 315.9, 376.4, 377.9	350.0	33.5	9.6

With the exception of results obtained at 12-15°C, the C.O.V. is less than 10% indicating that temperature has little effect on reproducibility.

The accuracy of the automatic integrator was checked by measuring the area of paper enclosed by the curve obtained during a tack determination and comparing with the indicated area. The area was conveniently determined firstly by cutting out and weighing a known area of chart paper and hence deducing the weight per unit area.

The chart record of two tack energy determinations were cut out using a very sharp scalpel and these were weighed. From the energy count the area indicated by the integrator was deduced from the fact that 10^4 counts corresponded to 61214 mm². The results are indicated in Table IX.

TABLE IX

Comparison of determination of tack energy by
automatic and manual techniques (506.7mm²
chart paper $\equiv$ 0.0318g)

Automatic Determination		Manual Determination	
Counts Recorded	Indicated Area (mm ²)	Weight of Area (g)	Area (mm ²)
40	244.90	0.0150	239.0
15	91.82	0.0056	89.23

The results show that the integrator may be relied upon to give an accurate measure of tack energy within $\pm 3\%$

CHAPTER 4

MEASUREMENT OF TACK ENERGY OF POLY (ISOBUTYL VINYL ETHER) BY THE PROBE METHOD.

The procedure for measuring tack and the limits of accuracy of the method have been discussed in Chapter 3. The definition of tack quoted in Chapter 1 indicated that the substrate should contact the adhesive under a definite pressure. Figure 1. indicates the variation of tack energy with applied pressure (i.e. probe load) using three different adhesive film thicknesses. In each case, increasing probe load gives an increasing tack energy. This is related to the bonding process in which the adhesive wets the substrate. Huntsberger (1967) has stated that wetting is the process whereby adhesive and substrate come into sufficiently close contact for the adhesive bonding forces to operate as indicated in section 2.3.1. He stated that the driving force for the wetting process is the applied pressure and the time of application of this pressure. Obviously therefore, an increase in probe load will increase the speed of the wetting process and hence of bond formation. The process of wetting depends on the conformability of the adhesive to the contours of the substrate surface, and this conformability is a function of the adhesive compliance. The compliance of a visco-elastic material is not simply the reciprocal tensile modulus (Ferry 1961) hence there is no simple way of correlating the adhesive modulus with the extent of wetting.

A more serious defect of the probe technique is that the volume of adhesive involved in the tack test is unknown

and variable. Observation of the adhesive surface after the tack test showed a circular distortion of the film surface. The circle diameter was estimated using a travelling microscope and was found to vary with probe load and film thickness. The volume of adhesive involved in each tack determination was then estimated firstly by calculating the area of the circle and assuming cylindrical geometry, multiplying this area by the film thickness.

The results are indicated in Table X

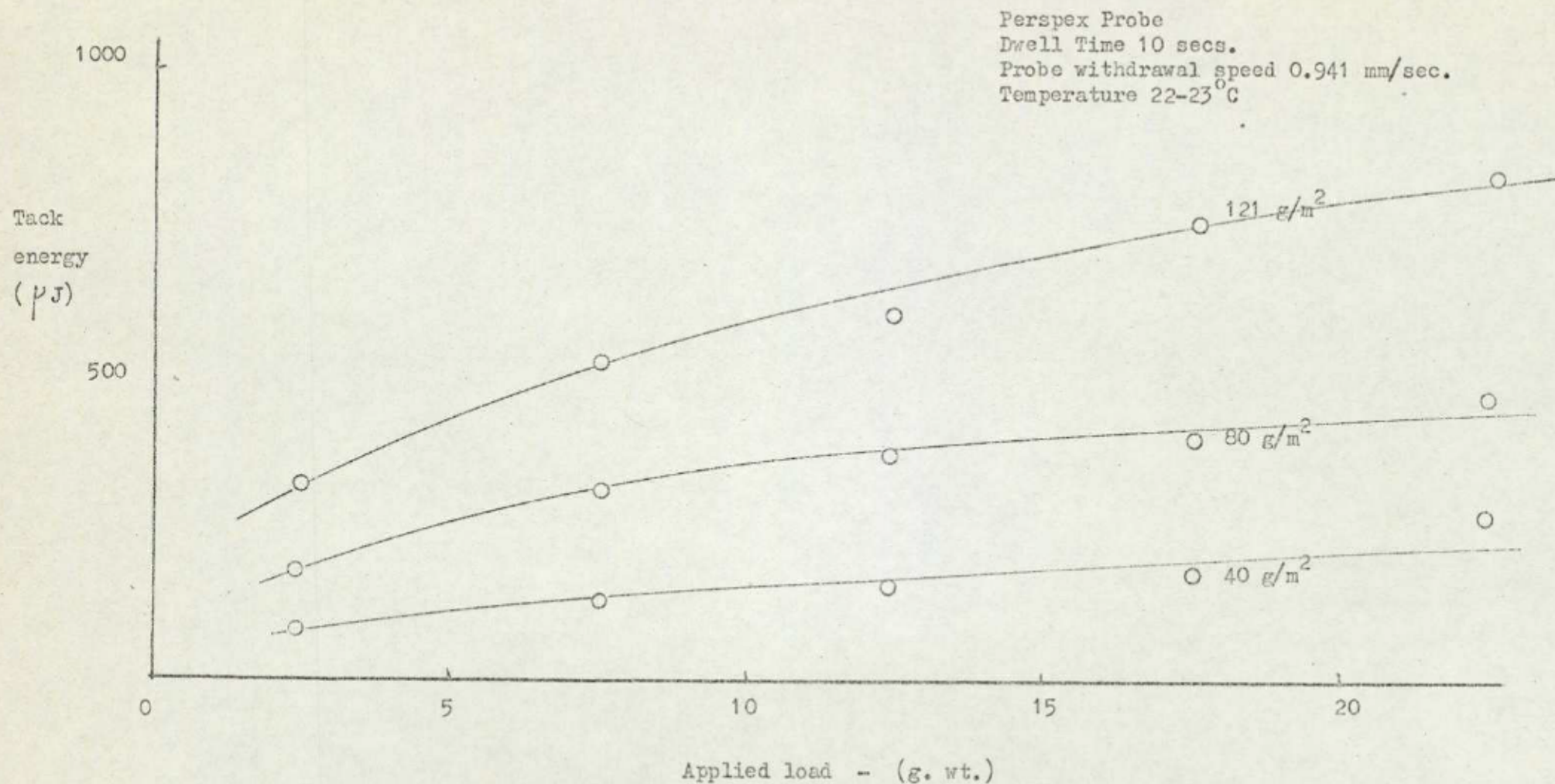
TABLE X

Estimation of the volume involved in the tack test at constant dwell time. probe withdrawal speed, temperature and probe composition

Probe Load (g)	Estimated volume $\text{cm}^3 \times 10^6$			
	Film Thickness (mm)	0.49	0.99	1.48
2.5		14.3	42.6	95.2
7.5		21.8	66.0	146.7
12.5		23.1	81.5	164.6
17.5		27.9	90.5	188.4
22.5		28.0	100.0	209.0

Comparing the data in Table X with figure 1, the effect of increasing probe load and film thickness is to increase the volume of adhesive involved in the tack test as well as the observed tack energy. However, the variation of tack energy per unit volume with probe load is not constant but increases with probe load.

Figure 1. Variation of tack energy with probe load and film thickness



Using constant dwell time, temperature and adhesive film thickness, the variation of tack energy with probe withdrawal speed was observed at five different values of probe load and the results are indicated graphically in Figure 2. In every case, the effect of increasing probe speed is to increase the tack energy, and reflects the fact that tack energy (being a function of adhesive modulus) is strongly rate dependant. This bears out Dahlquist's view (1959) that tack is strongly dependant on the adhesive's mechanical properties.

One other feature of Figure 2 is that increasing probe load increases the observed tack energy and that this effect is observed over a wide range of probe withdrawal speeds. In arriving at a definition of tack, it is therefore difficult to define a unique and significant bonding pressure, or debonding rate.

Figure 3 and 4 indicate that as the dwell time increases so does the observed tack energy. Measurements were made over a wide range of dwell times and probe withdrawal speeds. Again, the strong rate dependancy of the tack energy is apparent. The dwell time is of significance in the bonding stage as during this interval, interfacial contact of adhesive and substrate is increasing, which in turn will result in greater observed bond strength (i.e. tack energy) at the debonding stage. At long times, the increase of tack energy with dwell time is much less marked than at short times. For instance, referring to Figure 4 at 57 mm/min probe withdrawal speed, the observed tack energy at 10 seconds dwell time is approximately half that observed at 60 seconds dwell time. This suggests that ultimately at very long dwell times bond formation will be complete and no further increase of tack energy with dwell time will be observed. This would be achieved at times

Figure 2. Variation of tack energy with probe load and withdrawal speed

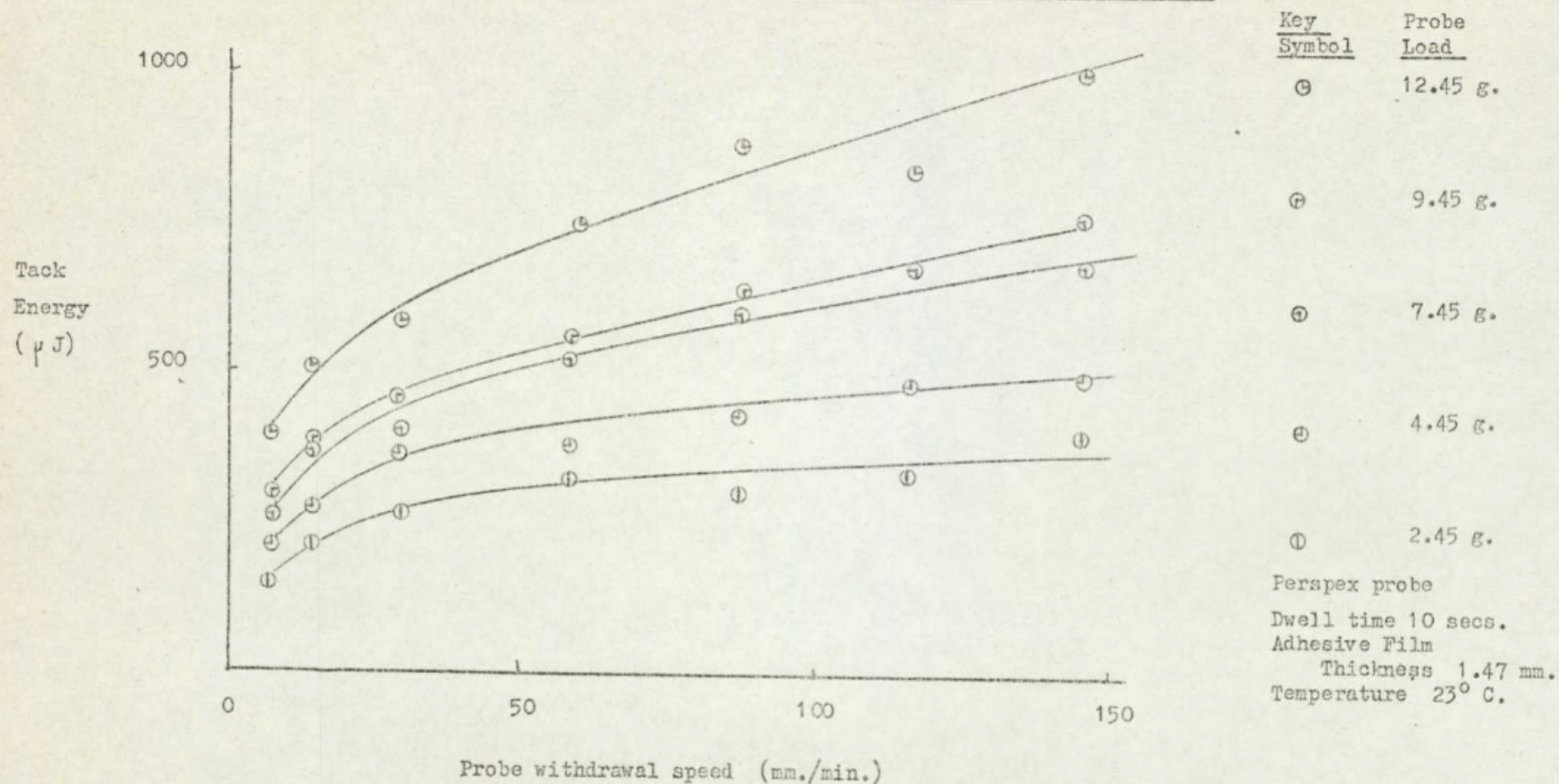


Figure 3. Variation of Tack Energy with Dwell Time and Probe Withdrawal Speed

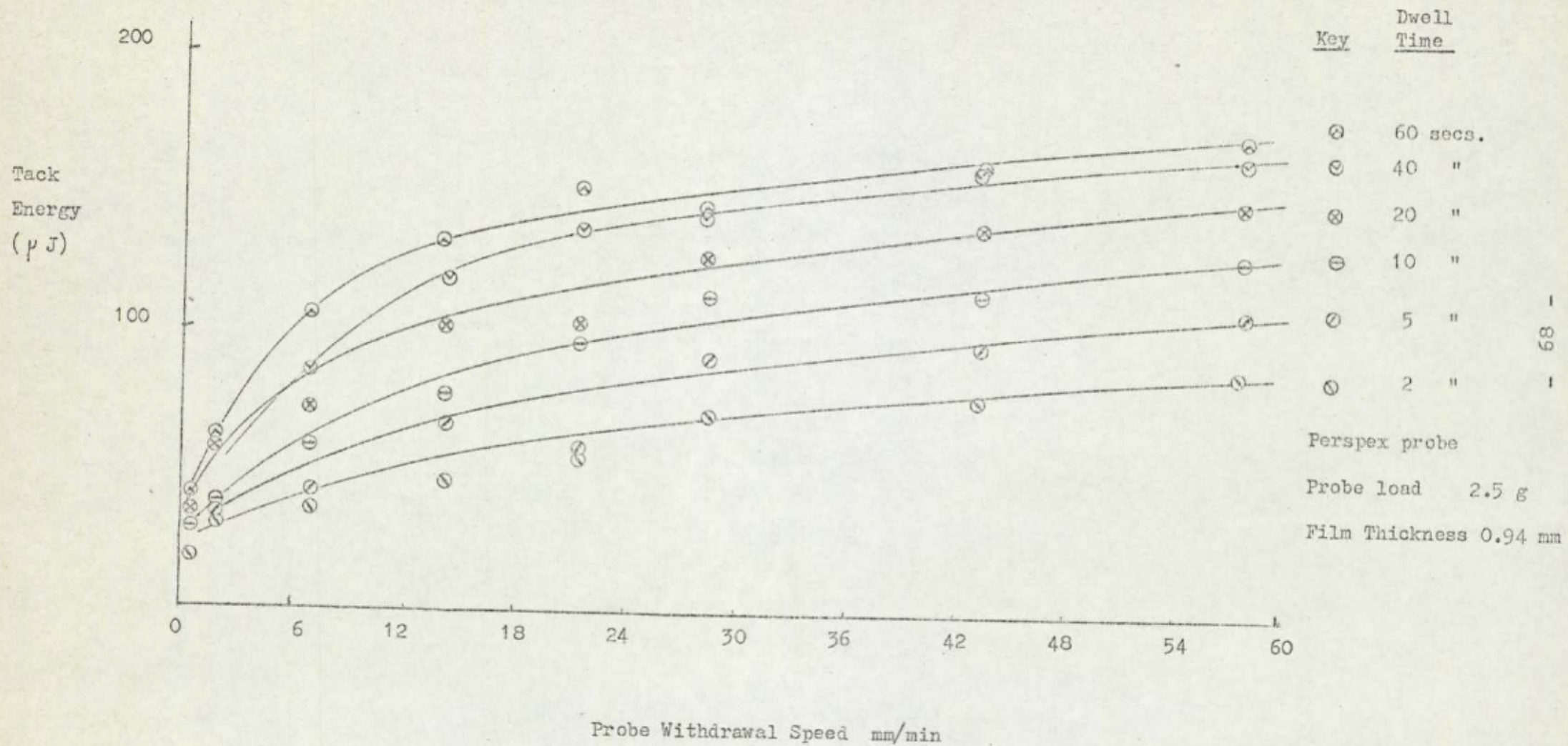
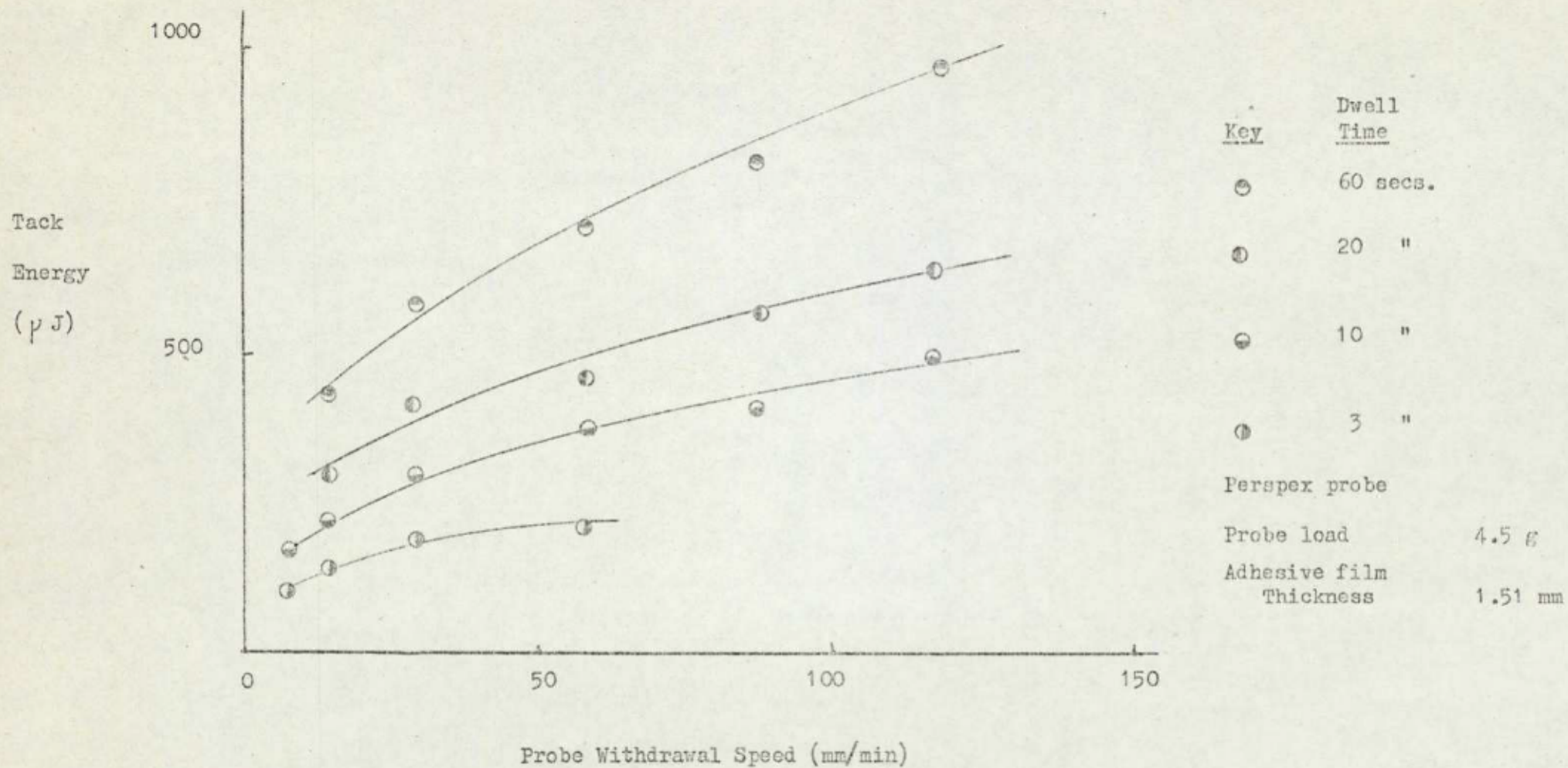


Figure 4. Variation of Tack Energy with Dwell Time



in excess of the maximum relaxation time, τ_m . This value of τ_m represents the time at which the elastic component of stress within the adhesive has decayed to zero due to viscous flow processes and at this point wetting is complete.

The dependance of tack energy on temperature is indicated in Figures 5 and 6. The tack energy in Figure 5 is zero at temperatures below 270°K due to the fact that the adhesive is no longer able to form an adhesive bond. A fairly steep increase in tack energy occurs in the temperature range 270 - 295°K then a gradual decrease in tack energy occurs in the temperature range 295 - 320°K. Above this temperature, cohesive failure occurred in the adhesive film.

This behaviour was observed by Dahlquist (1969) using rubber/resin mixes and was explained on the basis of two conflicting processes. As temperature decreases in the range 270 - 295°K, the elastic component of the adhesive modulus increases giving an increase in the stored elastic energy and hence tack energy. A concurrent decrease in viscous flow occurs. This viscous flow process is responsible for the wetting process consequently as temperature falls so does the extent of wetting, but this is compensated for by a large increase in stored elastic energy. Below a certain temperature, the extent of bond formation becomes so limited that a decrease in tack energy occurs even though the stored elastic energy is rapidly increasing. This temperature is 295°K for the poly isobutyl vinyl ether adhesive used in this work.

Further decrease in temperature reduces bond formation still further until below 270°K bond formation is no longer possible even though the adhesive can at this point store

Figure 5. Variation of Tack Energy with Temperature

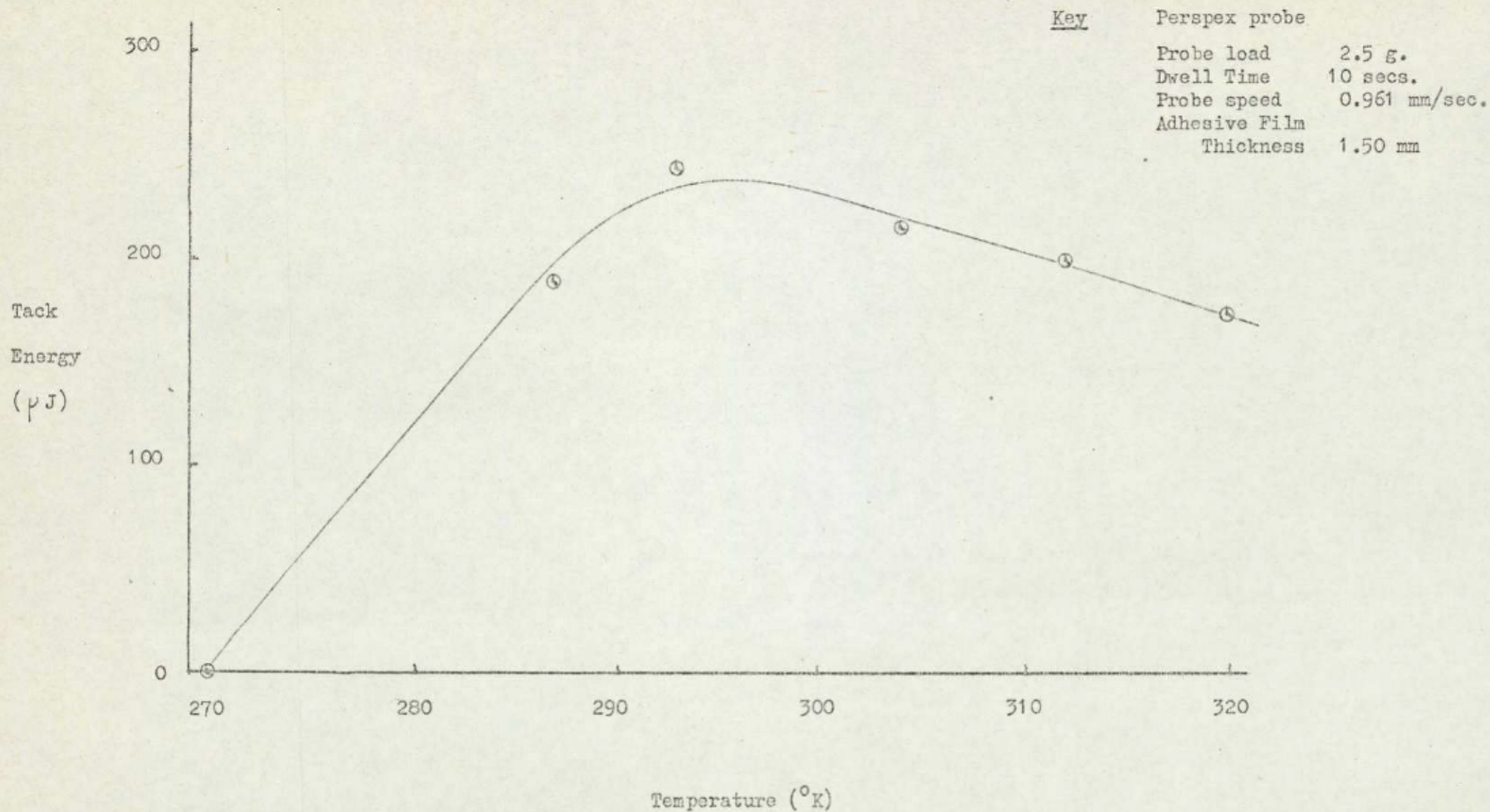


Figure 6. Variation of Tack Energy with Temperature

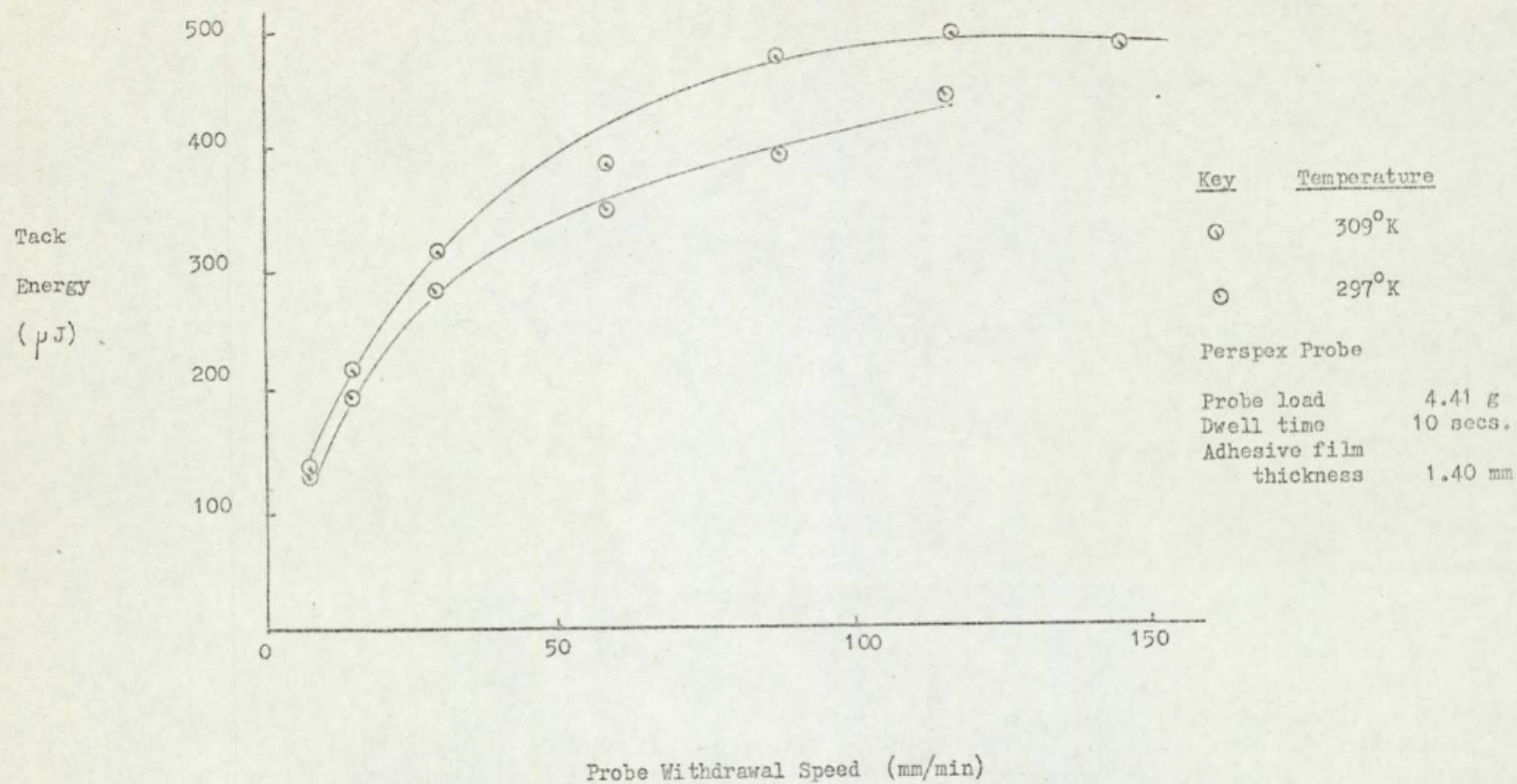
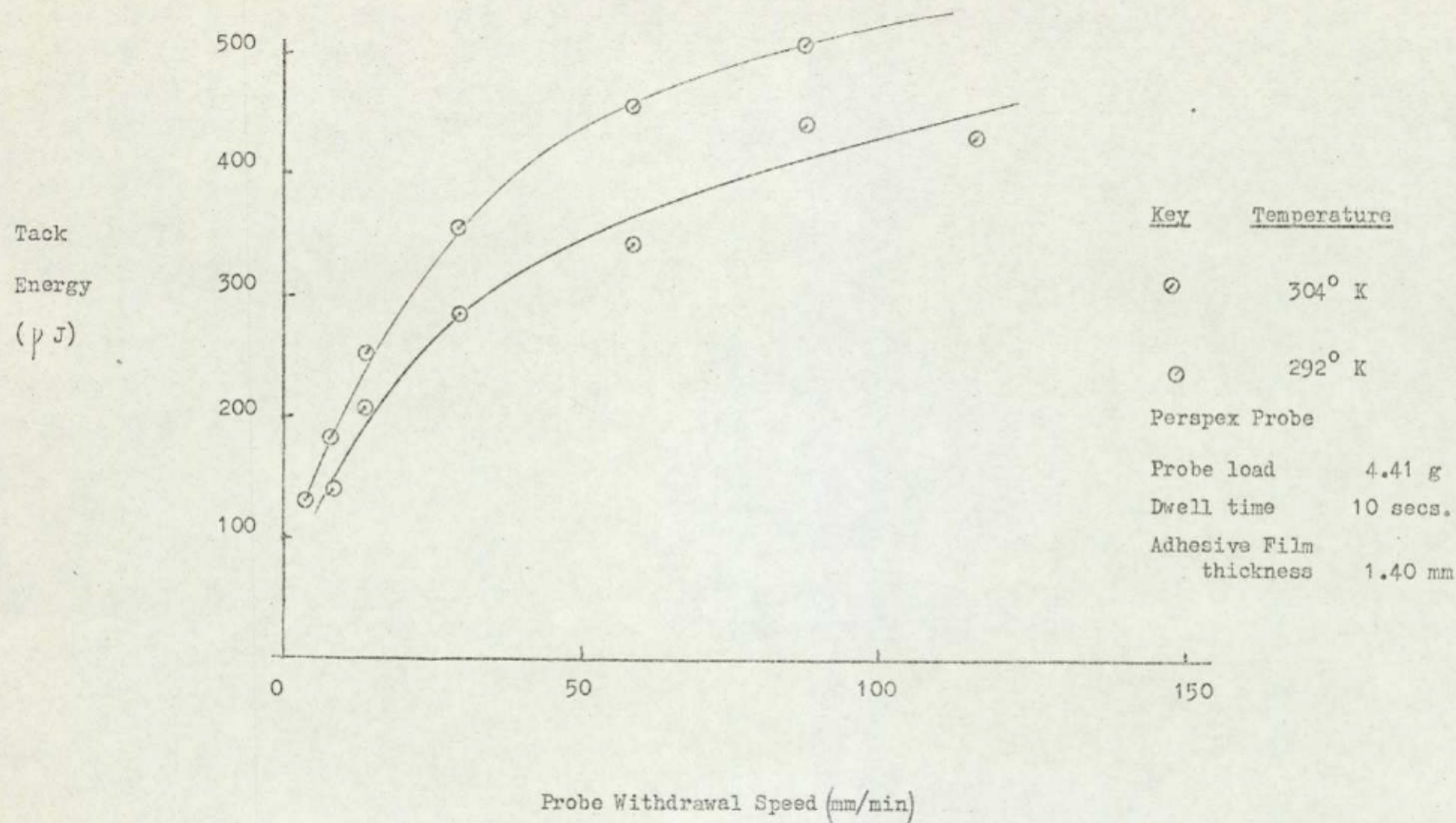


Figure 6. Variation of Tack Energy with Temperature and Probe Withdrawal Speed



a substantial amount of elastic energy.

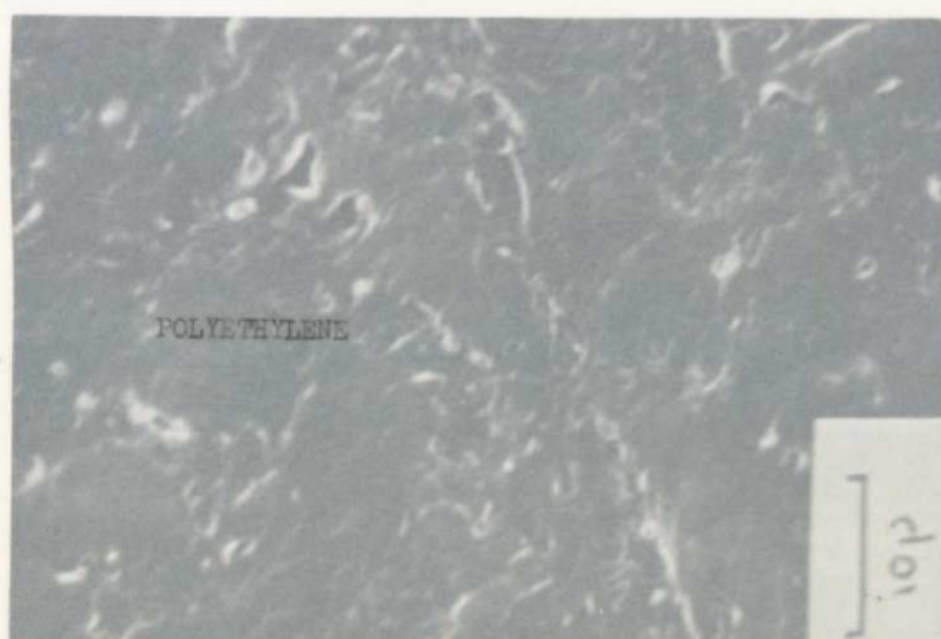
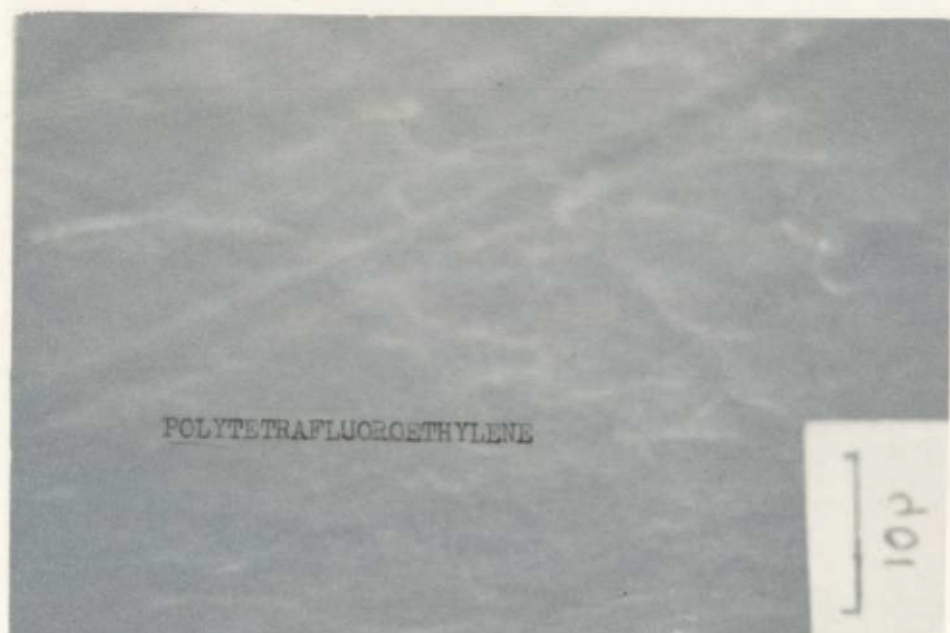
In figure 6, four temperatures were selected (292°K , 297°K , 304°K , 309°K) to study the effect of varying probe withdrawal speed as temperature varied. Since tack energy is varying relatively slowly with temperature, the tack energy curves are closely spaced but the order of tack energy is maintained through the whole range of speeds examined.

The variation of tack energy with differing probe composition was studied using varying dwell times (Figure 7) and varying probe withdrawal speeds (Figure 8). The objection to this procedure is that varying probe material not only varies probe surface free energy but also surface roughness (Hammond, 1963). The surface roughness of four probe materials were examined by electron microscopy by G.E.C. Power Engineering Ltd., Stafford, and the Author wishes to acknowledge with thanks the help of the Company. The probe materials were degreased by wiping the surface with lens tissue soaked in methyl ethyl ketone then polished with polishing alumina grade 3/50 using a polishing cloth. The probes were then in the condition in which they were used for the tack test.

The probe surfaces were then vacuum coated with aluminium to provide a conductive surface assuming that the metal surface closely followed the surface contours of the underlying probe materials. Photographs were then taken of the stereoscan electron micrographs and are indicated in Plate III.

Probe surface roughnesses were not identical and polyethylene was particularly rugose. The surface

PLATE III



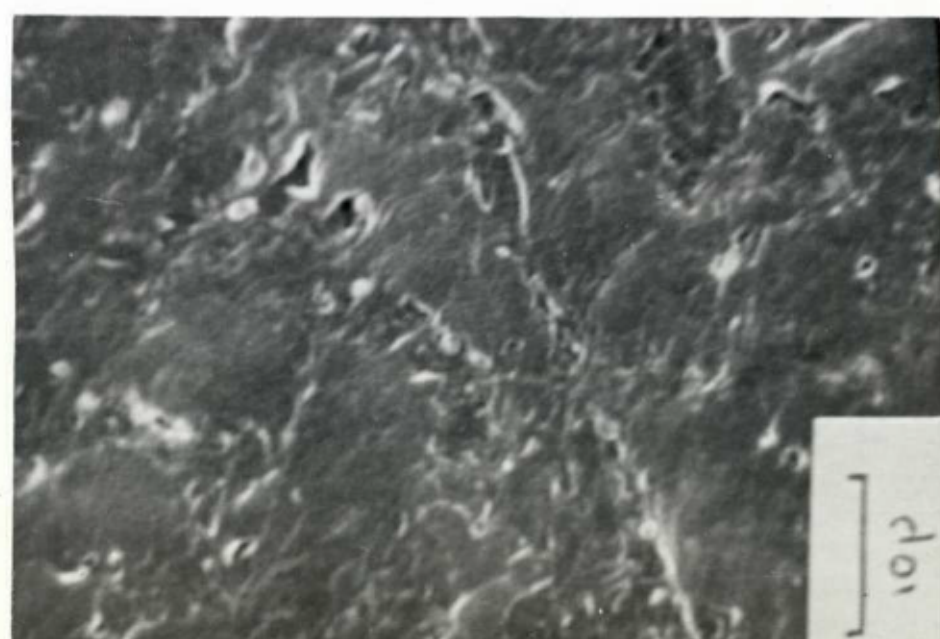


PLATE III

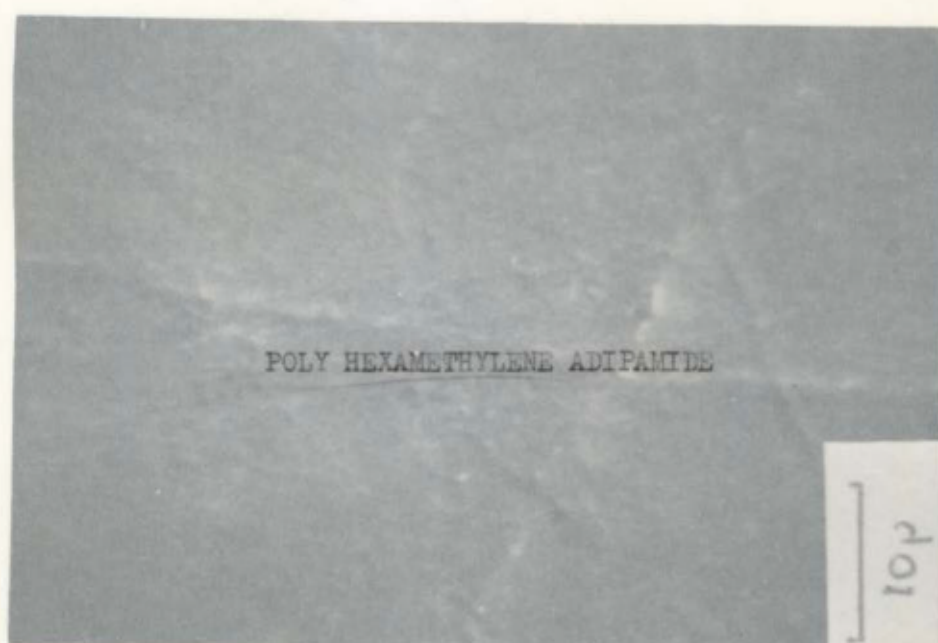
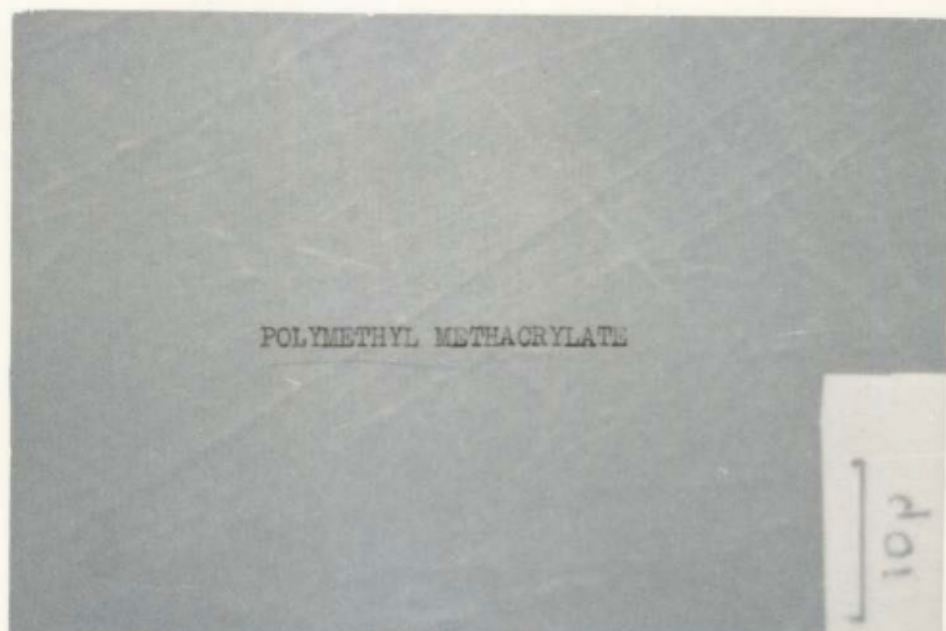




Figure 7. Variation of Tack Energy with Dwell Time and Probe Composition

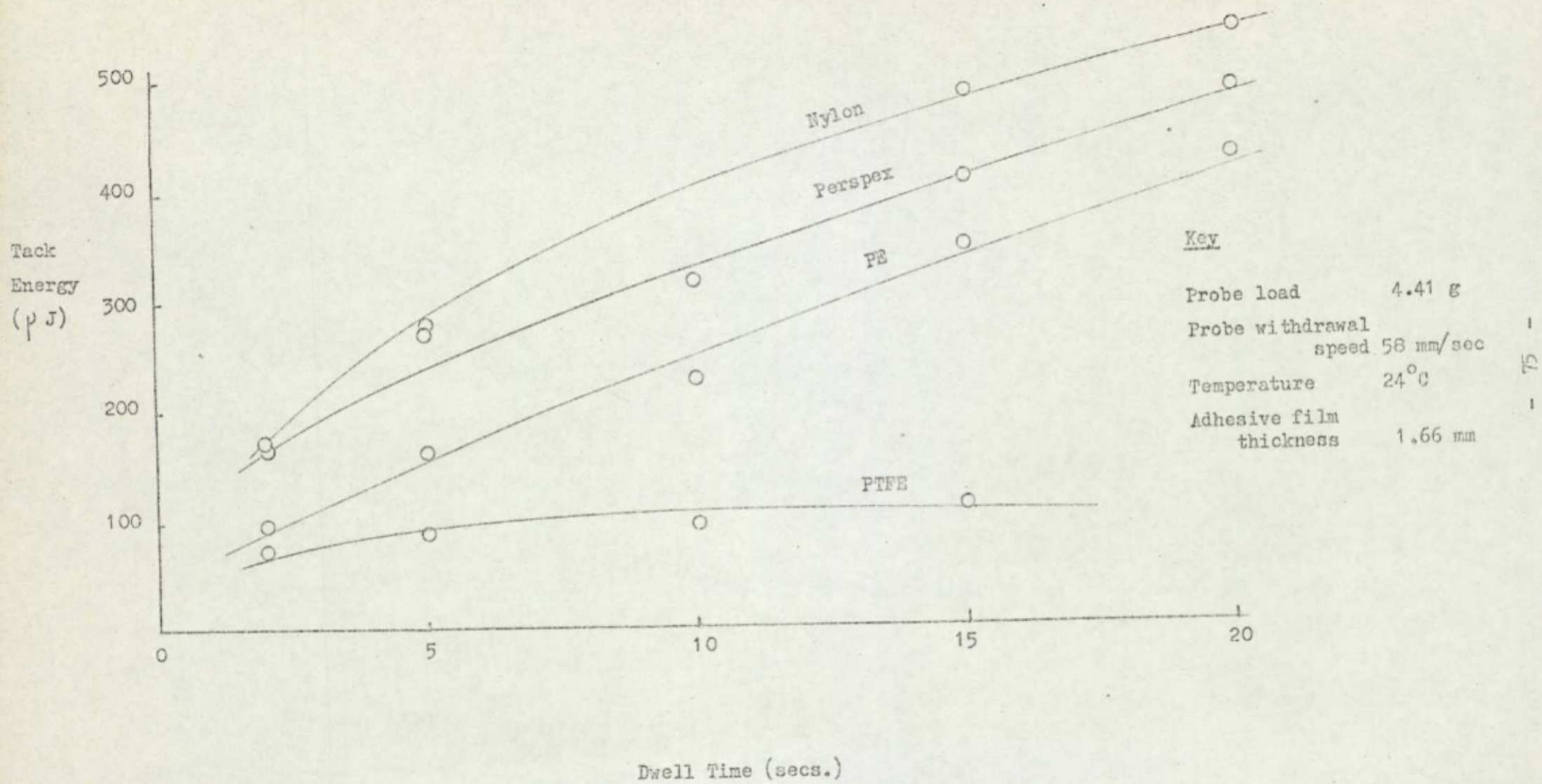


Figure 8. Variation of Tack Energy with Probe Withdrawal Speed

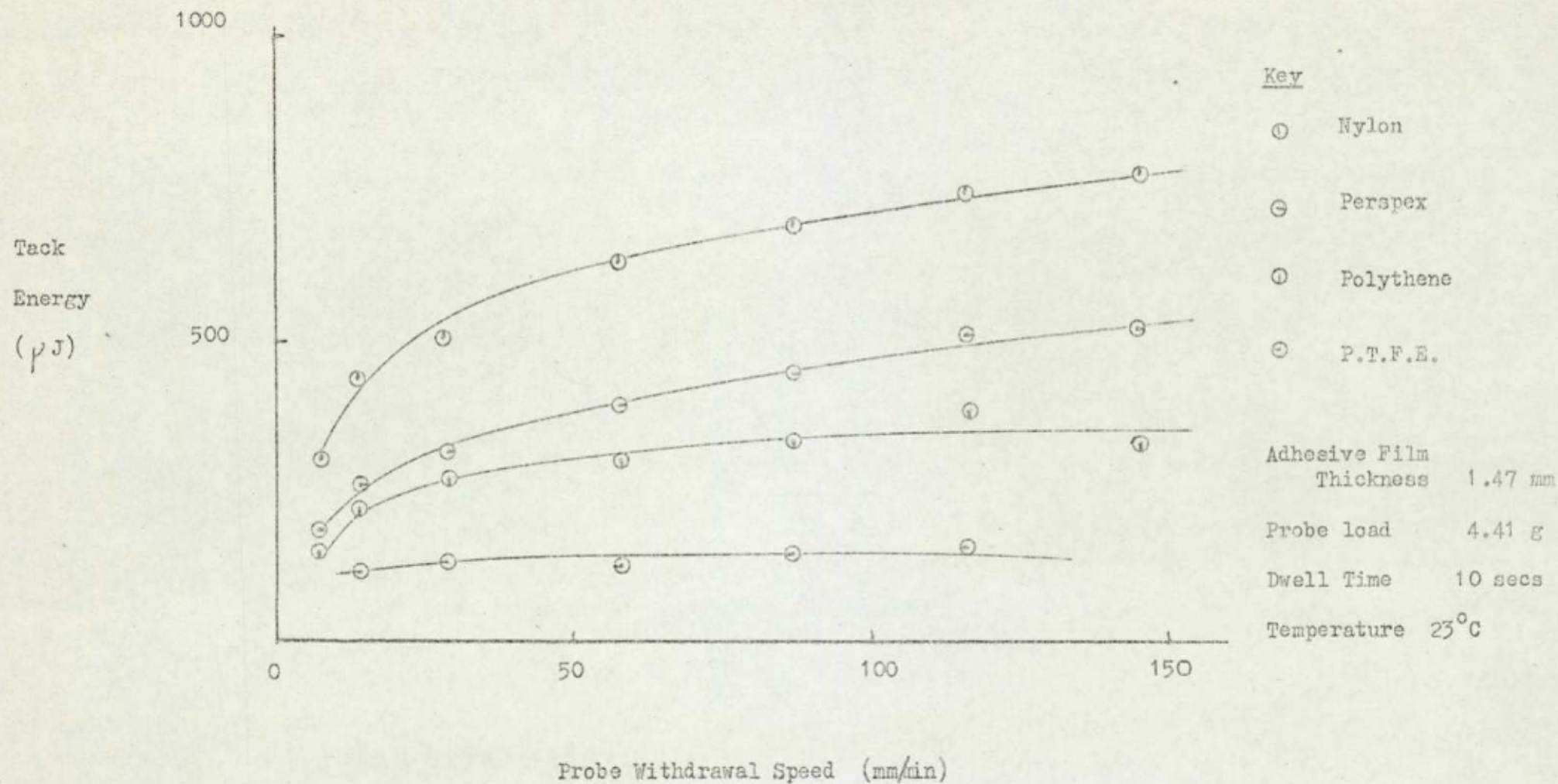
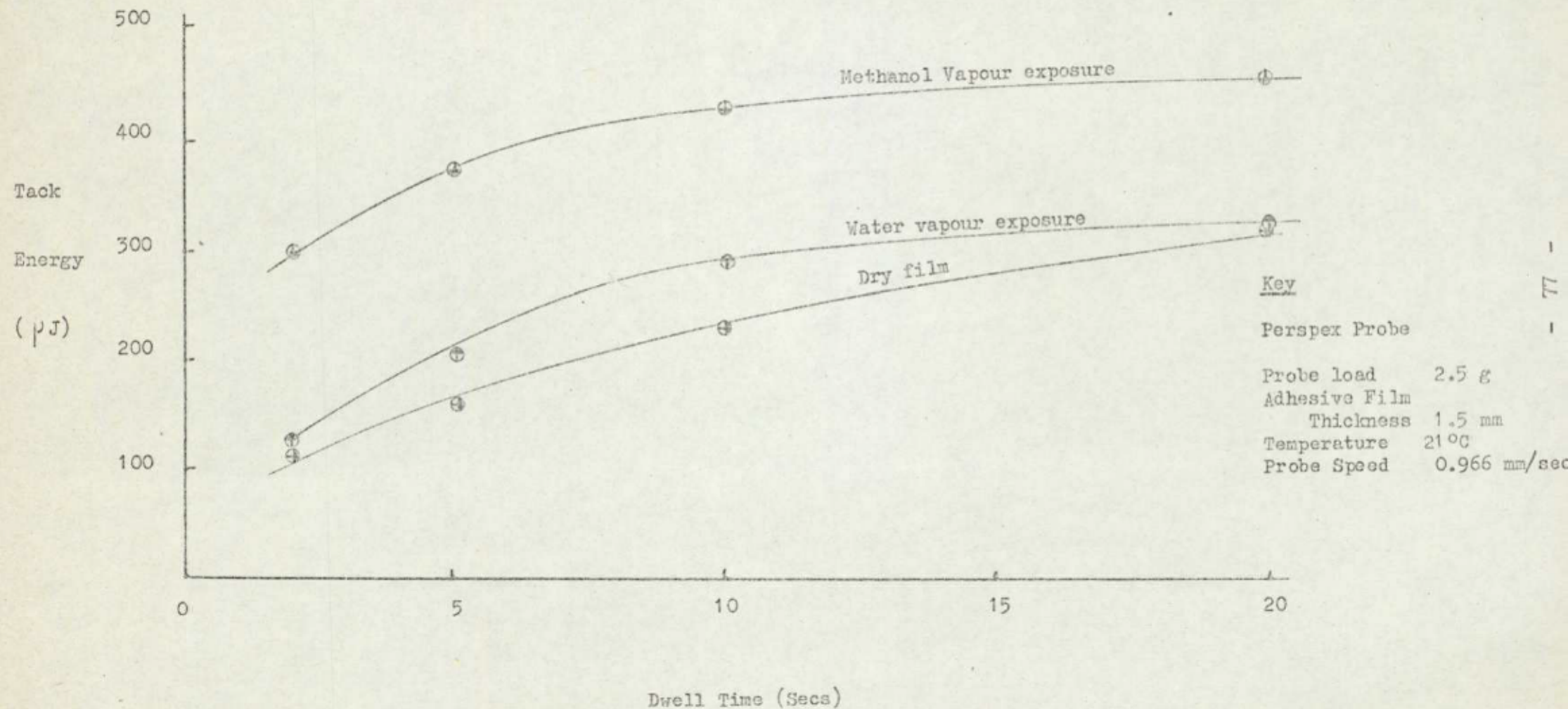


Figure 9. Variation of Tack Energy with Dwell Time in hostile environments



roughness of P.T.F.E., Perspex and Hexamethylene adipamide (Nylon 66) were less rugose than polythene and surface roughness was of a similar order of magnitude. The perspex probe was fairly smooth except for thin scratch marks, the origin of which are presumably the polishing process. The P.T.F.E. probe had less well defined and larger groove marks superimposed on a fairly irregular surface. The Nylon 66 probe also exhibited broad groove marks on a fairly smooth surface which had irregular pock marks in it.

Ranking the probes in order of surface roughness does not give the same ranking as in tack energy determinations in Figures 7 and 8, and it must be concluded that the magnitude and type of surface roughness observed is insufficient to cause gross distortion in the tack energy behaviour of the adhesive system used.

Figure 8 indicates conclusively that the observed order of tack energy is maintained over a wide range of probe withdrawal speeds. This contrasts sharply with the results of Kambe and Kamagata (1969) who used an adhesive based on poly isobutylene.

They concluded that at high probe withdrawal speed, tack force is not ranked according to probe γ_c , but, more significantly, that the order is altered at low probe withdrawal speeds (see section 2.3.1.)

Toyama, Ito, Moriguchi (1970 a, b) concluded that a maximum in tack force is observed where the critical surface tension γ_c , of the probe is identical to that of the adhesive. In a more recent paper, Sherriff Knibbs and Langley (1973) have shown that for resin/rubber mixes a maximum in tack force does not occur where the γ_c of the

probe is identical to that of the adhesive.

The γ_c of the probes used in the work described here and of the adhesive, were determined by the Zisman method indicated in section 2.2.4 using the liquids indicated in Table XI.

TABLE XI

Liquids used to determine probe and adhesive
critical surface tension (γ_c)

Liquid	* Measured surface tension (23°C) γ_L , mJ/m ²	Literature value (20°C) Fowkes (1967)
Tritolyl phosphate	44.3	40.9
Formamide	58.6	58.4
Glycerol	68.0	64.3

* by Searle Balance.

The γ_c of probe and adhesive materials is indicated in Table XII.

TABLE XII

Critical surface tension of probe and adhesive materials by Zisman sessile drop technique

Material	γ_c (23°C) mJ/m ²	γ_c (Fowkes 1967) 20°C
Adhesive	29 [±] 2	-
P.T.F.E.	18.5	18.5
Polyethylene	34.0	31.0
Perspex	42.0	39.0
Nylon 66	43.5	46.0

Inspection of Table XII indicates that the results obtained here agree with those obtained by Sherriff, that is that no peak in tack energy occurs where the γ_c of the probe is equal to γ_c adhesive and also the results in Figures 7 and 8 are ranked in order of probe γ_c , that is, as probe γ_c increases, so does the observed tack energy.

The effect of hostile environments on bond strength is to cause a rapid decrease in bond strength proportional to the intensity and duration of exposure of the bonded assembly to the environment. A brief examination of the effect of water and methanol vapour on observed tack energy was studied and the results are indicated in Figure 9. In this case however, the adhesive was exposed to the hostile environment prior to adhesion tests rather than exposing a previously bonded assembly to the environment for subsequent debonding.

Water and methanol are only very slightly soluble in poly isobutyl vinyl ether. Three films of adhesive mounted on glass plates were placed in three separate dessicators, one dessicator contained a moisture scavenger (molecular sieve), one dessicator contained air at 100% relative humidity and the third dessicator contained air saturated in methanol vapour.

After three days storage of the films in the three environments for three days, the films were removed and the tack energy determined immediately at 23°C and 50% relative humidity. The tack energy of the film stored at 100% relative humidity was slightly higher than the film stored at 0% relative humidity. The adhesive stored in methanol vapour gave tack energy values considerably higher than those of the film stored at 0% relative humidity.

Subsequent storage of the films in water and methanol yielded films which failed cohesively when subjected to the tack test indicated a general softening of the films undoubtedly due to absorption of vapour.

Since in all other experiments described in this work the films were stored in vacuum prior to tack energy determinations, it may be concluded that the effect of humidity on the films was not significant since exposure to water vapour was for short periods of time only.

The adhesive formulation was normally prepared as a toluene solution and the toluene was removed by drying the cast film firstly for 24 hours at room temperature at 760 mm mercury pressure then for 72 hours at room temperature at 5 mm mercury pressure. This was thought to be adequate to remove at least 99% of the solvent.

However, when the adhesive was cast from solutions in various solvents, significant differences in tack energy were observed though all other parameters such as temperature, adhesive film thickness etc. were identical. These results are indicated in Figure 10, where the solvents are ranked in order of solubility parameter δ .

$$\delta = \left(\frac{\Delta E_{\text{vap}}}{V_m} \right)^{\frac{1}{2}} \quad \dots\dots\dots (43)$$

ΔE_{vap} is the molar energy of vaporization of the liquid and may be re-expressed as the heat of vapourization ΔH_{vap} as follows:

$$\Delta E_{\text{vap}} = \Delta H_{\text{vap}} - RT \quad \dots\dots\dots (44)$$

where R = universal gas constant
and T = temperature

In equation 43, V_m is the molar volume of the solvent.

A peak in tack energy occurs when δ is approximately 530 ($\text{J}^{\frac{1}{2}} \text{mm}^{-3/2}$). Previous work (Tobolsky, 1960 b) has suggested that swelling of lightly cross-linked polymers in solvents of varying solubility parameter is a useful technique for determining the solubility parameter, δ , of the polymer since a maximum in swelling occurs when the solubility parameter, δ , of the polymer and solvent are very similar. Tobolsky quoted the solubility parameter of various polymers derived by this method and the results are indicated in Table XIII.

TABLE XIII

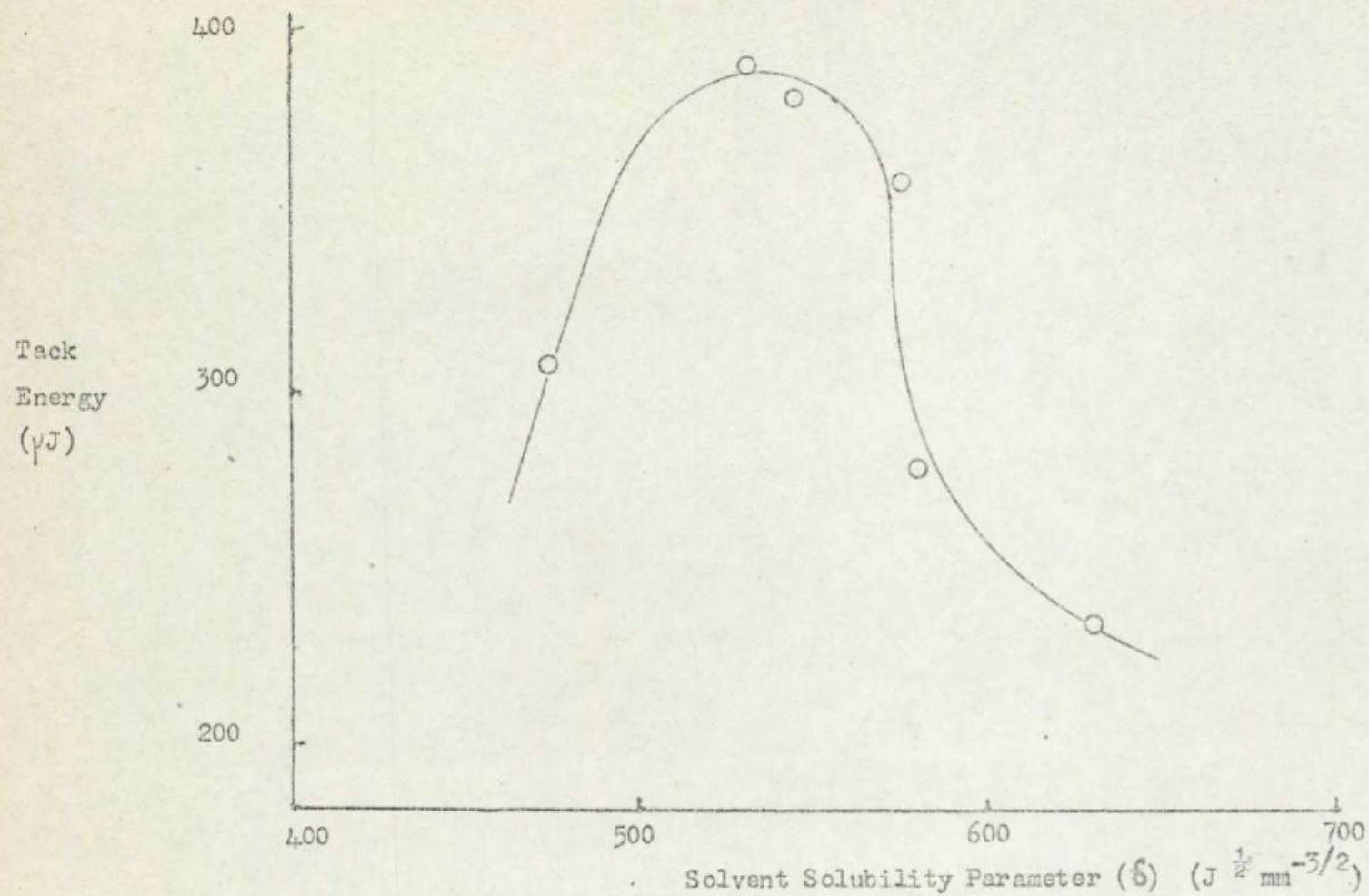
Solubility parameter, δ , of certain polymers
determined by solvent swelling technique
(Tobolsky, 1960)

Polymer	Solubility Parameter, δ , $\text{cals}^{\frac{1}{2}} \text{cm}^{-3/2}$
Polyethylene	7.9
Poly isobutylene	7.8
Poly isoprene	8.1
Polystyrene	8.6
Poly vinyl acetate	9.4

It would at first sight be attractive to correlate the variation in tack energy with solvent solubility parameter in an analogous way and to suggest that the peak in tack energy occurs at the point where the solubility parameter of the adhesive and solvent were equal. However, it is not certain that all traces of solvent were removed from the films. Gas liquid chromatography on the films of adhesive was used to try to estimate quantitatively the amount of residual solvent. However, it was not possible to obtain a useful estimate of the residual solvent by pyrolysis because a reliable decomposition trace of the adhesive itself could not be obtained.

The residual solvent was certainly below 0.1% but even at this level, remaining solvent could still greatly affect tack by slightly plasticizing the adhesive film. The variation of tack energy with film solvent is therefore most probably associated with the plasticizing effect of residual solvent in the adhesive film.

Figure 10. Variation of Tack Energy with solvent solubility parameter.



Key

Temp.	20 - 21°C
Probe load	2.5 g.
Probe Speed	0.966mm./sec.
Adhesive film thickness	1.45mm.
Perspex probe dwell time	10 sec.

The solvents used are indicated in Table XIV.

TABLE XIV

Solvents used in solubility parameter work
(Hoy, 1970)

Solvent	Abbreviation used	δ cals ^{1/2} cm ^{-3/2}
Methyl iso- butyl Ketone	MIBK	8.44
Toluene	-	8.93
Cyclohexane	-	8.19
Ethyl Acetate	Et Ac	8.91
Methylene Dichloride	Me Cl ₂	9.88

The order of tack energy observed is as follows:

MIBK > Cyclohexane > Toluene > Ethyl Acetate > Methylene
Dichloride

To the Author's knowledge, the effect of solvent on tack energy of the dry adhesive film has not been mentioned in the literature up to the time of writing. Iyanger and Erickson (1967) have shown that adhesion force measurements in peel experiments are at a maximum when the solubility parameter of the substrate is equal to that of the adhesive.

CHAPTER 5

MEASUREMENTS OF THE MODULUS PROPERTIES OF POLY (ISOBUTYL VINYL ETHER) BY TORSION PENDULUM

The literature on tack (Dahlquist, 1959) and the strong dependence of tack energy on temperature and speed of probe withdrawal indicated in Chapter 4, has indicated that the modulus of the adhesive has a strong influence of the tack of the adhesive.

A machine was not available so a simple free swinging torsion pendulum was constructed. The principle of the instrument is that the damping of oscillations induced in an assembly of which the adhesive is part, is proportional to the ratio of storage and loss moduli of the adhesive.

Consider a rectangular shaped specimen clamped rigidly at one end but able to undergo torsional oscillation at the other end about the axis running the length, l , of the specimen. Provided that l is much greater than the width a and that the width in turn is greater than three times the specimen thickness b then the instantaneous torque ξ is related to the angle of twist, ϕ , by the stiffness S^1 of the specimen as follows, provided that the cross sectional area of the sample remains constant:

$$\xi = S^1 \phi \quad \dots\dots\dots (45)$$

The stiffness is in fact the directional moment of the system and is related to modulus by a factor dependant on the geometry of the specimen. The induced, damped oscillations are in fact an example of simple harmonic

motion (that is the acceleration at any point is proportional to the amplitude of oscillations) then the periodic time T of the oscillations

is given by

$$T = 2\pi(I/S^1)^{\frac{1}{2}} \dots\dots\dots (46)$$

where I is the moment of inertia of the system.

This is strictly correct only if damping does not occur, i.e. the material is perfectly elastic. To accommodate the damping effect, a correction factor is applied:

$$\left(1 + \frac{\Lambda^2}{4\pi^2}\right)^{\frac{1}{2}} \text{ where } \Lambda \text{ is a measure of the damping and}$$

is defined as the natural logarithm of the ratio of consecutive amplitudes of oscillations:

$$\Lambda = L_n\left(\frac{h_n}{h_{n+1}}\right) \dots\dots\dots (47)$$

h_n is the amplitude of the n^{th} oscillation

h_{n+1} is the amplitude of the $(n+1)^{\text{th}}$ oscillation.

In practical situations $\Lambda \ll 2\pi$ and hence to a good approximation equation (46) is valid.

By rearranging equation (46) the stiffness S^1 can be expressed in terms of the moment of inertia, I , and the periodic time T .

The above theory is only valid if φ is small and that the specimen is subjected to very light loads. The weight on the specimen may be reduced by counterbalancing the

weight of the system and this procedure was adopted for this work.

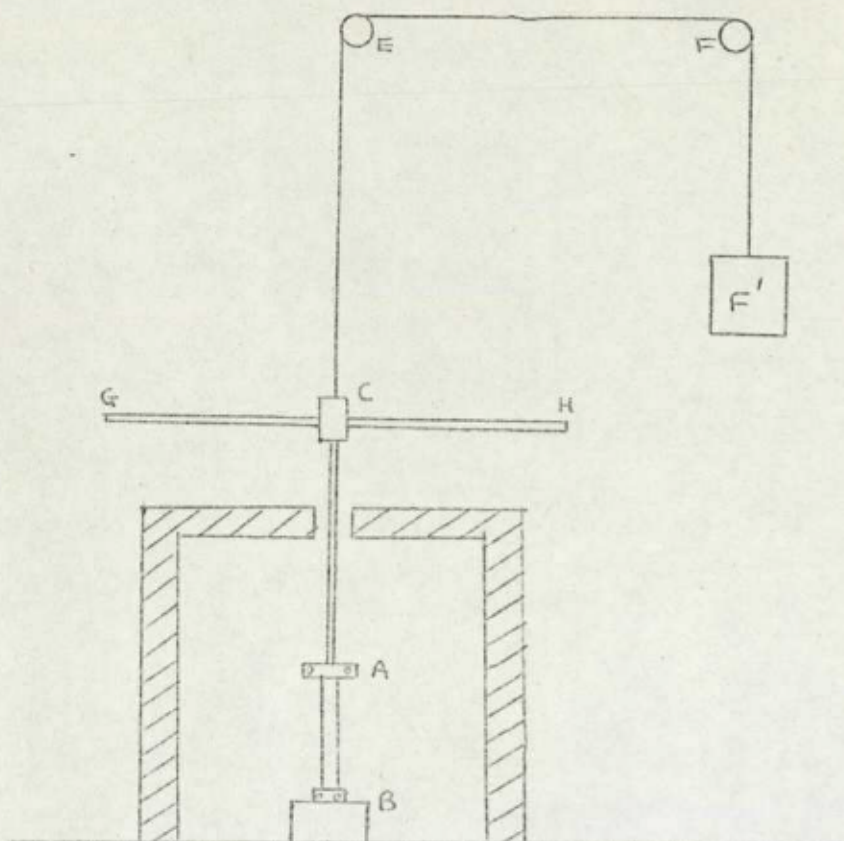
However, the use of materials such as pressure sensitive adhesives is not easy. Firstly, since the adhesive is fabricated in solution, the solvent must be removed and its removal is only efficient if very thin films are cast. The resulting dried films were too thin to use in torsional oscillation experiments so the film was built up by laminating together several dry films until a thickness of about 1.5 mm was obtained. During lamination, extreme care was taken to avoid the inclusion of air bubbles in the sample.

The aggressive tack and easy deformation of the film made its subsequent handling very difficult. Accurate measurement of the dimensions of the sample was not possible because of its tack, hence the calculation of the storage modulus G^1 from the stiffness S^1 was not possible. However, since it is the change in G^1 which was of interest rather than its absolute value, the measurement of S^1 was an adequate indication of the change in modulus properties.

The adhesive specimens used in stiffness determinations were of approximate dimensions $l = 100\text{mm}$, $a = 5.0\text{ mm}$, $b = 1.5\text{ mm}$.

A diagram of the apparatus is shown below.

DIAGRAM 6



B is a rigidly fixed clamp to which a specimen is held. A is a freely oscillating clamp in which the other end of the specimen is held. CA is a metal extension rod rigidly fixed to clamp A. At C, a cylindrical inertia bar GH is attached by means of a collar. Addition of weights to the inertia bar permits a variable moment of inertia to be used maintaining a constant frequency of oscillation (0.35 Hz). The amplitude of oscillations is monitored by reflecting a pencil beam of light onto a small mirror attached to C then reflects this onto a scale. The sample and clamps A are maintained at constant temperature in a thermostatic oven whilst the remainder of the apparatus is outside the oven. The weight of the assembly CA is counterbalanced using a thin high tensile steel wire and pulleys E and F with a counterbalancing weight F' .

The moment of inertia of the whole assembly ($I_1 + I_2$) is related to the moment of inertia of the inertia rod GH, I , by the formula

$$\frac{T_2^2}{T_{(1+2)}^2} = \frac{I_2}{I_1 + I_2} \dots\dots\dots (48)$$

where T_2 is the period of oscillations of the apparatus without inertia bar GH and $T_{(1+2)}$ is the period of oscillation of the whole apparatus.

I_1 was calculated from the mass M of the inertia rod its length, l , and radius of cross section, a , using the formula

$$I_1 = M \left[\frac{a^2}{4} + \frac{l^2}{12} \right] \dots\dots\dots (49)$$

At each temperature of test, the total moment of inertia ($I_1 + I_2$) was adjusted to give a constant frequency of test 0.35 Hz. The moment of inertia was determined on each occasion by the procedure outlined above and from this the stiffness S^1 was calculated.

At each temperature the damping was recorded as the amplitude of several consecutive oscillations on one side of the rest positions. Let these amplitude readings be $h_1, h_2, h_3, \dots h_{n-1}, h_n$

then the logarithmic decrement, Δ , was calculated from the following:

$$\Delta = \ln \frac{h_1}{h_2} = \ln \frac{h_2}{h_3} = \ln \frac{h_3}{h_4} = \ln \frac{h_4}{h_5} \dots\dots \frac{h_{n-1}}{h_n} \dots\dots\dots (50)$$

Finally S^1 and Δ were recorded graphically against temperature.

The glass transition temperature, T_g , of the adhesive was then determined as the peak in the graph of Δ against temperature, see Figure 11, which occurred at 259°K .

The variation of tack energy with temperature described in chapter 4, Figure 5, indicated that the adhesive had zero tack energy at 270°K which is the temperature at which the logarithmic decrement is rapidly increasing in Figure 11. The loss in tack energy is therefore associated with the loss of molecular mobility indicating clearly that molecular mobility is essential in the tack mechanism.

The stiffness-temperature properties of the adhesive cast from different solvents was determined at constant frequency and the results are indicated in Figure 12.

At temperatures above 263°K no differences in stiffness S^1 were detected. It is not clear whether this is a real effect or whether the apparatus is insufficiently sensitive to detect these differences. At temperatures below the glass transition temperature differences in the stiffness S^1 were detected and ranking in order of magnitude yields the following sequence:

Methylene Dichloride > ethyl acetate > toluene > Cyclohexane
= M.I.B.K.

High stiffness lower
—————→ stiffness

This is the reverse order for the tack energy results and could be explained as a bonding rather than debonding effect. The adhesive of higher stiffness would store

Figure 11. Variation of Stiffness S^1 and logarithmic Decrement with temperature at 0.357 Hz

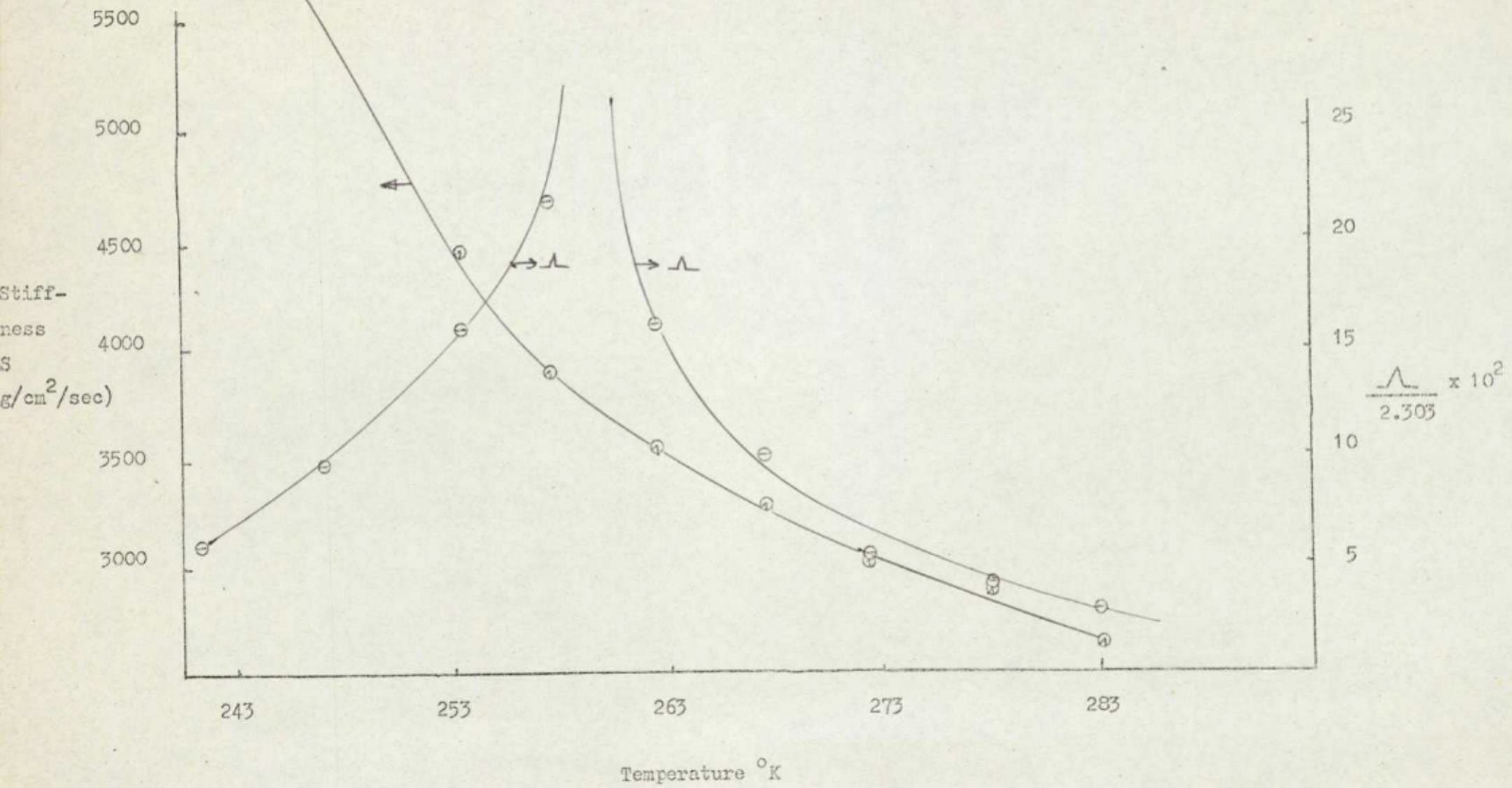
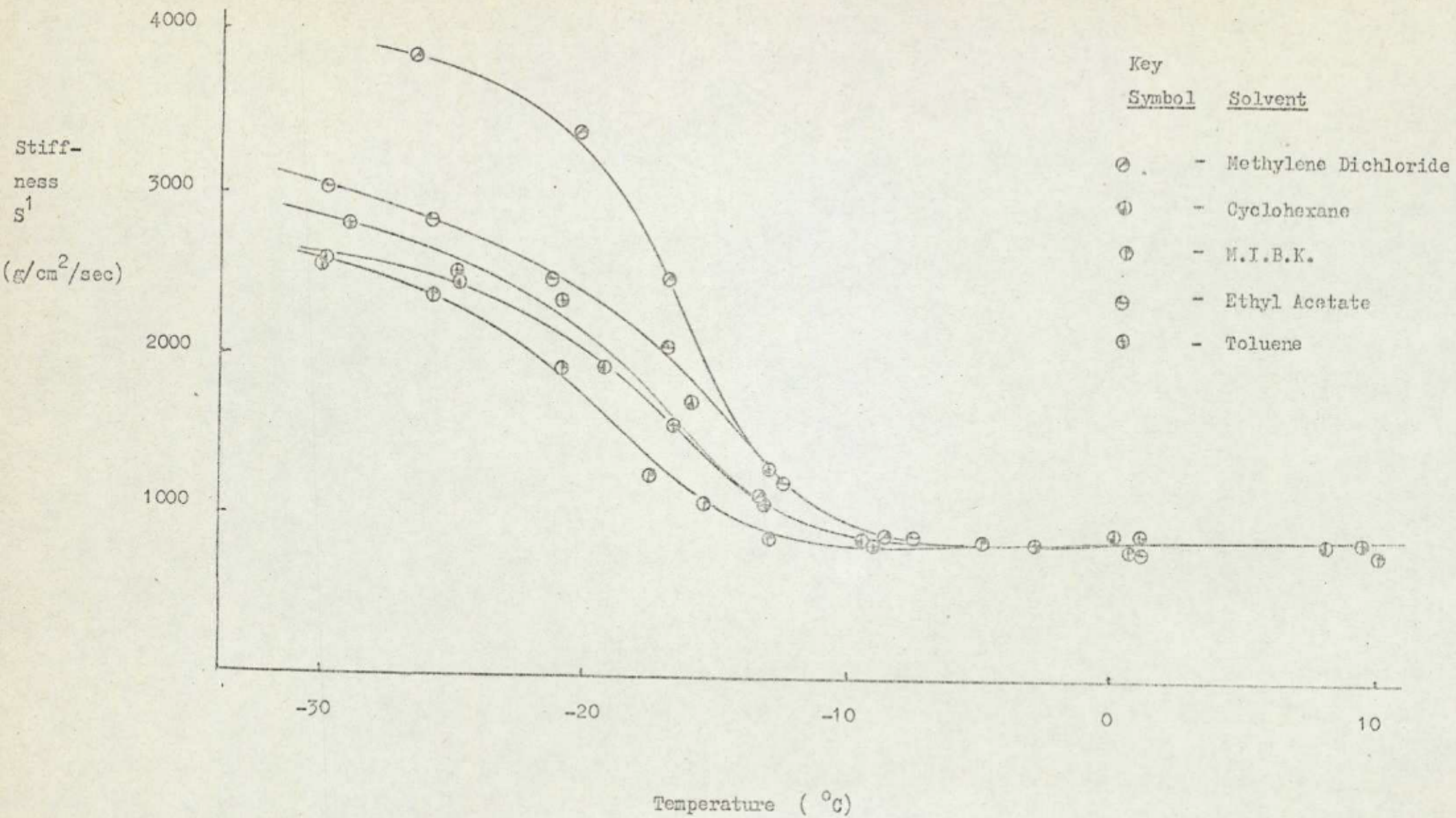


Figure 12. Variation of Stiffness S^1 with film solvent and temperature.



the most elastic energy but would conform less easily to the substrate than the adhesive of lower stiffness, i.e. wettability and bond formation would be reduced. The effect of solvent variation would be therefore to influence more strongly the bonding step rather than the debonding step.

FURTHER DISCUSSION OF THE TACK ENERGY MEASUREMENTS6.1 INTRODUCTION

As discussed in Chapter 2, section 3, workers in the field of polymer testing have demonstrated that the temperature of test and the rate (or time) of test has an important bearing on the results obtained with polymers in the viscoelastic state. Further, it has been demonstrated that both theoretically and experimentally the rate of test and temperature are equivalent and any polymer property which depends on these two variables can be expressed in terms of a single variable termed the reduced rate.

This is mathematically expressed by the W.L.F. equation which in effect states that the effect of varying temperature is to multiply the time scale of the experiment by a constant factor proportional to that temperature.

Kaelble, in a series of publications, analysed theoretically and experimentally the rate and temperature dependence of peel adhesion showing that peel adhesion follows the rate-temperature equivalence in the same way as the basic modulus properties of the adhesive despite the fact that the two phenomena are very different.

The work of Gent (1971, 1969, 1972) further extended the work to cover several modes of substrate/adhesive debonding.

Again, rate and temperature were shown to be equivalent and independent of geometry of debonding. In addition; he and subsequent authors (Andrews and Kinloch 1973) varied the surface free energy characteristics of the substrates and found that at each value of substrate γ_c , a reduced rate curve is obtained which is strictly parallel to curves found at different value of γ_c . Gent proposed that adhesive debonding could be explained in terms of a characteristic failure energy per unit area of interface θ_0 which was a constant over a wide range of rates and temperatures and that the total observed debonding energy, θ , was this factor multiplied by an hysteresis factor, H , associated with the rate dependence of viscoelastic properties. At an infinitely slow rate of test this hysteresis factor would become unity and the characteristic failure energy θ_0 would be equal to the thermodynamic work of adhesion between substrate and adhesive:

$$\theta = H \theta_0 \quad \dots\dots\dots (51)$$

H is the hysteresis factor which is strongly rate sensitive.

6.2 Tack Energy and Rate of Test

The tack energy data indicated in Figures 2, 3, 4, 6 and 8 indicate quite clearly that tack energy is strongly dependent on probe withdrawal speed and hence rate of test. If the results are quoted using $\log_{10}$ (probe withdrawal speed) as a common abscissa, then a similar procedure to that used by Kaelble may be followed.

Rate of Test in fact is the debonding speed divided by

Figure 13. Variation of Tack Energy with $\log_{10}$ (probe withdrawal speed) and film thickness.

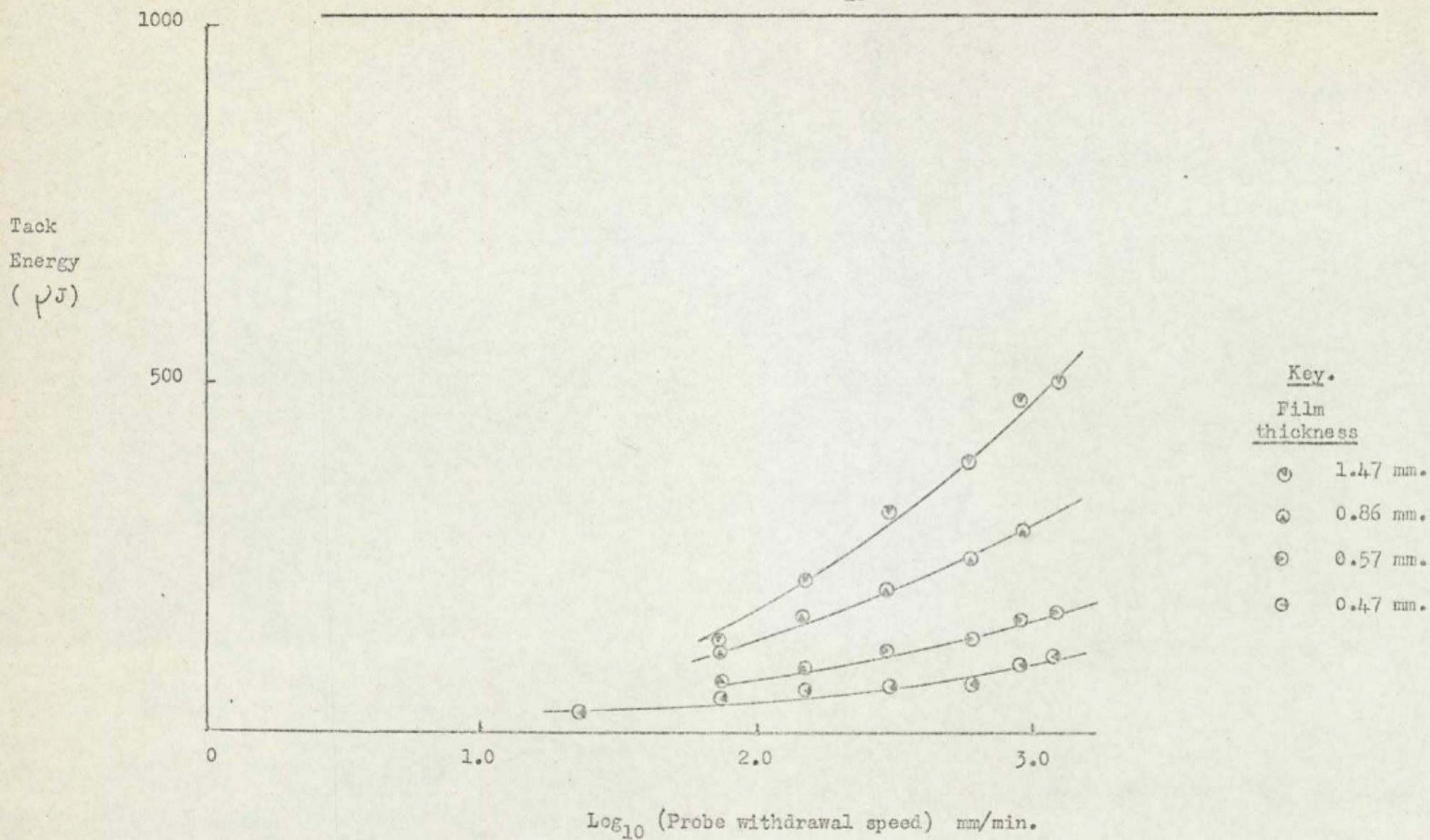
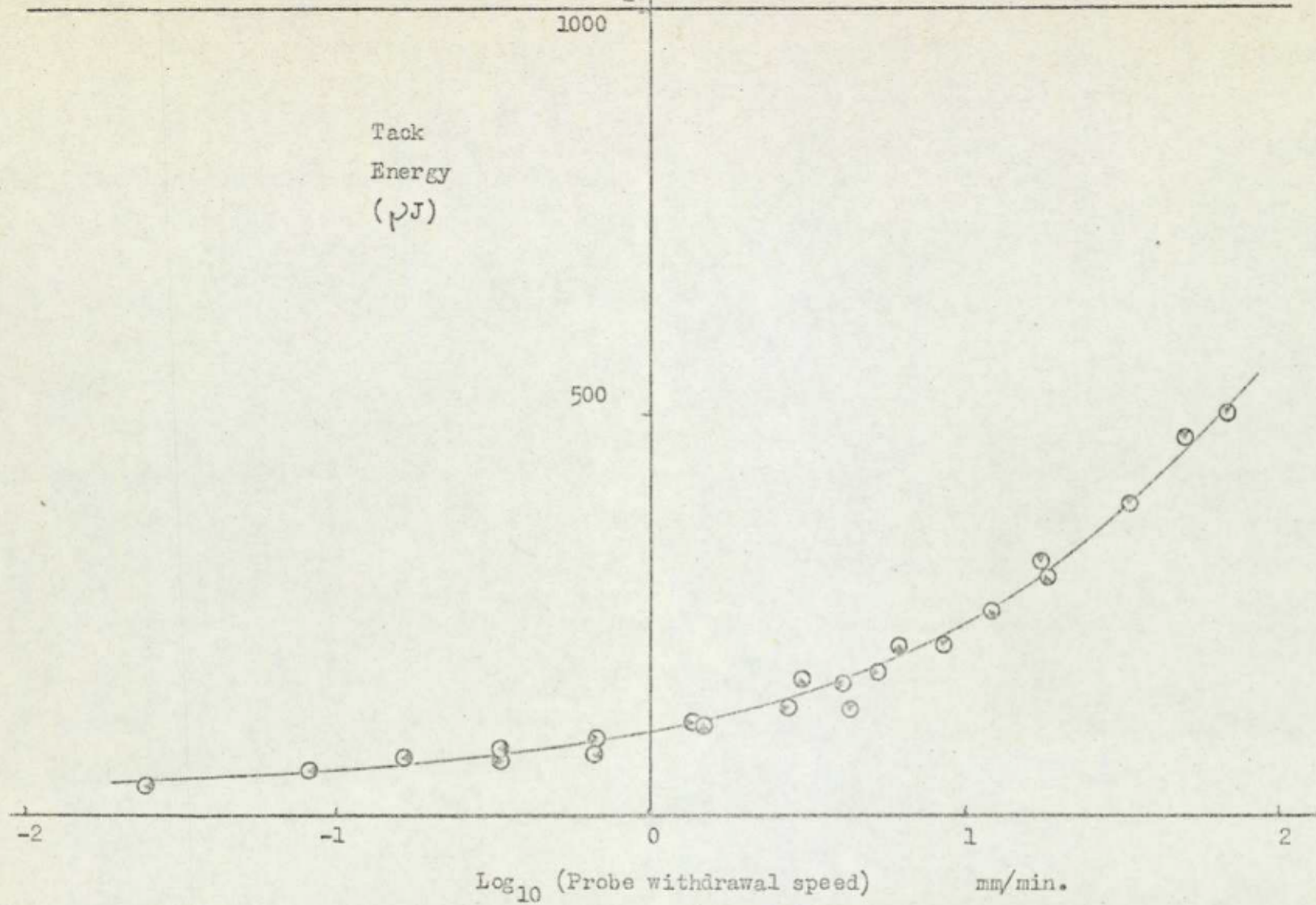


Figure 14. Variation of Tack Energy with $\log_{10}$ (speed) and film thickness. Key: as figure 13.



the adhesive film thickness, that is it is the rate of strain and has the units of reciprocal time. In the tack test this rate of strain is not known due to the complex geometry of the test procedure.

To investigate the interrelation of rate of probe withdrawal and adhesive film thickness, four different adhesive film thicknesses were used at varying probe speeds and results indicated in Figure 13 are expressed in terms of $\log_{10}$ (probe withdrawal speed).

Four smooth curves were obtained which were superimposable to form a single continuous curve (Figure 14) by horizontal shifting of the curves on the $\log_{10}$ (speed) axis. The relative shift factors used to derive Figure 14 are indicated in Table XV.

TABLE XV

Relative shift factors used to derive Figure 14
from Figure 13.

Film Thickness (mm)	1.49	0.866	0.571	0.471
$\Delta \log_{10}$ (Speed)	0	-0.55	-1.10	-1.40

The significance of this procedure is made more obvious by expressing $\log_{10}$ (speed) as a function of $\log_{10}$ (film thickness and this is shown in Figure 15.

In the simplest case

$$\begin{aligned}
 \log_{10} \left(\frac{\text{strain}}{\text{rate}} \right) &= \log_{10} (\text{speed of test}) - \log_{10} (\text{Film thickness}) \\
 &= \log_{10} \left[\frac{\text{speed of test}}{\text{film thickness}} \right] \dots \dots \dots (52)
 \end{aligned}$$

Figure 15. Variation of $\log_{10}$ (Probe withdrawal speed)
with adhesive film thickness.

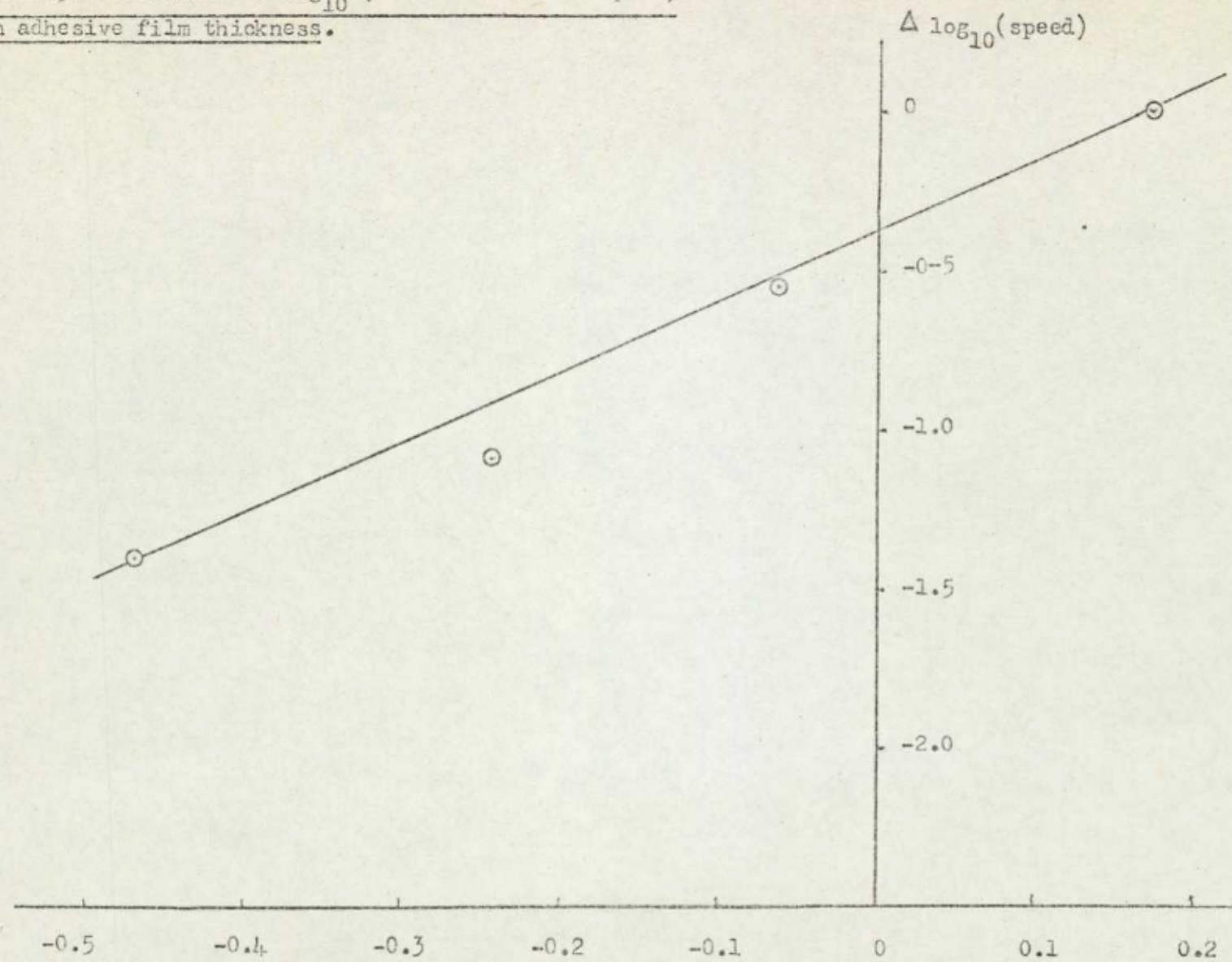


Figure 16. Variarion of tack energy with $\log_{10}$ (Probe withdrawal speed) and dwell time.

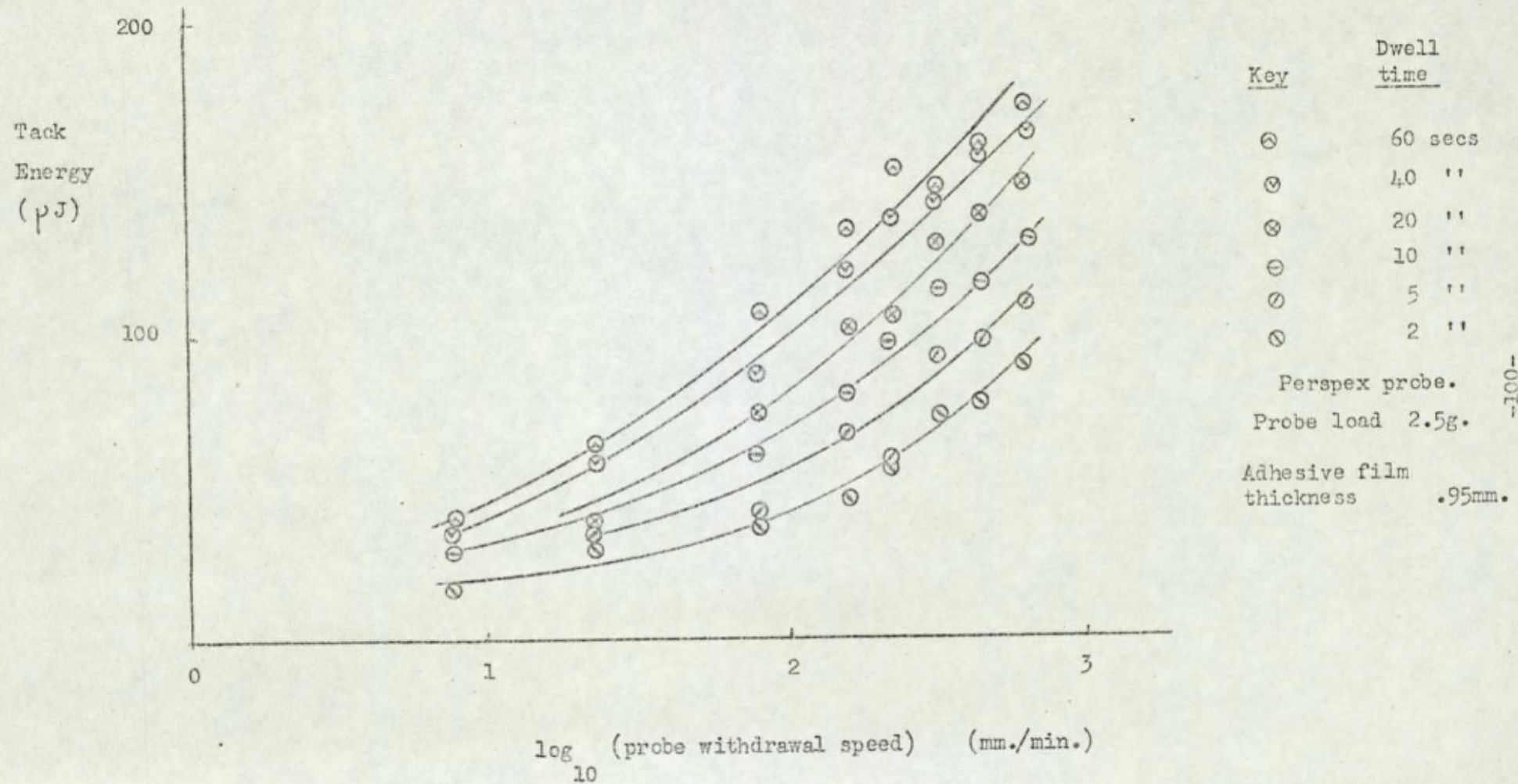


Figure 17. Variation of Tack Energy with $\log_{10}$ (Probe withdrawal speed) and Dwell Time

Key as Fig: 16.

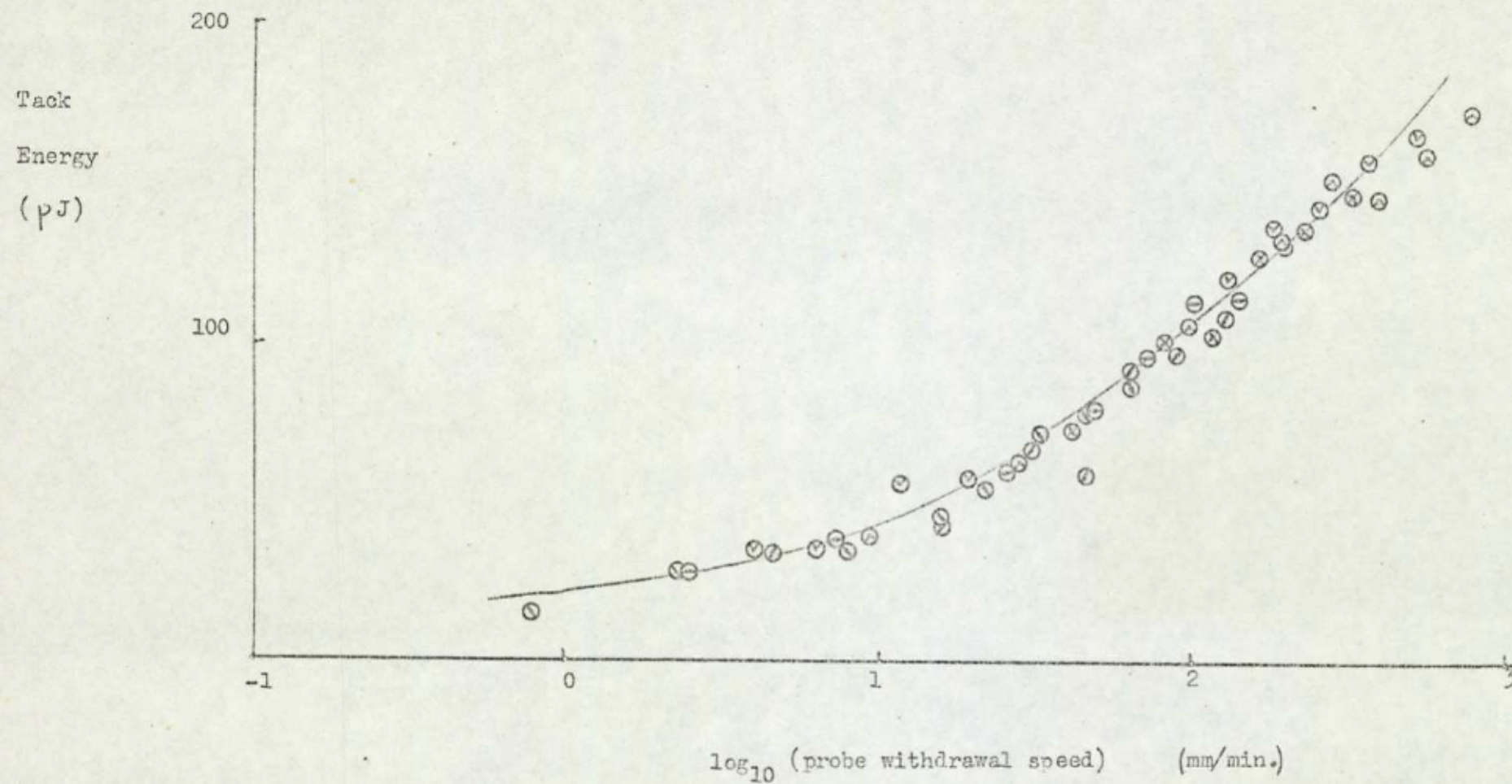
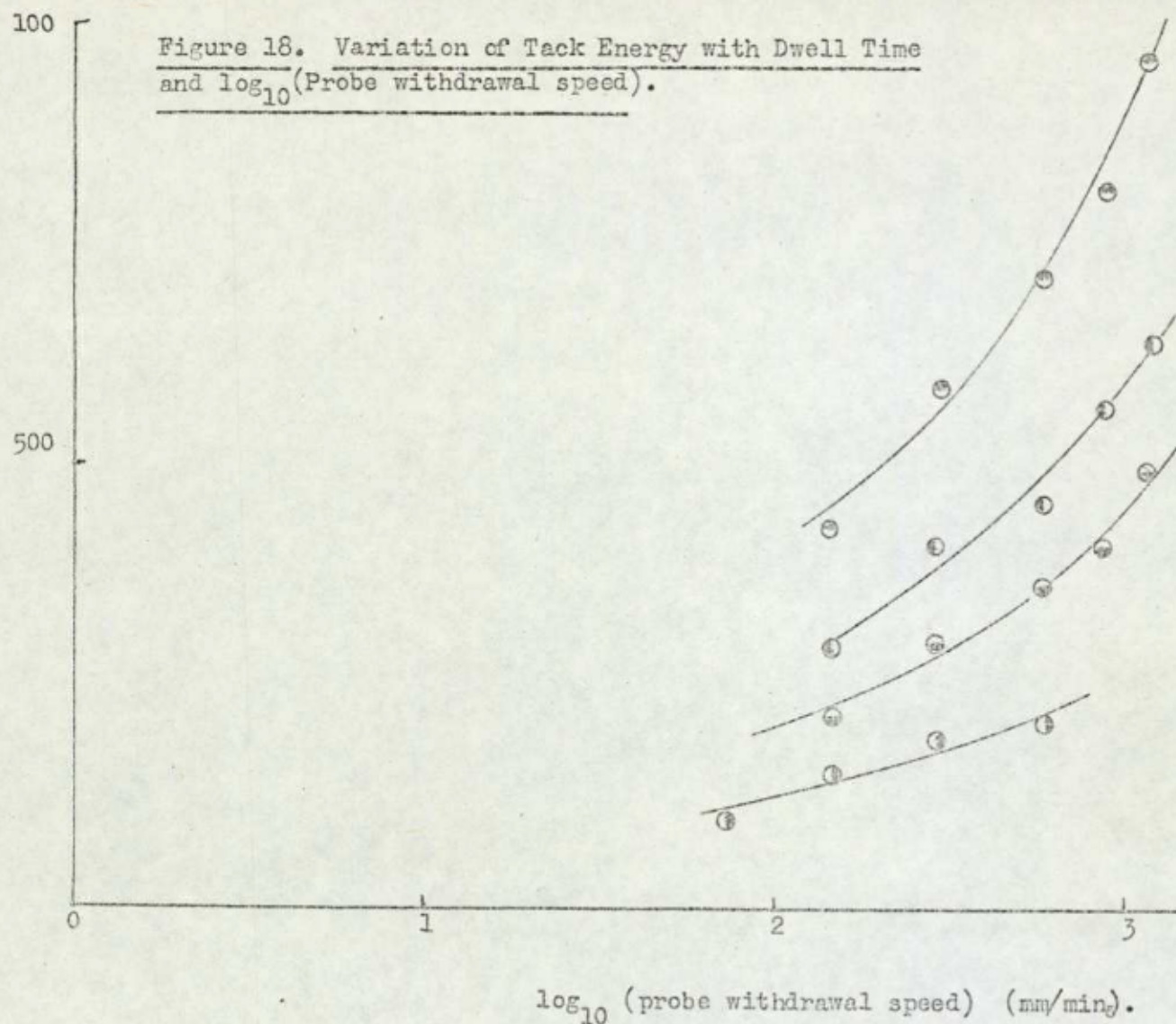


Figure 18. Variation of Tack Energy with Dwell Time and $\log_{10}$ (Probe withdrawal speed).

Tack
Energy
(μJ)



Key Dwell time

⊙ 60 secs

⊙ 20 "

⊙ 10 "

⊙ 2 "

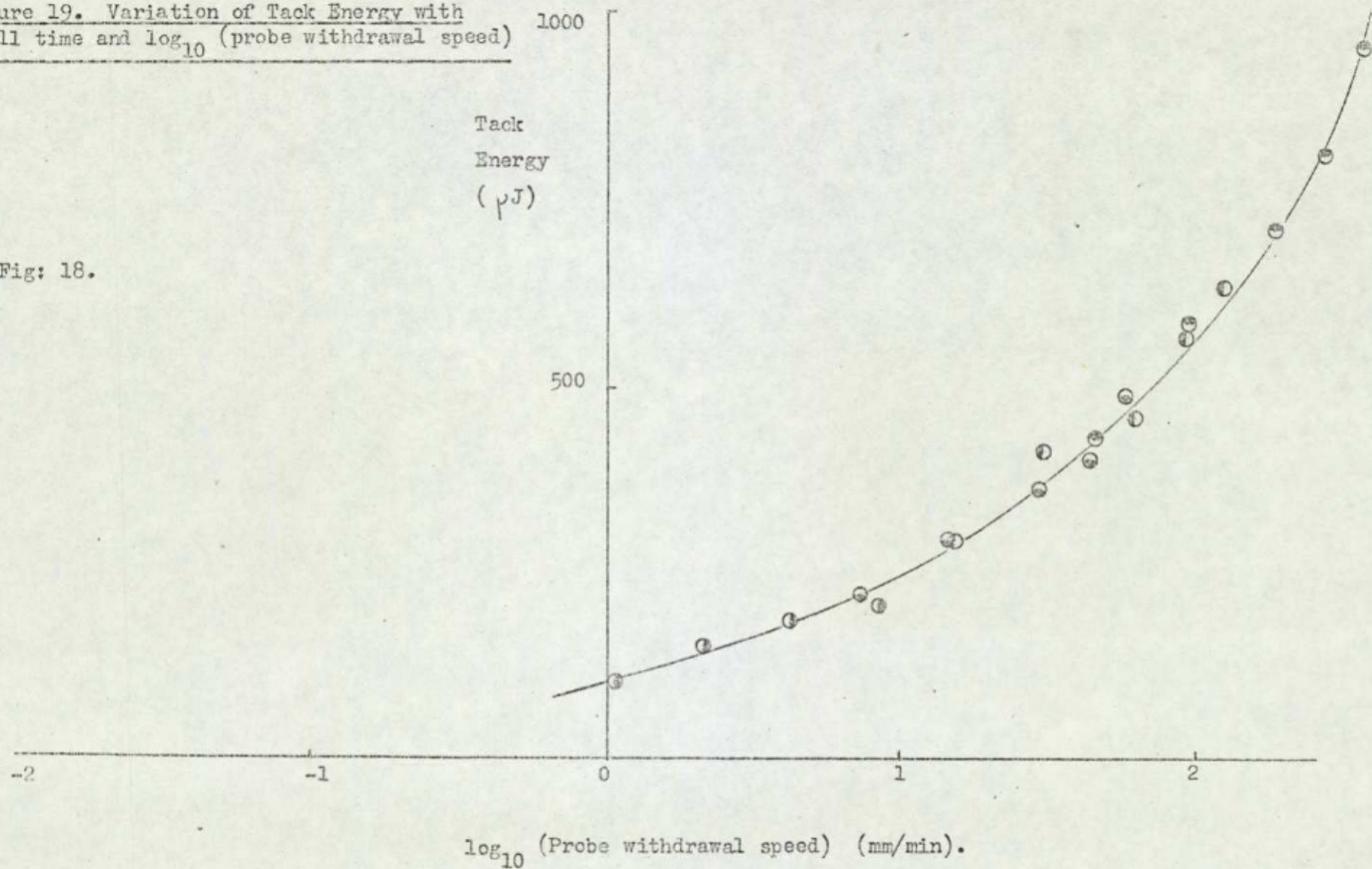
Adhesive film
thickness 1.50 mm.

Perspex probe
probe load 4.41g.

Figure 19. Variation of Tack Energy with
Dwell time and $\log_{10}$ (probe withdrawal speed)

Key

As Fig: 18.



By referring to Figure 15, the slope is in fact equal to $\log_{10}$ (strain rate) in the above equation. The value of K is 0.209 which means that the variation of speed of test with film thickness differs from the strain rate by a factor of $\text{antilog } 0.209 = 1.62$. This is presumably related to geometry during test.

3

Reduction of Variables in the Probe Tack Test

On an entirely empirical basis, it was found that by expressing the abscissae in Figures 2, 3, 4, 6 and 8 as $\log_{10}$ (probe withdrawal speed) superposition of data analogous to the rate-temperature superposition was possible.

Figure 16 is derived from Figure 4 and a series of curves is obtained. By the horizontal shift procedure it was possible to form the single continuous curve indicated in Figure 17. The shift factors used are indicated in Table XVI.

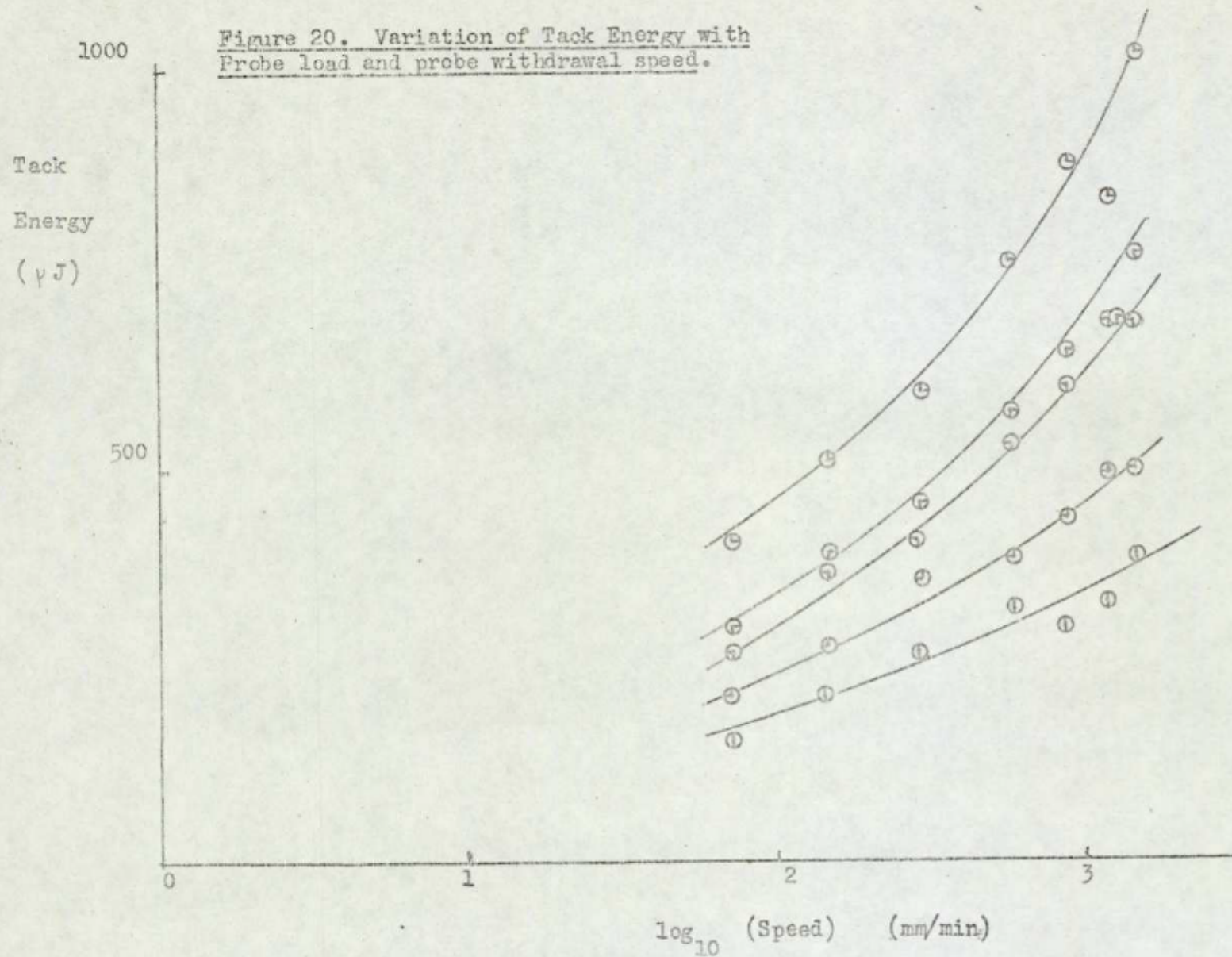
TABLE XVI

Shift factors used to derive Figure 17 from Figure 16.

Dwell Time (secs)	2	5	10	20	40	60
$\Delta \log_{10}$ (probe speed)	0	0.275	0.48	0.68	0.89	0.05

To extend this procedure over a wider range of rates, further dwell time/probe speed data were obtained using a differing adhesive film thickness (Figure 3) and this data is indicated in Figure 18. Again, a single continuous curve is obtained by the shift procedure and this is indicated in Figure 19. The shift factors used

Figure 20. Variation of Tack Energy with Probe load and probe withdrawal speed.



Key	Load/Dwell time
⊕	12.45g/20 secs
⊗	9.45g/10 secs
⊙	7.45g/10 secs
⊖	4.45g/10 secs
⊙	2.45g/10 secs

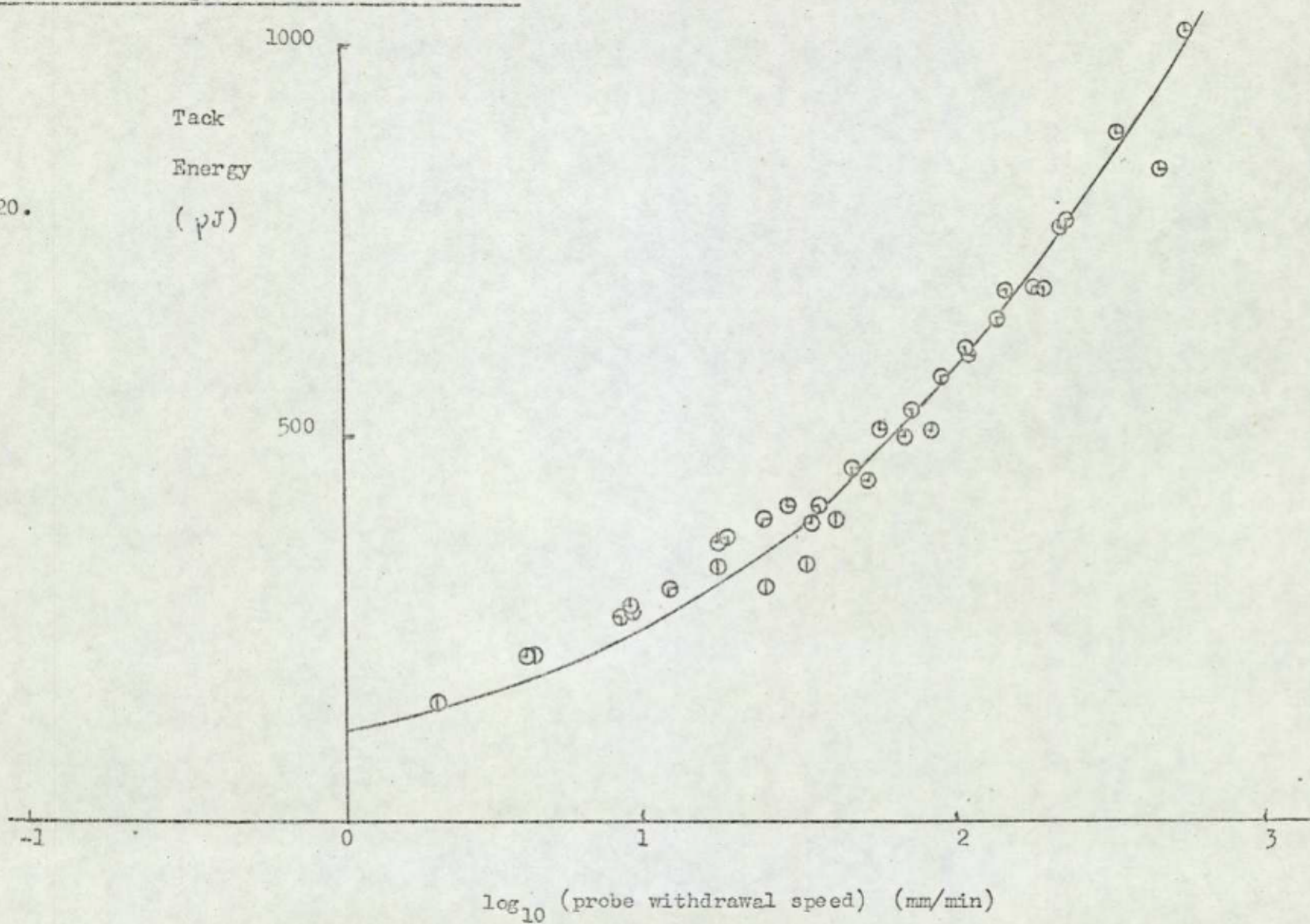
Perspex Probe
Adhesive film
thickness 1.46mm.

Figure 21. Variation of Tack Energy with
Probe Load and $\log_{10}$ (Probe withdrawal speed)

Key

As Fig: 20.

Tack
Energy
(μJ)



are indicated in Table XVII.

TABLE XVII

Relative shift factors used to derive Figure 19
from Figure 18

Dwell Time (secs)	3	10	20	60
$\Delta \log_{10}$ (probe speed)	0	-0.47 ₍₅₎	-0.80	-1.35

Empirically therefore, variation in dwell time during bonding is equivalent to variation in the probe withdrawal speed. This is useful for two reasons. Firstly it indicates the interrelation of bonding and debonding parameters and secondly represents a considerable simplification in the presentation and interpretation of the data.

The basis for the equivalence of dwell time and rate variation is the time dependent compliance of the adhesive. The effect of increasing dwell time is to increase the compliance of the adhesive and the value of compliance at the instant debonding commences strongly influences the energy stored during debonding.

The effect of probe load on tack energy was indicated in Figure 2. Expressing the probe withdrawal speed on a logarithmic curve yields figure 20. A family of curves is obtained which by the shift procedure yield the single continuous curve of Figure 21. This indicates that a

second bonding parameter can be expressed in terms of a debonding parameter. Table X (Chapter 4) indicated that as probe load increases, so does the volume of adhesive involved in the debonding procedure. This effect which is a function of adhesive compliance, is to simplify the expression of results by reducing the variables involved to a single variable.

The relative shift factors used to derive Figure 21 from Figure 20 are indicated in Table XVIII.

TABLE XVIII

Relative shift factors used to derive Figure 21
from Figure 20

Probe load (g)	2.45	4.45	7.45	9.45	12.45
$\Delta \log_{10}$ (Speed)	-1.12	-0.79	-0.50	-0.39	0

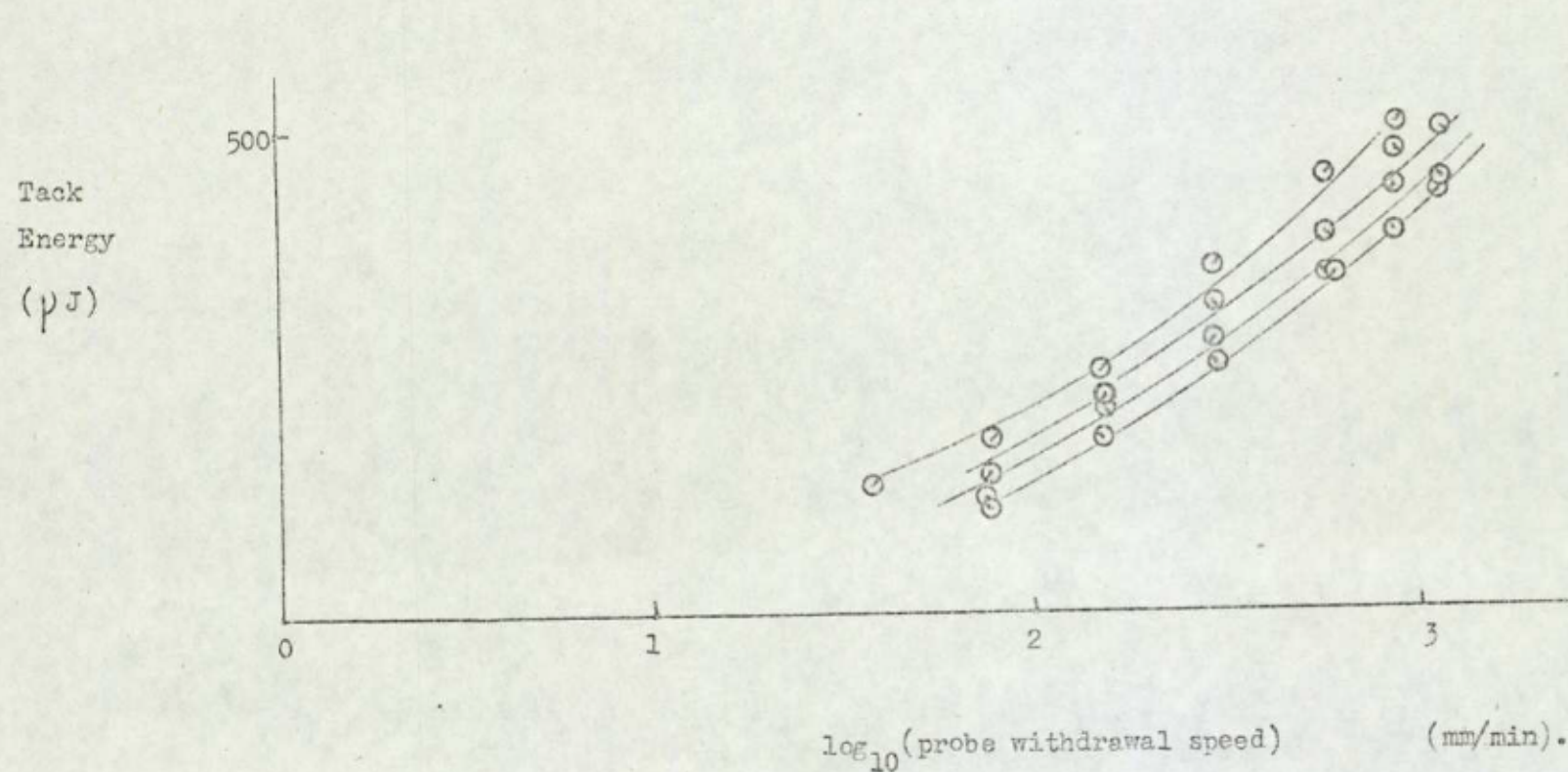
The variation of temperature and probe speed indicated in Figure 6 is expected to yield a single continuous curve by superposition as a direct result of the superposition principle. This is found to be the case and the results are indicated in Figures 22 and 23, and the appropriate shift factors are indicated in Table XIX.

TABLE XIX

Relative shift factors used to derive Figure 23
from Figure 22

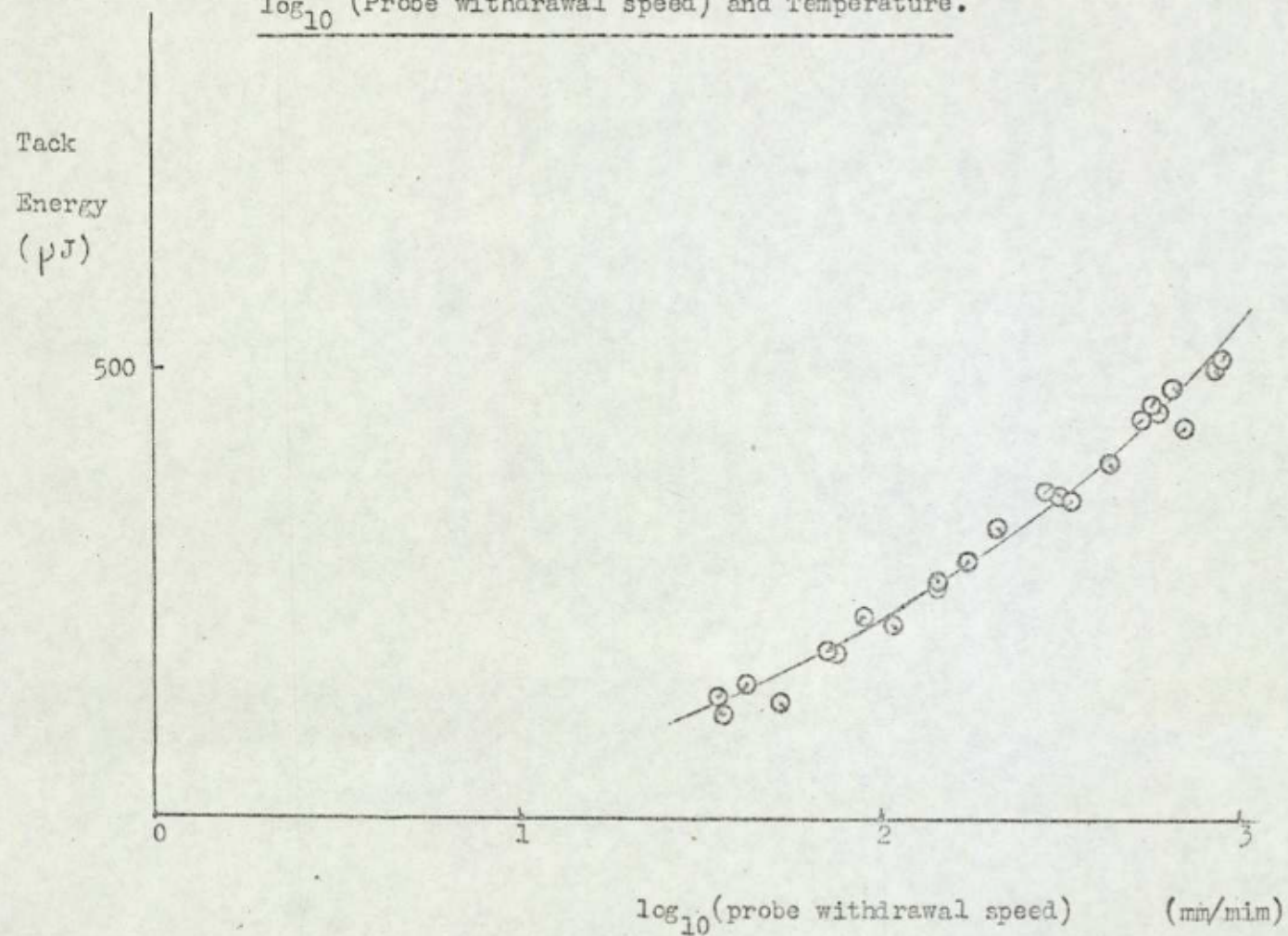
Temperature °K	292	297	304	309
$\Delta \log_{10}$ (Speed)	0	-0.11	-0.22	-0.30

Figure 22. Variation of Tack Energy with $\log_{10}$ (Probe withdrawal speed) and temperature



Key	Temperature
○	282°K
⊙	304°K
⊖	297°K
⊗	309°K
Adhesive film thickness 1.39mm	
Dwell time 10 secs	
Perspex probe	
Probe load 4.41g.	

Figure 23. Variation of Tack Energy with
 $\log_{10}$ (Probe withdrawal speed) and Temperature.



Key:

As Fig: 22

Finally, the data of Figure 8 may be expressed using $\log_{10}$ (probe withdrawal speed) as abscissa and this is shown in Figure 24. Again by superposition procedure the curves may be superimposed to yield a single curve indicated in Figure 25. The relative shift factors used are shown in Table XX.

TABLE XX

Relative shift factors used to derive Figure 25
from Figure 24

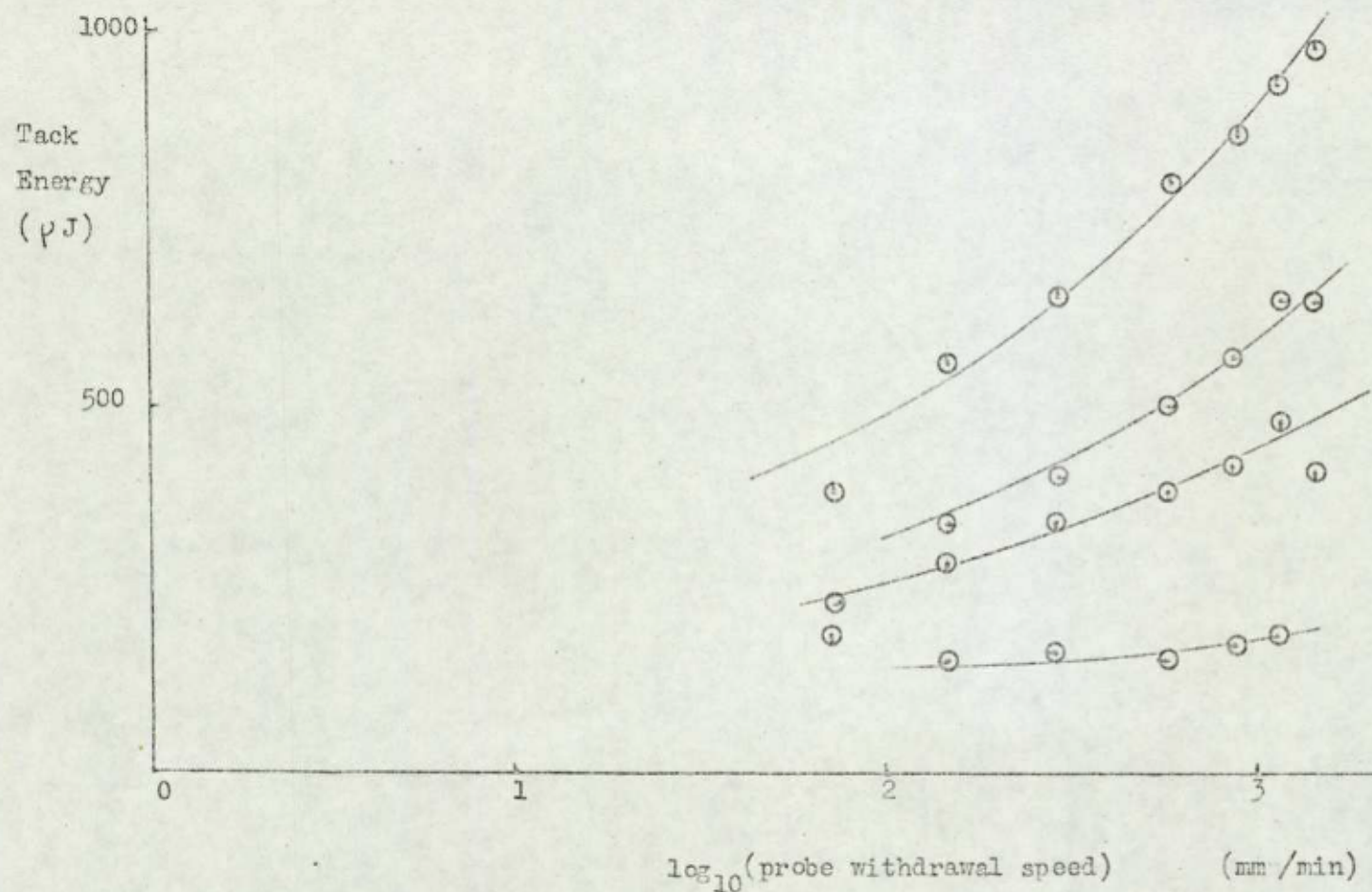
Probe	Nylon 66	Perspex	Poly-ethylene	P.T.F.E.
Probe γ_c , mJ/m ²	43.5	42.0	34.0	18.5
$\Delta \log_{10}$ (Speed)	0	-0.51	-0.81	-1.65

There is no theoretical justification or precedent for this procedure in literature. A theoretical justification is derived in Chapter 7.

6.4 Summary of the proposed superposition technique for Tack Energy results

The superposition of dwell time with rate, probe load with rate, adhesive film thickness with rate and temperature with rate has been interpreted in terms of the bulk modulus properties of the adhesive which are rate sensitive.

Figure 24. Variation of Tack Energy with $\log_{10}$ (Probe withdrawal speed) and Probe Composite.



Key

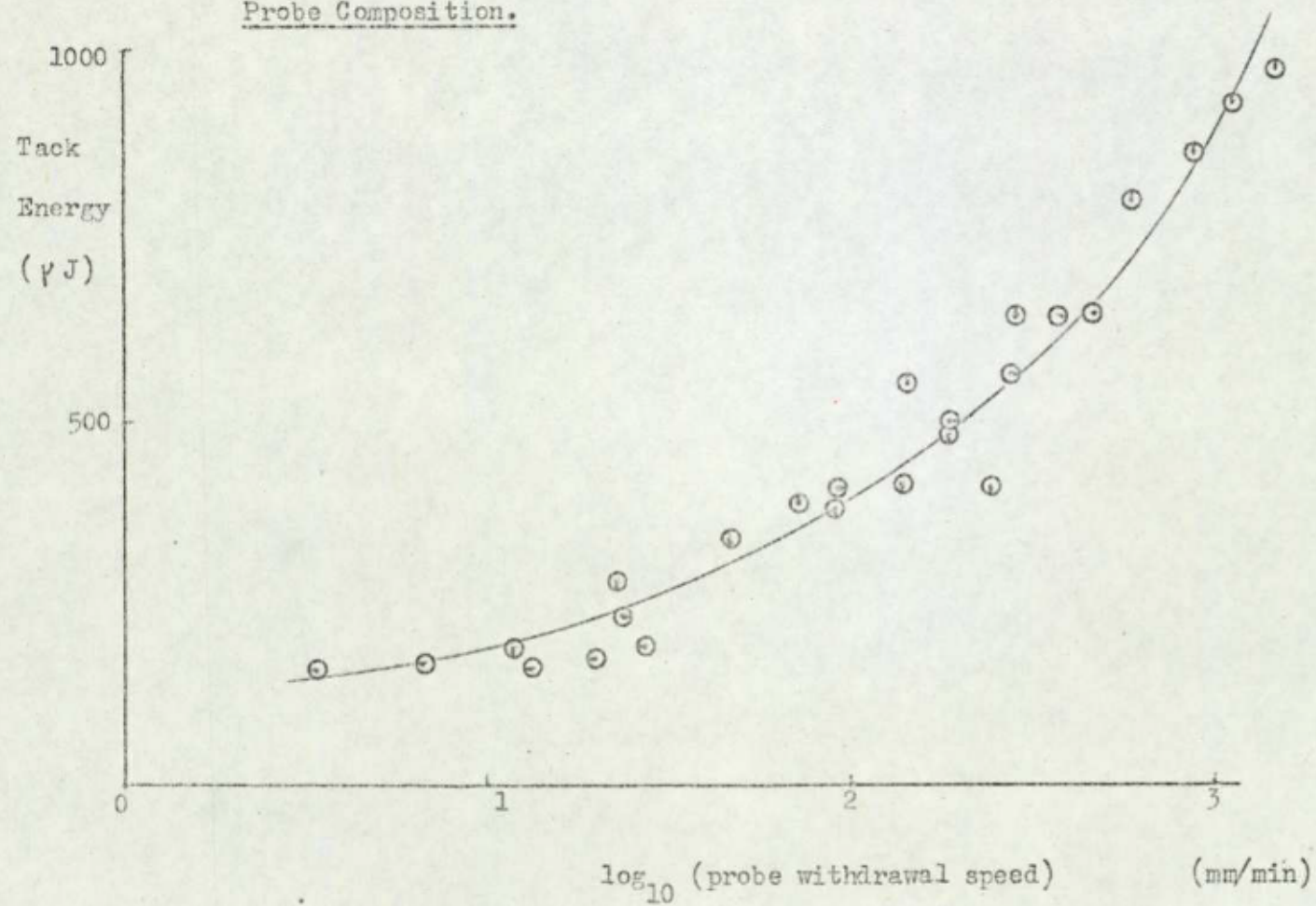
- Nylon 66
- ⊖ Perspex
- ⊙ Polyethylene
- ⊗ P.T.F.E.

Adhesive film thickness 1.45mm.

Probe load 4.41g.

Dwell Time 10 secs.

Figure 25. Variation of Tack Energy with Probe Composition.



Key

As Fig: 24.

This has resulted in a simplification in presentation of the tack energy data. However, the superposition of probe composition effects has no clear interpretation but certainly is to some extent a function of the interfacial properties of substrate and adhesive during bonding and debonding.

Empirically, however, the superposition of tack data can be taken a step further. If the curves derived in Figures 25, 23, 21, 19 and 17 are shifted horizontally, it is possible to form a single continuous master curve and this is shown in Figure 26. The curve obtained is of the form

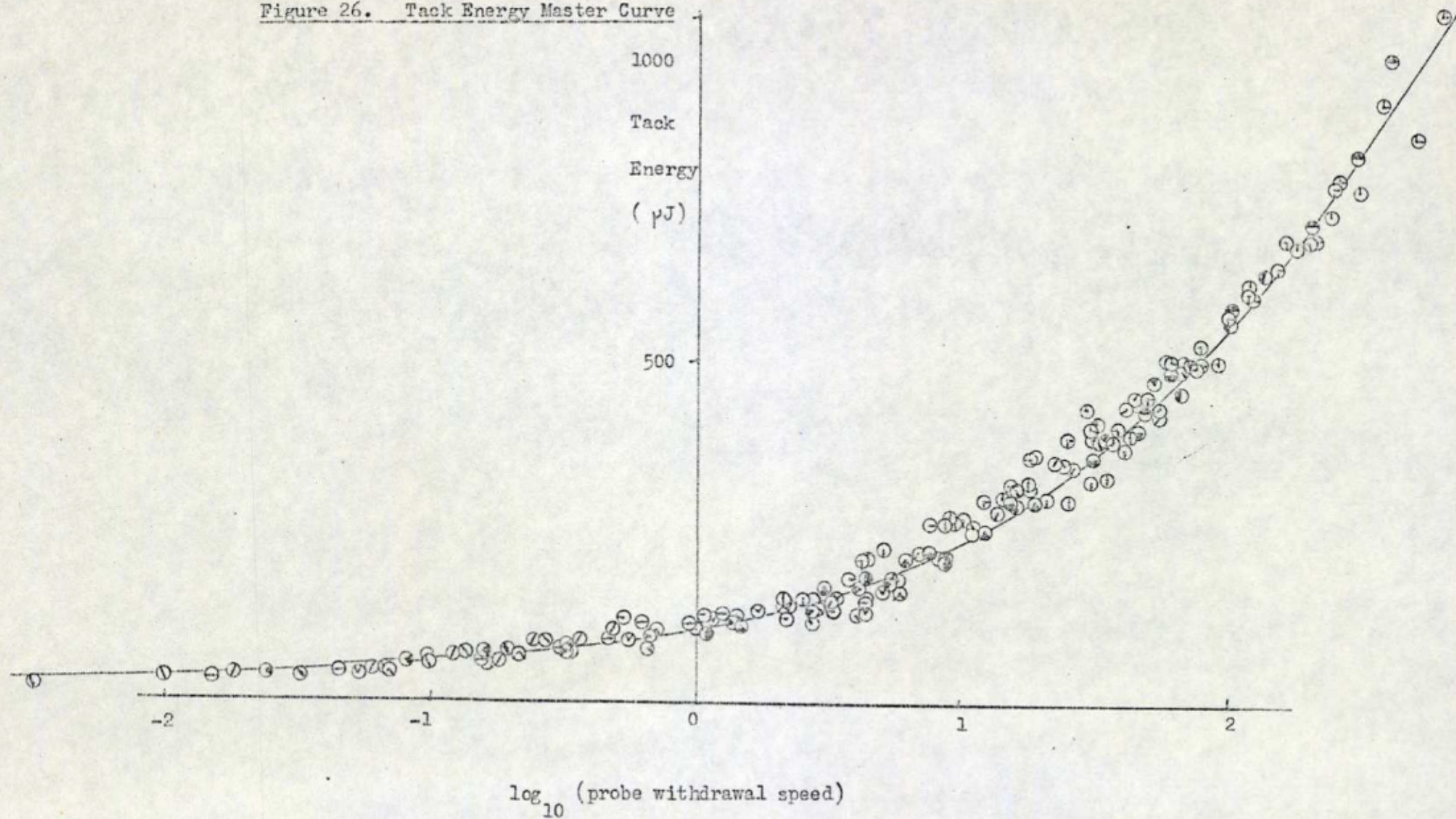
$$y = A \exp (mx)$$

where y is tack energy, x is $\log_{10}$ (probe speed) and A and m are constants.

To construct Figure 26 it was arbitrarily decided to give the constant A the value of $100\mu\text{J}$ whence it is found that the value of m is 0.90.

This single master curve represents the tack energy - rate variation of the adhesive over a wide range of parameters. The effect is to reduce all variables in the probe tack method to a single variable ($\log_{10}$ probe speed) which to the Author's knowledge, has not been reported previously. A considerable simplification in the expression of tack data results, which also raises several important theoretical points which are discussed in Chapter 7.

Figure 26. Tack Energy Master Curve



CHAPTER 7

THEORETICAL CONSIDERATION OF TACK ENERGY REDUCED VARIABLE TECHNIQUE

7.1 INTRODUCTION

The shift factors used to derive the single master curve indicated in Figure 26 are entirely empirical as is the derived tack equation

$$y = A \exp (mx).$$

The procedure combines both bonding and debonding effects into one single equation which has not been reported previously. This raises several important considerations.

Predominantly, previous work has dealt with the formation of an adhesive bond which is then debonded after adhesive and substrate have achieved equilibrium such that all observed debonding phenomena can be clearly linked with the debonding step and the nature of the equilibrium attained after bonding.

The essence of the tack test is that debonding is carried out after a relatively short period of bonding - so short in fact that the bonding process has not been taken to completion. The debonding process is therefore sensitive to the extent to which bonding has taken place, since the time and pressure of bonding strongly influence the compliance of adhesive and also the wetting process.

7.2 The Nature of the Debonding Stage in Adhesive Testing.

Current thinking on the debonding stage has focussed attention on a characteristic failure energy, θ_0 , per unit

area of interface as discussed in Section 6.1. At infinitely slow rates of test θ_0 is identified with the thermodynamic work of adhesion. Williams (1972) has similarly proposed a failure energy based on fracture mechanical considerations. In any material there are discontinuities of composition which are the cause of weaknesses in that material when it is subjected to stress. These weaknesses or flaws are of a finite size, the average of which may be related to the magnitude of stress (termed the critical stress) required to cause increase of the flaw size to the extent that the material fractures. Williams has described two types of flaw size. Firstly, a small size which is a feature of brittle materials and large flaw size, both of which govern the type of failure observed. In the large flaw size region, the failure of the material is not due to the fact that the applied stress exceeds the critical stress but failure is a function of the energy expended in applying stress. This is termed the energy balance criterion.

When an adhesive/substrate interface is present, the flaw distribution becomes denser and/or of larger than the average size than for a single uniform material.

For a crack length of a the strain energy of deformation, u , is a function of critical stress σ_c , Young's modulus E and a as follows:

$$U = \frac{\pi a^2 \sigma_c^2}{E} \dots\dots\dots (53)$$

$$\text{Then } \frac{\partial U}{\partial a} > \frac{\partial 4a\theta_c}{\partial a} \dots\dots\dots (54)$$

$$\text{and hence } \sigma_c > \left[\frac{2}{\pi} \cdot \frac{E\theta_c}{a} \right]^{\frac{1}{2}} \dots\dots\dots (55)$$

where θ_c is the cohesive fracture energy density.

When failure occurs at an interface Williams (1972) has shown that the only significant change is that the adhesive fracture energy θ_a is substituted for θ_c .

Williams went on to show that for an adhesive in the viscoelastic state, both the modulus E and the adhesive fracture are time dependent:

$$\sigma_d(t) = K \left[\frac{E(t) \theta_a(t)}{a} \right]^{\frac{1}{2}} \dots\dots\dots (56)$$

He was able to show that the time dependent crack position may be deduced by applying a time dependent form of the energy balance criterion.

In addition, the velocity of crack growth after fracture initiation may be deduced. The work of Andrews and Kinloch (1973) and Williams (1972) has conclusively shown that the debonding stage is strongly time dependent and in particular the surface energy effects are linked with this time dependency.

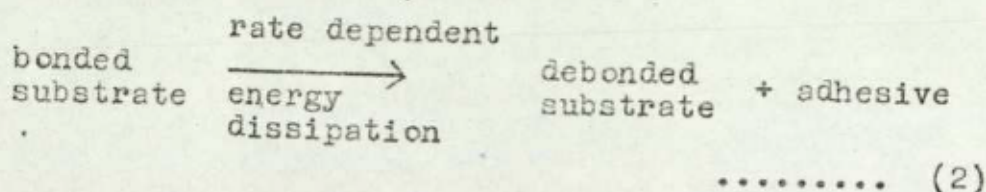
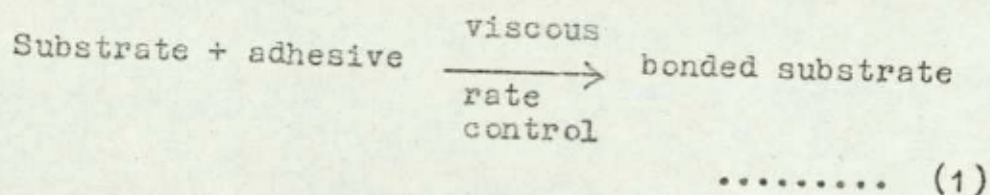
In the tack test, the interfacial debonding rate (crack growth rate) is not measured and is probably not constant under the conditions used. The rate measured is the rate of strain in the main bulk of adhesive. The energy measured is therefore stored viscoelastically in the transient network set up on debonding. However, it has been shown that the nature of the substrate affects the observed energy of tack. During the debonding stage, this interfacial effect is related to the fracture energy considerations indicated above. The nature of surface effects during the bonding stage is considered in the next section.

Nature of the Bonding Stage in the Tack Test and
its Relation to the Debonding Stage.

Comparatively little information on the mechanisms involved in the bonding stage for liquid adhesives has been reported in the literature. Schonhorn (1966) and Cherry (1969) have studied the wetting process of polymeric liquids to various substrate using a contact angle technique. They have shown that the wetting process is time dependent and that a shift factor (a_T) may be defined which is a function of adhesive viscosity, adhesive surface tension, γ_a , and a reciprocal length which is a function of the nature of the interface. This evidence points to a viscous flow process of wetting and Cherry has explained the wetting process using Eyring's theory of viscosity in terms of an activated rate process in which the activation energy barriers are the same as those which oppose viscous flow, from which an important point arises.

It is known that surface rugosity of the substrate influences contact angle measurements in low viscosity fluids and Cherry (1969) states that the activation energy barriers of spreading are due solely to rugosity and in this instance, rate controlling. In the case of high viscosity materials, the rate controlling step is the viscosity activation energy barrier.

It has been observed in the course of this present work that probe surface roughness did not apparently influence the observed tack energy. This implies that the bonding stage in the tack test is viscosity controlled.



The above scheme indicates the steps involved in the tack test. In stage (1) bonding is controlled by a viscosity activation energy barrier and stage (2) depends on time dependent modulus and fracture energy parameters.

Since both stages are time dependent, it is apparent that time is the common variable to which all parameters may be related. This is the justification for the superposition procedure as it applies to the tack test.

4 The nature of the Activation Energy Barriers in the bonding stage

4.1 Introduction

It is the purpose of this section to define more clearly the relationship of the activated flow process of bonding to the total bulk properties of the substrate/adhesive assembly.

Firstly, it is assumed that the adhesive is in the visco-elastic state, well above the glass transition temperature. Secondly, it is assumed that Eyring's theory of absolute reaction rates may be applied to the bonding stage at the interface and Ferry's free volume concept of viscosity may be applied to the bulk adhesive viscosity.

As indicated in section 2.5, Eyring (1941) from Quantum Mechanical considerations derived an expression for the rate of reaction of a molecule in the gas phase which was of the form

$$\text{Rate} = C_0 \frac{kT}{h} \exp \frac{-\Delta F^\ddagger}{RT} \dots\dots\dots (57)$$

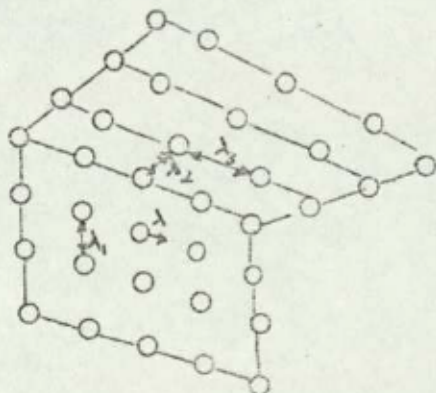
The rate constant was expressed as

$$\text{Rate constant} = K^1 = \frac{kT}{h} \exp \frac{-\Delta F^\ddagger}{RT} \dots\dots\dots (58)$$

These considerations were applied to many rate processes and of interest here is its application to viscosity. The resistance to flow encountered by a molecule moving through a matrix of similar molecules is expressed in terms of the potential energy surfaces (or barriers) which require an activation energy in order that the molecule may pass over the barrier. In viscous flow, this activation energy is supplied by the applied stress.

7.4.2 Application of the rate theory to viscosity

If the process of flow is assumed to be governed by activation energy criteria, then a molecule must move against the potential energy barrier of its neighbours. Consider a three dimensional array of molecules as follows:



A force, f , is necessary to move a molecule in the direction of the force. The effect of the force is to reduce the activation energy $\Delta F^\ddagger$ in the direction of the force by a factor $(f \frac{\delta}{2})$ and to increase the activation energy in the reverse direction by the same factor, where δ is related to the shape of the activation energy barrier. The equilibrium is therefore altered such that the molecule moves in the direction of the applied force. Reciprocal viscosity is related to the applied force, f , and the velocity gradient, $\frac{\Delta u}{\lambda_1}$, is as follows:

$$\frac{1}{\eta} = \frac{\Delta u}{\lambda_1 f} \quad \dots\dots\dots (59)$$

Eyring suggested that the velocity is related to the net rate of movement as follows:

$$\Delta u = \lambda [K_f^1 - K_b^1] \quad \dots\dots\dots (60)$$

K_f^1 is the rate constant for the forward reaction

K_b^1 is the rate constant for the backward reaction

$$K_f^1 = \frac{kT}{h} \exp\left(\frac{-\Delta F^\ddagger}{RT}\right) \exp\left(\frac{f \lambda_1 \lambda_2 \lambda_3}{2 kT}\right) \quad \dots\dots (61)$$

$$K_b^1 = \frac{kT}{h} \exp\left(\frac{-\Delta F^\ddagger}{RT}\right) \exp\left(\frac{-f \lambda_2 \lambda_3 \lambda_1}{2 kT}\right) \quad \dots\dots (62)$$

$$\text{hence } \eta^{-1} = \frac{\lambda_1^2 \lambda_2 \lambda_3}{\lambda_1 h} \exp \left(\frac{-\Delta F^\ddagger}{RT} \right) \dots\dots\dots (63)$$

$$\approx \frac{V}{Nh} \times \exp \left(\frac{-\Delta F^\ddagger}{RT} \right) \dots\dots\dots (64)$$

$$\text{Finally } \eta = \frac{Nh}{V} \times \exp \left(\frac{\Delta F^\ddagger}{RT} \right) \dots\dots\dots (65)$$

where N is Avogadro's number and
V the volume of the system

Eyring went on to show that the activation energy is comprised of the work required to create free volume for a molecule to jump into available free volume and the work required to free the molecule from its immediate environment to enable it to jump. In practice the former is predominant and is a constant fraction of the energy of vaporization of a molecule ΔE_{Evap}

$$\eta = K \exp \frac{\Delta E_{\text{Evap}}}{nkT} \dots\dots\dots (66)$$

where K and n are constants.

This important conclusion is of fundamental significance in the following analysis.

7.4.3 Consideration of Bulk and Interfacial Viscosities

In an adhesive bond, the adhesive mass is adsorbed onto the substrate surface by a viscous flow process at the interface (Cherry, 1969). The rheological behaviour at the interface during this flow process will be

governed by the applied stress and surface energy effects. In this case the work required to alter the free volume at the interface will be greater than in the bulk by a factor proportional to the energy of adsorption ΔE_{ads} . In other words, flow at the interface is governed by activation energy barriers associated with the energy of adsorption whilst flow in the bulk is governed by the available free volume.

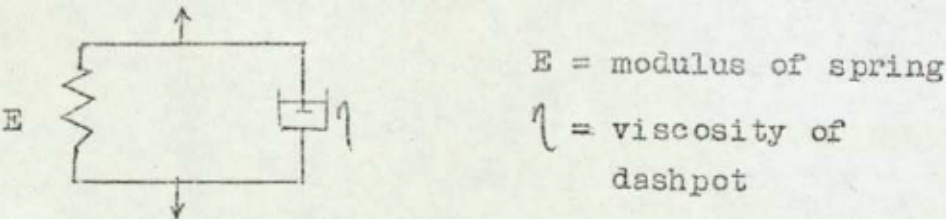
Let η_s be the surface viscosity

Let η_B be the bulk viscosity

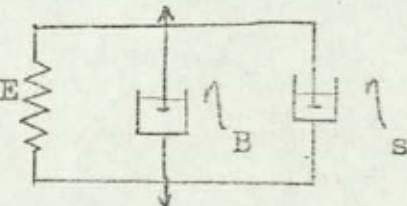
then
$$\frac{\eta_s}{\eta_B} = \exp \frac{\Delta E_{ads}}{nkT} / \exp \frac{1}{f} \dots\dots\dots (67)$$

hence
$$\eta_s = \eta_B \exp \left[\frac{\Delta E_{ads}}{nkT} - \frac{1}{f} \right] \dots\dots\dots (68)$$

This concept may be extended to linearly viscoelastic adhesives by employing a Voigt model which is a Hookean spring in parallel with a Newtonian dashpot



In the tack bonding situation, a constant applied load causes a surface flow in addition to a bulk flow component. The second flow component may be represented by an additional dashpot in the Voigt model in parallel with the first



The stress, σ , in the model is the sum of the stresses in each element hence

$$\eta_B \frac{d\epsilon}{dt} + \eta_s \frac{d\epsilon}{dt} + E\epsilon = \sigma \dots\dots\dots (69)$$

where σ = stress ϵ = strain t = time

Since however it is postulated that η_s is related to η_B by equation (68) then

$$\sigma = \eta_B \frac{d\epsilon}{dt} \left[1 + \exp \left(-\frac{E\epsilon s}{nKT} - \frac{1}{F} \right) \right] + E\epsilon \dots\dots (70)$$

For simplicity, let the exponential term in equation (70) be represented by A then

$$\eta_B \frac{d\epsilon}{dt} (1 + A) + E\epsilon = \sigma \dots\dots\dots (71)$$

$$\therefore \frac{d\epsilon}{dt} + \frac{E\epsilon}{(1+A)\eta_s} = \frac{\sigma}{\eta_s(1+A)} \dots\dots (72)$$

This equation may be solved by multiplying both sides by $\exp \int \frac{E}{(1+A)\eta_s} dt$

$$\frac{d\epsilon}{dt} \exp \int \frac{E}{\eta_s(1+A)} dt + \frac{E\epsilon}{\eta_s(1+A)} \exp \int \frac{E}{\eta_s(1+A)} dt = \frac{\sigma}{(1+A)\eta_s} \exp \int \frac{E}{\eta_s(1+A)} dt \dots\dots\dots (73)$$

$$\text{i.e. } d \left[\epsilon \exp \int \frac{Edt}{\eta_s(1+A)} \right] = \int \frac{\sigma}{\eta_s(1+A)} \exp \int \frac{Edt}{\eta_s(1+A)} dt \dots\dots\dots (74)$$

$$\epsilon \exp \frac{Et}{\eta_s(1+A)} = \frac{\sigma}{E} \exp \frac{Et}{\eta_s(1+A)} + C \dots\dots\dots (75)$$

Where C is an integration constant which may be evaluated by applying the boundary conditions

$$\sigma = \sigma_0 \quad t = 0 \quad \epsilon = 0$$

$$\text{Hence } C = - \frac{\sigma_0}{E} \quad \dots\dots\dots (76)$$

$$\epsilon \exp \frac{Et}{\eta(1+A)} = \frac{\sigma_0}{E} \exp \left(\frac{Et}{\eta(1+A)} \right) - \frac{\sigma_0}{E} \quad \dots\dots\dots (77)$$

$$\text{Finally} \quad \epsilon = \sigma_0 J \left[1 - \exp \frac{-t}{(1+A)\tau} \right] \quad \dots\dots\dots (78)$$

where J is the compliance of the element

and $\tau = \eta/E$ is called the retardation time and is the time taken by the model to dissipate stored elastic energy.

Comparing this result with a Voigt model containing one dashpot, the only difference is that the retardation time τ is multiplied by a factor $(1 + A)$.

The Boltzmann principle outlined in Chapter 2, section 2.3 enables the viscoelastic properties of a real polymer system to be expressed in terms of an infinite number of Voigt elements in series.

Equation (78) becomes

$$\epsilon_t = \sigma_0 \int_0^\infty J_t \left[1 - \exp \left(\frac{-t}{\tau(1+A)} \right) \right] d\tau \quad \dots\dots\dots (79)$$

The important point is that the retardation times τ_1 are multiplied by a constant factor $(1+A)$

$$\text{Mathematically } \tau = \tau_0 (1+A) \quad \dots\dots\dots (80)$$

where τ_0 = retardation time observed in the bulk polymer

τ = retardation time when surface flow occurs, eg. due to adhesive bond formation.

If the same adhesive is applied under constant stress to two different substrates 1 and 2, then the surface viscosities will be altered by a factor proportional to ΔE_{ads}^1 and ΔE_{ads}^2 . The effect is to alter the retardation times τ_1 and τ_2 as follows

$$\tau_1 = \tau_0 (1 + A_1) \quad \dots\dots\dots (81)$$

$$\tau_2 = \tau_0 (1 + A_2) \quad \dots\dots\dots (82)$$

$$\text{where } A_1 = \exp \left(\frac{\Delta E_{ads}^1}{nkT} - \frac{1}{f} \right), \quad A_2 = \exp \left(\frac{\Delta E_{ads}^2}{nkT} - \frac{1}{f} \right)$$

that is

$$\frac{\tau_1}{\tau_2} = \frac{1 + A_1}{1 + A_2} \quad \dots\dots\dots (83)$$

Now the ratio is a particular form of the superposition principle due to Williams - Landel - Ferry (1955) which states that the effect of varying temperature is to multiply or divide the time scale by a constant factor at each value of temperature.

This constant factor is termed the shift factor a_T

$$a_T = \frac{\tau(T)}{\tau(T_0)} \dots\dots\dots (84)$$

In this case however, the shift is due to variation of substrate to which a linear viscoelastic adhesive is brought into contact. The effect of varying substrate is therefore to multiply the time scale of an experiment by a constant factor related to the energy of adsorption. Let this shift factor be denoted by a_Y

$$a_Y = \frac{\tau_1}{\tau_2} = \frac{1 + A_1}{1 + A_2} \dots\dots\dots (85)$$

Expanding A_1 and A_2 yields

$$a_Y = \frac{1 + \exp\left(\frac{\Delta E_{ads}^1}{nkT} - \frac{1}{f}\right)}{1 + \exp\left(\frac{\Delta E_{ads}^{11}}{nkT} - \frac{1}{f}\right)} \dots\dots\dots (86)$$

where ΔE_{ads}^1 is energy of adsorption with
substrate 1

ΔE_{ads}^{11} is the energy of adsorption with
substrate 2

$$a_Y = \frac{\exp \frac{1}{f} + \exp\left(\frac{\Delta E_{ads}^1}{nkT}\right)}{\exp \frac{1}{f} + \exp\left(\frac{\Delta E_{ads}^{11}}{nkT}\right)} \dots\dots\dots (87)$$

In principle therefore, the shift factor associated with the bonding process may be deduced from the fractional free volume at the temperature of test and the energy(s) of adsorption.

The above treatment has several limitations. The Voigt model or any modification of it is a convenient mathematical fiction and has no basis in physical reality. Nevertheless, the equation 7 is entirely independent of the model used to derive it and hence subsequent equations are also independent of the method of derivation.

The model is strictly applicable to the linear viscoelastic region only where strains are of the order of 1 to 2%. In practice, and the conditions employed during the tack test provide a good example, strains are much higher than this. In this region, the response of the material is certainly non-linearly viscoelastic. A comparatively simple modification of the model is to allow for non-linear behaviour as follows:

$$\text{Elastic strain in spring element} = \epsilon_e = \frac{\sigma}{E} + \frac{K_1}{(m+1)} \left(\frac{\sigma}{\psi} \right)^{m+1}$$

$$\text{Viscous strain rate in dashpot} = \frac{d\epsilon_v}{dt} = K_2 - \left(\frac{\sigma}{\omega} \right)^n$$

where

E, ψ, ω, m and n are related material parameter

K_1 is taken as $+1$ for compression (bonding)

K_2 is taken as -1 for tension

hence

$$\frac{d\epsilon}{dt} = \frac{d(\sigma/E)}{dt} + K_1 - \left(\frac{\sigma}{\psi} \right)^m \frac{d(\sigma/\psi)}{dt} + K_2 \left(\frac{\sigma}{\omega} \right)^n \dots \dots \dots (88)$$

This non-linear differential equation is considerably more complex but analysis shows that when applied to the modified

Voigt element the same conclusion is reached, that is the time scale is altered by a factor $(1 + A)$.

Even this modification is an over-simplification, since in the non-linear region, the Boltzmann superposition principle does not apply. The value of the Voigt element is principally in giving a simple convenient approximation to the experimentally observed facts, provided that the real molecular system can be represented by a properly chosen set of springs and dashpots. A more realistic model would consider first the response of the individual chains in the material and then the response of the network entanglements or junctions. The problem of network junction response has not yet been solved but in any case would be formidable in its complexity. The value of the model is to circumvent these difficulties until a quantitative model of molecular behaviour has been worked out.

The assumption in Eyring's treatment of viscosity that activation energies are related to either the energy of vapourization or adsorption is supported by rather tenuous experimental evidence. It works to a reasonable degree of accuracy considering the simplifications made in applying activation energy concepts to viscosity for simple liquids but for high polymers which have ordered structures an activation energy approach is generally less sound. The expression of the energy of activation as an entropy of activation may be more realistic, but the relationship of entropy of activation to adsorption energies is unclear. In any case the constant, η , can only have a value which is experimentally inaccessible.

The assumption that surface viscosity η_s is related to

bulk viscosity η_B as indicated in equation 68 is also open to discussion. The main assumption is that the pre exponential term is unity. Fortunately it is the term in the exponential function which has the more important effect on the properties of the function. The use of energy terms and free volume terms in the exponential functions may at first sight appear incongruous. However, the energy term is in some way related to free volume since energy is required to create free volume. The energy of adsorption in practice is not a constant but usually the mean value of many energies of adsorption which result from surface roughness and defects.

7.5

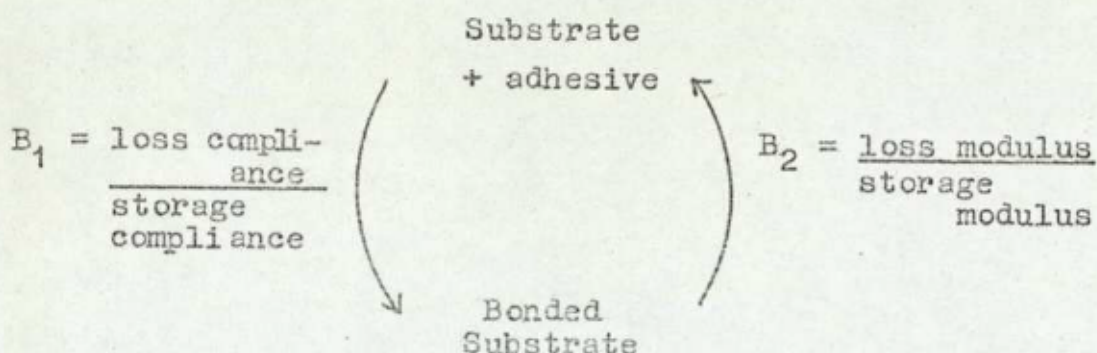
Nature of the constants in the Tack Equation

The observed tack energy is an exponential function of probe withdrawal speed. The constant m , remains constant over a wide range of probe speeds. It is also constant for dwell time, probe load, temperature and probe composition. This suggests that m is a characteristic of the adhesive material.

The properties of the equation also suggest that a high value of m , that is above approximately 0.5 indicates high energy dissipation during the tack test. Now it is well known that the energy dissipated in a viscoelastic material is related to the loss factor B . This loss factor is the ratio of dissipated energy to stored energy and is hence an indication of the extent of liquid like behaviour. Low energy dissipation (low value of B) is indicative of predominantly elastic behaviour of material and conversely high energy dissipation (high value of B) is indicative of predominantly liquid like behaviour.

It is therefore apparent that the constant m is related to the loss factor B . A high value of m indicates

predominantly elastic behaviour. This conclusion fits in well with the view of tack stated by Salomon, (1965). Note however, that there are two dissipative processes involved in the tack test. Firstly during bonding, energy is dissipated when substrate is mechanically contacted with adhesive and secondly during debonding energy is dissipated. The loss factor B is different during these two processes. The tack is therefore a function of these two values of B in the following cycle



In practical terms therefore, an evaluation of m leads directly to a picture of the tack behaviour of a material and it is now proposed that it might be termed the "tack parameter".

A feature^{of} tack testing is the concept of dwell time. Previous literature has always emphasised that tack is particularly associated with the rapid development of measurable bond strength. This is an important feature of tack but no agreed standard dwell time has ever been adopted, with the result that a wide range of arbitrary dwell times have been adopted.

The present work on tack has shown that tack is related to the loss factor at bonding and debonding stage. The dwell time is related to the loss factor during debonding but there is no particular value of dwell time which is of significance, nor indeed applied bonding

pressure since both may be related to and expressed in terms of the rate of debonding. The definition of tack given in Chapter 1 is therefore inadequate except as a qualitative description of the phenomenon.

The constant A in the tack equation was arbitrarily fixed at 100γJ to fix a reference from which Figure 26 could be constructed. The physical significance of this may be arrived at by expressing the tack equation logarithmically then differentiating

$$\begin{aligned}
 \gamma &= A e^{mx} \\
 \log_e \gamma &= \log_e A + mx \qquad \dots\dots\dots (89)
 \end{aligned}$$

$$\frac{d \log_e \gamma}{dx} = m \qquad \dots\dots\dots (90)$$

Equation (90) yields equation (89) by integration and log_eA is the integration constant. The value given to A will depend on the compliance of the adhesive which in turn is a function of the radius of the hemispherical probe tip. The constant A is therefore related to this radius.

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER
WORK

8.1 CONCLUSIONS

The work on tack indicated here has concentrated on pressure sensitive adhesion of poly isobutyl vinyl ether. The literature on tack has been reviewed and as a result, a method of measuring tack energy has been developed. As indicated in Chapter 1, the significance of energy measurements are that they more adequately indicate the storage and loss of energy processes which occur in viscoelastic materials.

The accuracy of the method was evaluated and generally the coefficient of variation was 6% of the mean value in any set of tack energy data. Measurements were only made within the limits of test where this was true. A total of six variables were examined independently and in addition, the effect of hostile environments was also examined. The initial effect was to increase the observed tack energy but the long term effect was to render the adhesive unsuitable for use as a pressure sensitive adhesive within the scope of the definition used here.

The effect of adhesive solvent was examined and was found to influence strongly the observed tack energy. This was probably due to a small amount of residual solvent acting as a plasticizer for the adhesive.

The effect of substrate variations was examined. Previous work on tack had given conflicting evidence on the effect of probe critical surface tension. The results obtained in this work were found to agree with those of Sherriff Knibbs and Langley (1973).

The effect of probe surface roughness was found to be relatively insignificant. The work of Hammond (1963) had suggested it might be significant.

An empirical procedure was adopted to express the inter-relation of adhesive film thickness in terms of rate of test. Nominally the rate of test is the ratio of speed of test to adhesive film thickness. In the tack test a geometric factor of 1.6 was introduced.

The superposition technique was further extended to the remaining variables such as dwell time, probe load, temperature and probe surface free energy. This empirical procedure, was found to yield a simple continuous curve which was applicable over a wide range of tack variables. The curve was a simple exponential function:

$$\text{Tack Energy} = A \exp m (\log_{10} \text{probe speed})$$

where A and m are constants.

A was shown to be a geometric factor related to the probe dimensions. The constant m was linked to the storage and loss compliances during bonding and storage and loss moduli on debonding. It is thought that m is a unique feature of the tack behaviour of the adhesive material independent of the applied bonding or debonding parameters.

In particular, the effect of substrate surface free energy was discussed and by proposing a viscosity controlled bonding stage, an expression was derived which indicates why substrate variation may be linked to rate of debonding effects. The debonding stage is governed by fracture mechanical considerations and, at infinitely slow debonding rates, this is the work of adhesion.

The superposition of surface energy and rate of testing is a new concept not previously discussed in the literature.

The definition of tack suggested in Chapter 1 has been shown to be inadequate. Certainly it is a useful qualitative indication of the phenomenon, but the process has been shown to be a sophisticated process involved storage and loss compliances and moduli. A corollary to the initial definition could be 'that the energy dissipated on bonding and debonding is closely related to the rate of debonding'. However, the fact that tack is a term applied to a process involving several interacting parameters during both bonding and debonding, makes a brief succinct definition difficult.

8.2 Recommendations for further work

- 8.2.1 Further work initially on determining the variation of the constant A with probe geometry would be useful.
- 8.2.2. More extensive changes in composition could be made to investigate the basic structural parameters of the adhesive which influence the magnitude of m.

- 8.2.3 Concurrently with m, physical measurements of the loss factors at the bonding and debonding stage would lead to a precise knowledge of the relationship of m to these loss factors.
- 8.2.4 Further work could concentrate on measuring the rate of interfacial separation. This would require sophisticated experimental techniques, but would yield theoretically interesting results. With the apparatus used in this work, the tack energy at high rates of debonding could not be accurately measured. It would be useful to use energy measuring equipment capable of accurate measurement at high rates.
- 8.2.5 The flow theory of bonding has indicated the energy of adsorption is an important parameter in tack testing. Work on model compounds to deduce adsorption isotherms could possibly yield information on the precise influence of adsorption energies on adhesive behaviour in polymeric adhesives.

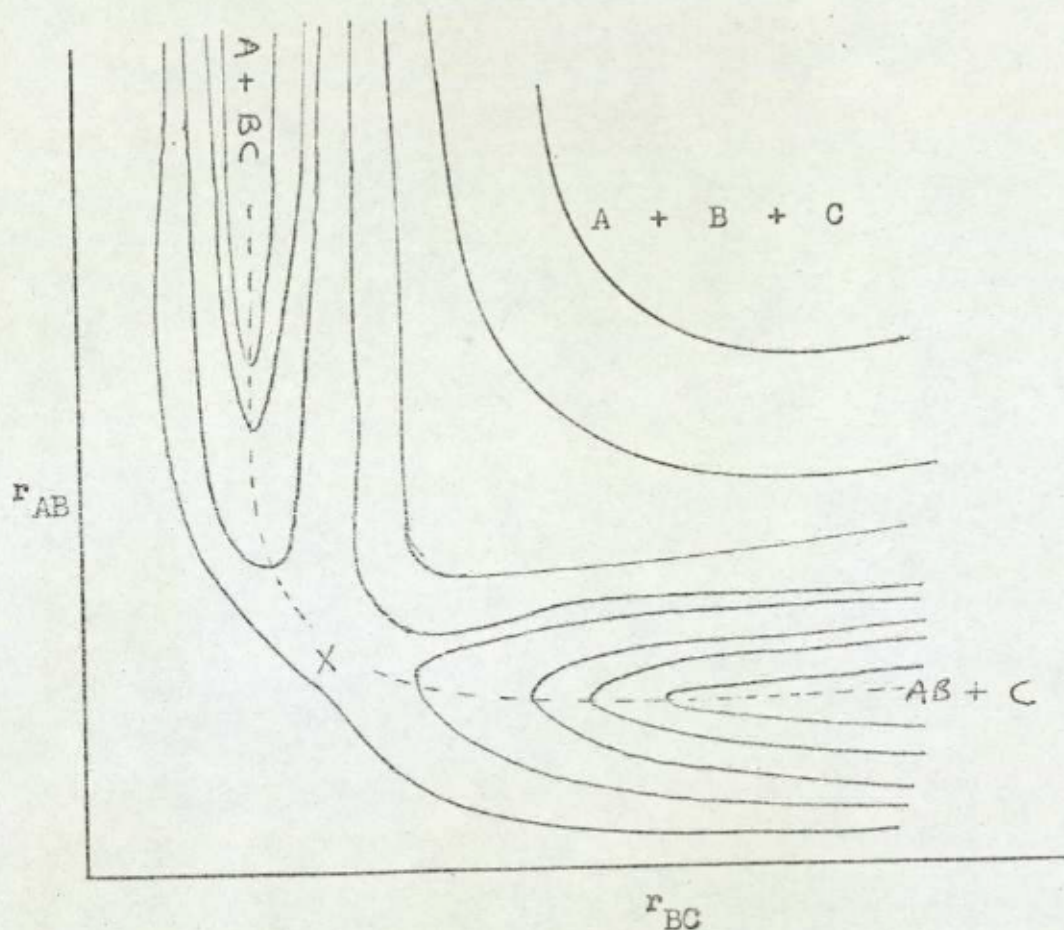
A P P E N D I X A

OUTLINE OF BASIC REACTION RATE THEORY

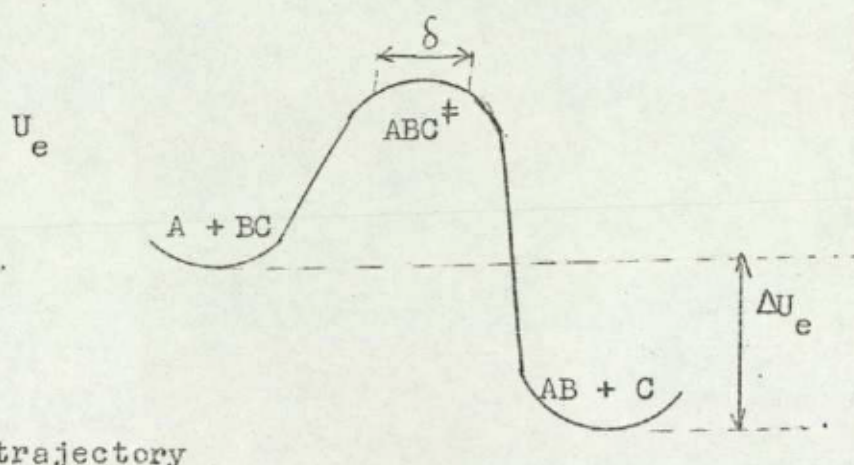
Eyring (1941) used a two stage analysis to predict reaction rates in the gas phase; a quantum mechanical calculation of the ground state electronic energy surface (potential surface) for the reaction followed by a statistical mechanical calculation of the reaction rate.

Calculation of potential energy surfaces is theoretically possible using Schrodinger's equation, but in practice is so difficult that approximation and simplification procedures are used. Using the Born - Oppenheimer approximation that the nuclei are stationary and only electrons are mobile, Eyring calculated the ground state electronic energy levels, U_e , for varying internuclear distances r . This ground state U_e is a function of r . The interactions which occur are electron-electron, electron-nucleus and nucleus-nucleus coulombic interactions which determine U_e . Additionally however, for polyatomic molecules, there are $(3_n - 5)$ linear or $(3_n - 6)$ non-linear degrees of freedom on which U_e depends. If $n \geq 3$ therefore, U_e is a function of at least three variables. Eyring used a semi empirical method of determining U_e from spectroscopic measurements and, by varying the internuclear distance, was able to construct potential surfaces, for instance in the reaction of A with BC to give products AB and C. In the following figure, let the y axis represent internuclear distance AB, and the x axis the internuclear distance BC. Then,

omitting for simplicity the AC axis, let the Z axis normal to the plane of the paper represent the potential energy axis U_e :



The dotted line represents the course of the particle on the potential surface and hence represents the reaction path. X represents the transition $A' - B - C$ which is termed the activated complex. Re-plotting the diagram along the trajectory of the particle yields the following curve:



The point x is a saddle point between the two states, reactants and products, but note that it is still a ground state energy.

Calculations of reaction rate was done using a statistical thermodynamic argument. Eyring postulated that the activated complex is in effect a stable molecule in equilibrium with reactants $A + BC$. This cannot be rigorously correct, but may be a close approximation if the molecules are activated and deactivated rapidly compared to the rate of decomposition of the activated complex. Treating the activated complex $ABC^\ddagger$ as a stable molecule permits the derivation of partition functions.

Eyring expressed the rate of reaction in terms of the activated complex $C^\ddagger$, velocity over the saddle point, $\bar{u}$, and saddle length as follows:

$$\text{Rate} = \frac{C^\ddagger \bar{u}}{\delta} \dots\dots\dots (91)$$

By normal co-ordinate analysis, Eyring showed that

$$\bar{u} = \frac{\int_0^{\infty} u \exp \left(\frac{-mu^2}{2kT} \right) du}{\int_{-\infty}^{\infty} \exp \left(\frac{-mu^2}{2kT} \right) du} = \frac{1}{\frac{m}{kT}} = \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}} \dots\dots\dots (92)$$

where m is the reduced mass of the activated complex. The equilibrium between reactants and complex is characterised by the constants K_a and the concentration of reactants C_o and complex $C^\ddagger$ as follows:

$$K_a = \frac{C^\ddagger}{C_o} \dots\dots\dots (93)$$

Now K_a contains a translational partition function derived as follows. The Wilson-Sommerfield extension of the Bohr quantization rule states that the energy of translation of a particle is the product of momentum and distance along the complete trajectory, i.e.

$$n_1 h = \oint p dq = 2m \dot{x} l \dots\dots\dots (94)$$

- where p = particle momentum
- dq = incremental distance
- $\dot{x}$ = velocity
- m = mass
- l = total distance travelled

$$\text{hence } \dot{x} = \frac{n_1 h}{2lm}$$

$$\text{The energy level is then } \epsilon_n = \frac{1}{2} m \dot{x}^2 = \frac{n_1^2 h^2}{8l^2 m} \dots\dots\dots (95)$$

and the associated translational partition function q_T is:

$$q_T = \sum_{n_1=1}^{\infty} \exp \frac{-\epsilon_{n_1}}{kT} = \sum_{n_1=1}^{\infty} \exp \frac{-n_1^2 h^2}{8l^2 mkT} \dots\dots\dots (96)$$

$$= \int_0^{\infty} \exp \left(\frac{-n_1^2 h^2}{8l^2 mkT} \right) dn_1 = \left(\frac{2\pi mk}{h^2} \right)^{\frac{1}{2}} l \dots\dots\dots (97)$$

In the case considered here $l = \delta$

$$\therefore q_T = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{1}{2}} \delta \dots\dots\dots (98)$$

and $K_a = q_T K^\ddagger$ where $K^\ddagger$ is a second equilibrium constant associated with the remaining partition functions

$$\therefore K_a = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{1}{2}} \delta K^\ddagger = \frac{C^\ddagger}{C_o} \dots\dots\dots (99)$$

$$\text{Rate} = C_o K^\ddagger \frac{\delta}{\delta} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{1}{2}} \left(\frac{k}{2\pi m} \right)^{\frac{1}{2}} \dots\dots (100)$$

$$= C_o K^\ddagger \frac{kT}{h} \dots\dots\dots (101)$$

The rate constant $K^\ddagger$ may be expressed as $\exp -\frac{\Delta F^\ddagger}{RT}$

where $\Delta F^\ddagger$ is the activation energy required to move reactants from the initial to the activated state.

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