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I hereby recommend that the thesis prepared under my supervision by Stanley W. Lasoski, Jr.

entitled Adhesion of Polyvinyl Acetate to Steel

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Approved by:

Walter Soller

Gerard Kraus

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ADHESION OF POLYVINYL ACETATE TO STEEL

A dissertation submitted to the

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DOCTOR OF PHILOSOPHY

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by

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TABLE OF CONTENTS

INTRODUCTION

The phenomenon of adhesion occurs in various systems, e.g., gas-solid, liquid-solid, solid-solid, etc.. When one realizes that despite our appreciable knowledge of molecular forces it is not possible to predict with certainty the miscibility of two liquids or the strength of a given material, the difficulty in formulating a generalized theory of adhesion becomes readily apparent.

Some investigators, notably W. D. Harkins[1], have provided the theoretical basis for the study of adhesion of the solid-liquid type. One might also note that it has been only recently that a reasonably accurate method of determining the surface area of a finely divided solid has become available in the multilayer adsorption theory of Brunauer, Emmett, and Teller[2]. This method offers a relatively simple means of determining the surface area of a powder which is necessary if thermodynamic variables are to be related on a unit area basis. Consequently, variables such as contact angle, surface tension, heats of wetting, total surface energy, etc., may be related[3] so as to calculate the energy of adhesion of a liquid to a solid.

However, such a treatment is not readily adaptable to a study of a solid-solid system because of the difficulties involved in measuring the pertinent variables, e.g., the surface tension of a solid. In addition, the difficulties are in various ways augmented by the fact that most practical adhesives and adherent coatings are high polymers which in the bonded structure exert their own mechanical properties. Also, the field of polymer chemistry is in a relative state of infancy. Consequently, such solid-solid adhesional studies as are reported in the literature have been mainly empirical and phenomenological in nature, particularly in the development and use of products in the aircraft industry[4-8]. To evaluate the effective adhesion empirical test methods such as scratch, shear, tensile, peel, strip, impact, etc., have been devised[9-16]. Generally, the force required for the ultimate separation of the adhesive-adherend layers is measured. Most systems investigated have been complex multicomponent formulas yielding little or no theoretical knowledge of the fundamentals of behavior or of adhesion per se.

However, with a better understanding of the properties and the behavior of polymeric materials it has been possible in recent years to construct rather simple two component systems which could be studied from a more theoretical viewpoint. Such investigations contribute greatly to our understanding of adhesional phenomena and indicate the way to future experimental studies.

SCOPE OF INVESTIGATION

The object of this investigation was to study a given polymer-metal system thoroughly with regard to: (1) failure at thin films and mechanism of failure; (2) correlation of bulk-properties of polymers with those of a polymer metal system; and (3) adhesional phenomena operating at the polymer metal interface.

The polymer chosen was polyvinylacetate for several reasons: (1) it is a linear, vinyl polymer with a relatively small degree of cross-linking and does not crystallize on extension; (2) data are available in the literature on its various properties; (3) it is a polar polymer and offers an extension of some work done by Kraus and Manson[17] on polystyrene and polyethylene; (4) it is generally recognized as having excellent adhesive properties and consequently offers a range of magnitude of adhesion over which the properties may be varied and measured; and (5) fractionation could be easily accomplished and molecular weights determined by a viscosity method since the constants have been evaluated by other methods.

The method used was the tensile technique utilizing films of polymers varying between 0.0005 and 0.010 inches in thickness.

THEORETICAL

I. Molecular Forces

In explaining chemical and physical phenomena it is convenient to recognize molecular forces as operative in two distinct types of bonds: primary and secondary. The basis of division is the magnitude of the interaction energies or dissociation energies characterizing each type. Primary bonds - heteropolar, homopolar, metallic - are characterized by energies of dissociation of about 50 to 150 Kcal./mole while secondary bonds have dissociation energies of 0-2 Kcal./mole. The secondary bonds are the so-called van der Waals forces which include the well-known dispersion[18,19], orientation[20], and induction[23] forces. Intermediate in magnitude are the energies (4-10 Kcal./mole) associated with hydrogen bonding which may be classified as a special type of dipole bonds[21,22]. Of these forces it is very doubtful whether primary forces are of any importance in adhesion[24]. Of the secondary forces the dispersion forces and hydrogen bonds are by far the most important. A calculation by London and Eisenschitz[25] shows that even in the case of high polarity the dispersion forces supply a considerable share of the total attraction. It is only in the cases of highly polar substances as H_2O, NH_3, and HCN that orientation forces equal or exceed dispersion forces while induction forces have only a minor influence.

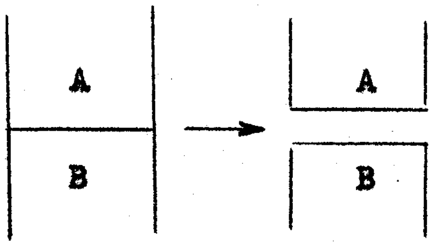
A fairly recent study on the adhesion of polymers to cellulose by McLaren and Hofrichter[26] has shown clearly the effect of hydrogen bonding. Their work reveals a linear relation between the logarithms of carboxyl concentration and the adhesion of that polymer to cellulose. Kraus[17] assuming only dispersion forces operative at the interface has calculated, using the same principle employed by Mark[27] and deBoer[28] for tensile strengths of polymeric materials, a theoretical adhesive strength of approximately 3000 kg./cm.^{2}. He has also calculated for a dipole-metal interaction a value ca 5% of that for dispersion forces. It should be pointed out that dispersion values are many times greater than the adhesion measured in the laboratory and even a small percentage of the theoretical adhesion would account for the effective adhesion measured. McLaren[29-31] stresses the importance of polar groups which become evident in their work with cellulose as the adherent.

II. Thermodynamical Aspects of Adhesional and Cohesional Failure

In the previous section, the molecular forces generally accepted as contributors to adhesion have been considered. However, unlike solid-liquid systems, no consideration of the thermodynamics of solid-solid systems and actual adhesional failure have been reported.

For a given substance, the molecules in the interior are completely surrounded by other molecules effecting a saturation of the interaction forces; however, for a molecule at the surface, there is an unbalanced met inward attraction. Consequently, the substance tends to contract to the smallest possible surface area. It is for this reason drops of liquid mercury will assume a spherical shape, gas bubbles in a liquid become spherical, etc.. In order to extend the area of surface it is necessary to do work to bring the molecules from the bulk into the surface against the inward attractive force; this work required to increase the area by one square cm. is called the "surface free energy." The tendency of a liquid to contract to a smaller area is a manifestation of free energy since approach to equilibrium is always accompanied by a diminution of free energy according to the second law of thermodynamics. Similarly, the work required to enlarge the surface of separation between two substances is called the interfacial free energy; this is generally less than the larger of the two surface free energies because the two surfaces exert mutual attraction across the interface and reduce the inward pull of molecules in the surface by those of its own kind.

In solid-solid systems surface energies are extremely difficult to measure; consequently, this aspect of adhesion with solids has been sidestepped. Analagous to Dupre's deduction for a solid-liquid system, the work of adhesion of two solids can be represented by the following process:



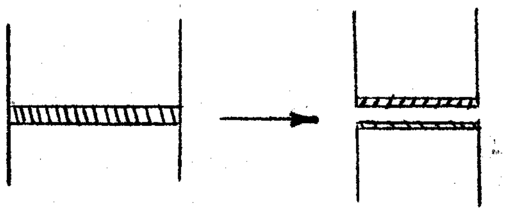
The work of adhesion is a measure of the energy required to separate the two solids and is given by

$$W_{Adh} \equiv \gamma_{Adh} = \gamma_A + \gamma_B - \gamma_{A/B} \qquad (1)$$

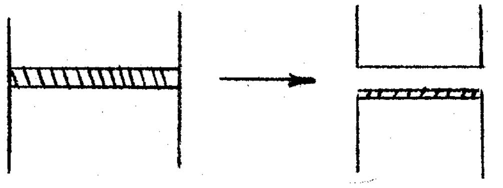
Similarly, the work of cohesion for a given solid(s) is:

$$W_{coh} \equiv \gamma_{coh} = 2\gamma_s \, . \qquad (2)$$

In the case of adhesion, the model must be modified to the extent of introducing an adhesive film between two solid specimens which may or may not be chosen to be the same. Now, rupture or separation may occur in the film (cohesive failure) or at the interface of the film and the solid (adhesive failure), viz:



$$\gamma_{coh} = 2\,\gamma_{film(p)} \qquad (3)$$



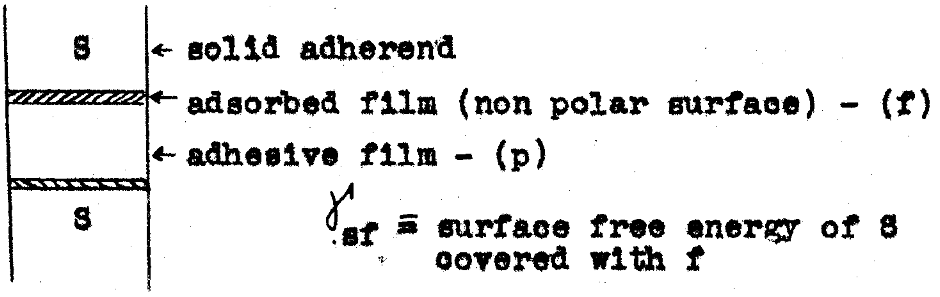
$$\gamma_{adh} = \gamma_s + \gamma_p - \gamma_{p/s} \qquad (4)$$

It is obvious then that the conditions for the two methods of failure are:

adhesional failure $\gamma_{adh} < \gamma_{coh}$

cohesive failure $\gamma_{coh} < \gamma_{adh}$

If one were able to measure the free energies or surface tensions indicated in (3) and (4), prediction of the type of failure would be relatively simple. Such data are not available and are unobtainable at present. However, since the surface energies of metals are quite high[32], it should be possible to evaluate such predictions by replacing the metal surface with one of low surface free energy, e.g., a non-polar surface, especially if failure occurs cohesively before alteration of the surface. Of course, this implies all other variables to be constant; this is a serious consideration in a mechanical test. Nevertheless, the model considered now is (greatly exaggerated):



$\gamma_{sf} \equiv$ surface free energy of S covered with f

whereby: $\gamma_{coh} = 2\gamma_p$

$$\gamma_{adh} = \gamma_p + \gamma_{sf} - \gamma_{p/f}$$

It is seen then that for adhesive failure

$$\gamma_{adh} < \gamma_{coh} \text{ or } \gamma_p > \gamma_{sf} - \gamma_{p/f} \qquad (5)$$

and for cohesive failure

$$\gamma_{coh} < \gamma_{adh} \quad \text{or} \quad \gamma_p < \gamma_{sf} - \gamma_{p/f} \qquad (6)$$

Since nonpolar surfaces have a low surface energy, it is quite possible to achieve the situation represented by equation (5).

III. Strength-Thickness Behavior of Adhesive Specimens

One of the common behaviors of adhesive joints is the increasing strength with decreasing thickness of the adhesive. This has been observed by a number of investigators[33-38]. At least, five theories have been proposed to explain such a behavior. The more pertinent theories shall be discussed briefly.

(a) Molecular Orientation of Adhesive. McBain and co-workers[39,40] have proposed that chains of molecules in the adhesive layer are oriented due to the force field of the adherend surface. Fields of force due to these oriented molecules at the surface cause a similar but reduced orientation in the next layer of adhesive, the molecules furthest away from the surface being least oriented. Such an explanation implies the force field operative over a distance many molecular layers. Investigations of Bulkley[41], and calculations of electrostatic attractions between surfaces and charged particles by Lennard-Jones[42] and Bowden[43] have shown the attractive forces to be quite weak beyond the first monolayer. In addition, this theory predicts failure in cohesion for all specimens since the weakest plane will be in the middle of the adhesive.

(b) Flaw Theory. Bikerman[34] suggested that the failure is due to flaws in the same manner that the increasing average strength of fibers has been related to the probability of the occurrence of a flaw of a given severity at which a given fracture is initiated[44-47]. The theory of flaws assumes a material to have a distribution of flaws of different size and failure is initiated or occurs with the strongest flaw (largest size). Therefore, the less material, the smaller the probability of a flaw.

(c) Non-tensile and Internal Stresses. This theory was arrived at independently by Kraus and Manson[17] and Meissner and Baldauf[48]. Internal stresses may be ascribed to solvent evaporation in the case of liquid adhesives or differential thermal contraction stresses in the case of a molded specimen. The force necessary to rupture such a specimen will therefore be smaller in the case of thicker adhesive films. In addition, due to the constraint of the adherend surface the stress concentration should be greater at the interface. The explanation may be extended further to the phenomena occurring during the actual deformation and rupturing of the test specimen. It is suggested that for a given load, the thicker the specimen the greater the "necking" of the adhesive. Consequently, at the interface around the edge, a force is exerted having a tensile and a shear component. With greater necking this shear component becomes larger in magnitude. The theory suggests a failure or at least an initiation in shear and is supported by the observance of peripheral rings of bare metal increasing in width with the thickness of the adhesive film. This also suggests that an extrapolation of the strength-thickness curve to zero thickness is an extrapolation out of the shear component; if so, "zero thickness" specimens would have only pure tensile stresses. The observations on very thin films (< 50 microns thickness) indicate cohesive failure in the film which would indicate also that thin film specimens should behave in the same manner that bulk properties of the adhesive film do.

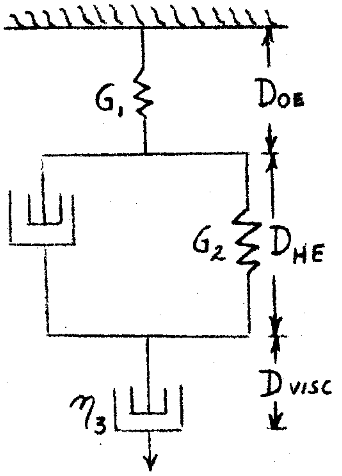
As will be shown in the present paper the authors' experimental evidence favors (c), with (b) exerting its influence to some extent.

IV. Mechanical Behavior of Polymeric Materials

Previously, it was suggested that "zero film thickness" of a polymer-metal system should behave in a similar manner to that of bulk polymers. Therefore, a brief description of their general behavior is necessary.

(a) Deformation[49-53].

The deformation behavior may be described by a mechanical model, according to Tuckett, as:



G = modulus
D = deformation
η = viscosity

The model has three components of the total deformation:

(1) Ordinary elastic deformation (D_{OE}) is an instantaneous elastic response by alteration of the bond angles and bond distances. The forces required to accomplish this are very high and are of the order of magnitude of Young's modulus for metals, ca 10^6 Kg./cm.^{2}. Such a deformation will appear or disappear on application or release of the load. It is independent of temperature.

(2) Highly elastic deformation (D_{HE}) is a retarded elastic response which manifests itself by the uncoiling of a polymer chain. The end-to-end distances of such chains follow a distribution law and also will have a definite range of end-to-end distances for a given temperature. Such a deformation requires energy to uncoil the chain and energy to overcome intermolecular interactions between points along the chain.

(3) Viscous deformation (D_{VISC}) is a flow phenomenon manifesting itself in the relative movements of chains along each other. Such a deformation occurs principally near or above the transition temperature and is analogous to the flow of viscous fluids under an applied stress. Therefore, this process is dependent on the length of time of application of the stress.

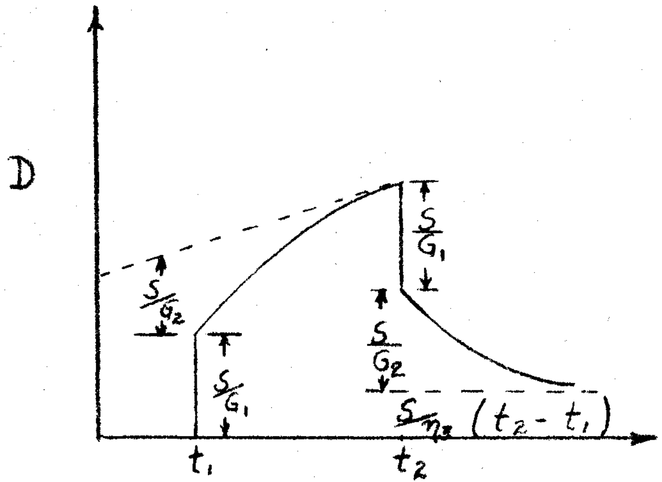
The total deformation may be described by the equation, which is the sum of the three displacements, as:

$$D = D_{OE} + D_{HE} + D_{VISC}$$

or

$$D = \frac{S}{G_1} + \frac{S}{G_2}\left(1 - e^{-\frac{t}{t_2}}\right) + \frac{S}{\eta_3}\,t \quad (7)$$

The behavior may be described thus: if a stress is suddenly imposed upon a polymer, there occurs an instantaneous elastic response of magnitude $\frac{S}{G_1}$. This will be followed by the uncurling and orientation of polymer molecules which is termed a retarded elastic response because it is time dependent approaching at infinite time the value S/G_2. The flow phenomenon goes on from the beginning at the rate S/η_3. When the stress is released, there results an instantaneous recovery, followed by a retarded recovery. The flow deformation is not recovered. Schematically it may be represented by:



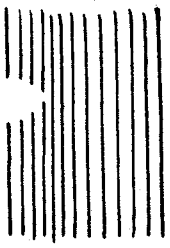
One would expect from this simplied model that the behavior of a polymer would exhibit temperature and time effects. For example, at high temperatures the material would behave as a liquid of viscosity η_3 which would obscure the first two components. At very low temperatures the instantaneous response predominates. At in between temperatures all three components come into play with the importance being continually shifted to the retarded elastic and the elastic element as the temperature is lowered.

Such effects are of utmost importance in a mechanical test in which the experimental time scale and temperature may be varied at will.

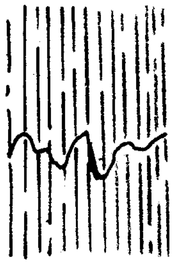
(b) Molecular Weight and Tensile Strength.

To consider the tensile strength one must consider the mechanism of fracture. Fracture may occur in either of two methods or the combination of the two, viz:

(a)



(b)



In (a) fracture has been depicted as rupturing primary bonds while in (b) the fracture is a result of slipping of chains over each other causing a fracture line at the ends of the molecules. In a polymer in which there are strong forces of interaction between neighboring chains, it is quite possible to have the cohesion energy higher than that of a primary valence bond and therefore rupture may occur by (a). Such internal cohesion is promoted by molecular symmetry and the presence of polar groups or hydrogen bonding groups as there are in polyamides and silk. On the other hand, an increase in molecular weight produces a similar effect simply by offering per one polymer molecule more interaction centers. The effect is more simply illustrated and more commonly known for liquids. As the molecular weight of a hydrocarbon increases, e.g., the boiling point increases, volatility decreases, solubility decreases, etc.. This is a reflection of the total intermolecular secondary bonding energy increasing with chain length. Hildebrand[54] has shown that the vaporization energy (ΔH_v-RT) for n-butane, n-hexane, and n-octane bear the ratios of 1:1.53:2.07, based on n-butane.

Therefore, it may be concluded that as the molecular weight increases the tensile strength will increase at a given temperature. Of course, since the thermal energy, reflected in vibrations, rotations, and translational movements of segments or chains, increases with increasing temperature, a polymer for a given molecular weight will exhibit an inverse relationship between temperature and binding forces, if only secondary bonds are the binding forces.

It is pertinent to mention, at this point, that attempts have been made to calculate theoretical tensile strengths of polymers[27,28,55]. In all cases, the calculated values considerably exceeded the observed values - some as much as 500 times. Several factors may contribute to this discrepancy: (1) All the bonds over the area of fracture do not break simultaneously as assumed; the rupture of bond increases the load on the others by $\frac{n}{n-1}$ where n is the number of bonds to be broken. In this way, the break may be propagated across the fracture line. (2) The structure may not be regular and it exhibits microscopic "flaws" which may be very low molecular polymers, voids, or impurities. Such "flaws" are regions of high stress concentrations which may initiate failure. The implications are that after initiation a tearing type mechanism propagates the stress resulting in failure.

(c) Temperature Effects.

In order to explain the phenomenon of polymers exhibiting increased strength or brittleness at lower temperatures it should be assumed[55-58] that the macromolecule in the molten or dissolved state can undergo two kinds of movements: (1) a macro-Brownian movement of the total molecule; (2) a micro-Brownian movement consisting of vibrations and rotations executed by segments of the molecule. The macro-Brownian movement is more or less free in the plastic state or in solution but cross links, e.g., by vulcanization, prevent this. The thermal micro-Brownian movements of the segments continually decrease on cooling. Fewer and fewer segments have sufficient energy to execute vibrations or rotations and the material becomes more viscous. Finally, when it has cooled to an extent that the micro-Brownian movement has practically stopped, the material is brittle and glasslike. This "freezing-in" takes place over a short range of temperature and is characterized in two different ways: determination of the second order transition point and determination of the brittle point.

(1) Second-order transition point (T_m). This point manifests itself as a sudden change of the temperature dependency of many physical properties such as: specific volume[56], specific heat[57], thermal expansion[58], refractive index[59], compressibility[60], etc.. It should be noted that each of these methods utilized approximately the same time-scale. The viscous flow is the factor that is supposed to be responsible for the manifestation of the second-order transition point. That this is a thermodynamic singularity has been the subject of much debate and discussion. It has been shown, for example, that polystyrene exhibits a change in the T_m as the rate of cooling is varied in specific volume measurements[61]. In fact, Boyer and Spencer[62] have shown that T_m disappears when measurements are sufficiently prolonged (e.g., 15 hours) to reach equilibrium. This temperature therefore may be defined[62] as the lowest temperature at which an observable amount of viscous flow can occur under the forces acting on the system and within the time limits of the experimental technique employed. When the rate of viscous flow, upon stiffening of polymer, becomes too small under experimental conditions, a T_m is found. Generally, a material at the transition point has a viscosity near 10^{13} poises[63].

(2) Brittle point (T_b). The basis of the brittle point determinations depends upon the fact that as the temperature is lowered the elastic properties disappear and embrittlement occurs. In general, the material has to react in a very short time during the applied test. If the elasticity is insufficient to yield to this force by deformation, the material will break. Therefore, the brittle point may be defined as[64]: temperature at which the time interval required by the specimen to undergo the necessary deformation is just equal to the experimental timescale. At higher temperatures, the time is more than sufficient to obtain a plastic deformation of the sample without breaking; at lower temperatures the material can not deform fast enough and it breaks.

The differentiation between the two temperatures discussed is determined by the fact that the second-order transition temperature is a viscous response to a stress while the brittle temperature is an elastic response. The brittle temperature (T_b) is always greater than or equal to T_m.

The most important factor that determines the position of T_m is the strength of the secondary bond energies[65]. Molecules with strong polar groups, which increase the secondary binding energies have high second-order transition and brittle-points, e.g. compare, polyvinyl alcohol

(T_m = 75° C.) and polyvinyl acetate (T_m = 28° C.).

(d) Plasticizer Effect.

The effect of a plasticizer essentially is the saturation of the active centers of the polymer chain and the spreading apart of the chains. By virtue of the reduced interchain molecular attraction, a polymer is rendered more flexible. This process is that of external plasticization. The same effect may be accomplished copolymerizing an inflexible polymer with a more flexible one (internal plasticization), e.g., vinylchloride-acetate copolymers.

As the percentage of plasticizer increases, the physical properties change. Of interest in this paper is the tensile strength which has been shown by Boyer[66] to be (theoretically) related to the weight percent of plasticizer by:

$$T \cdot S = a - \frac{b}{\bar{M}_2} - \frac{w_1}{M_1} \tag{8}$$

a, b = constants

$\bar{M}_2$ = no. average mol. wt. polymer

M_1 = mol. wt. plast.

In addition, it is predictable that as the plasticizer content increases, the second-order transition decreases since the plasticizer renders the polymer less brittle or decreases the internal viscosity.

RESULTS AND DISCUSSION

In Figure 1 are shown effective adhesion versus film thickness curves for a polyvinyl acetate fraction of viscosity average molecular weight 225,000. The curves are in all respects similar to those obtained with polystyrene and polyethylene[17]. At thin film thicknesses the effective adhesion is of the order of magnitude of the tensile strength of the bulk polymer and there is a decrease in adhesion with film thickness. Increasing the temperature decreases the effective adhesion and diminishes the rate of decrease with film thickness. The same behavior is exhibited by three other fractions of molecular weights 147,000, 77,000, and 54,000. The molecular weights of the fractions were computed from experimental intrinsic viscosities with the modified Staudinger equation using the constants reported by Wagner[67]:

$$[\eta] = 1.88 \times 10^{-4} M^{0.68} \qquad (9)$$

<u>The effect of molecular weight on effective</u> adhesion is shown in Figure 2 in which the data at 22° C. are plotted. Significantly, the data reveal a critical molecular weight above which the effective adhesion is not increased to any extent. The only other data in the literature revealing this behavior, to the author's knowledge, is that of McLaren[68] on the adhesion of polyvinyl acetate to

FIGURE I.

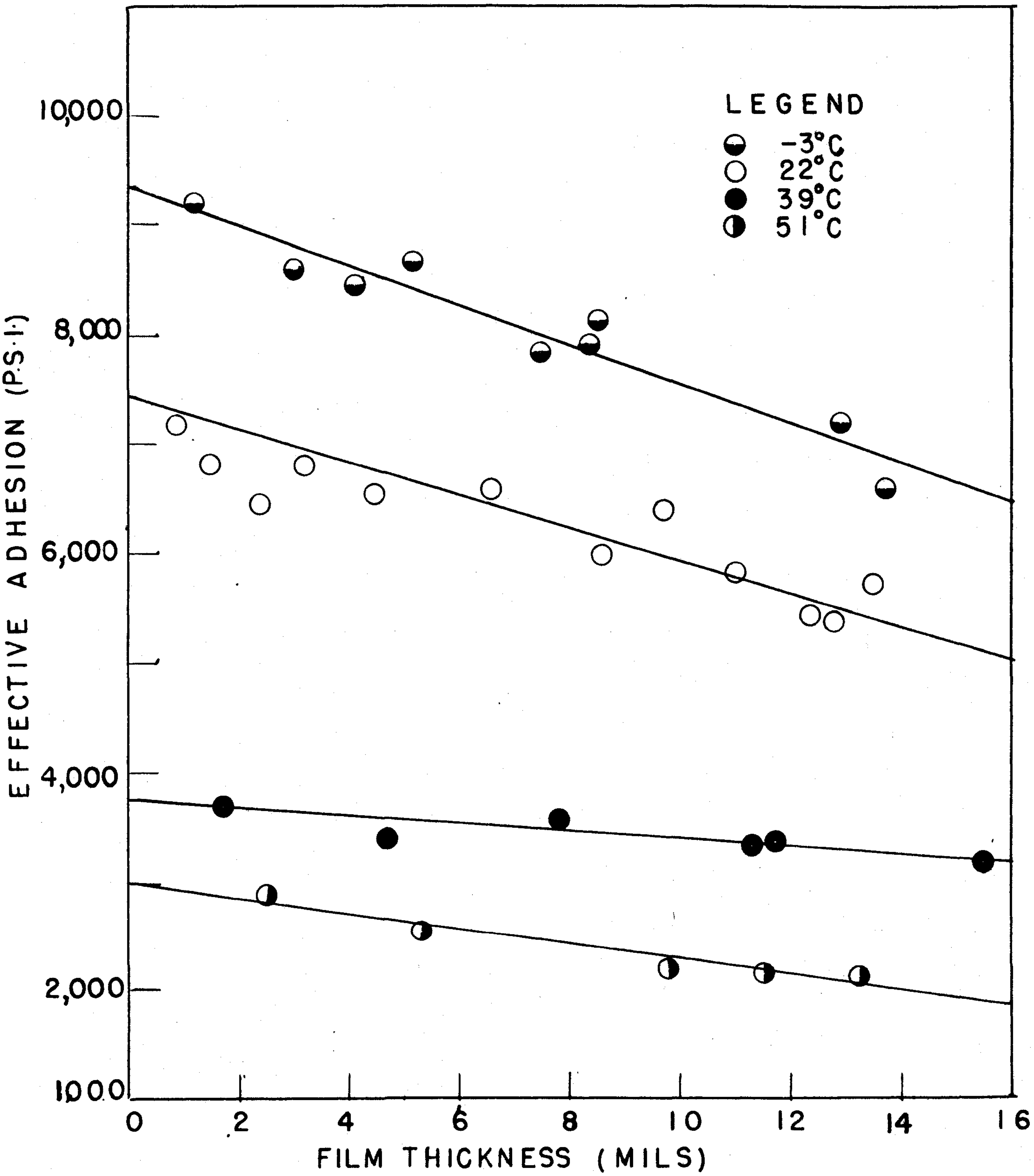
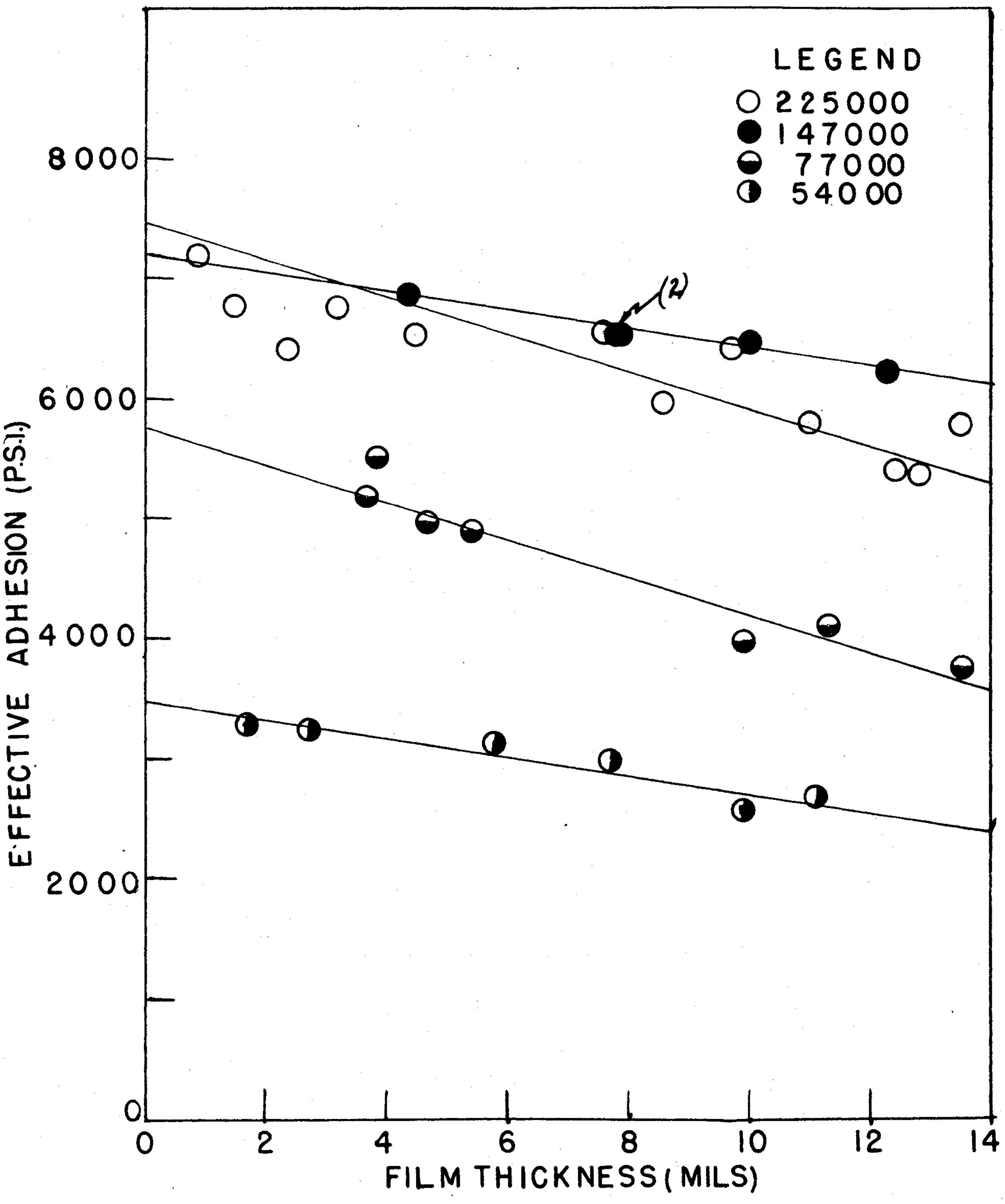

LEGEND
◒ -3°C
○ 22°C
● 39°C
◑ 51°C
EFFECTIVE ADHESION (P.S.I.)
10,000
8,000
6,000
4,000
2,000
1000
FILM THICKNESS (MILS)
0
2
4
6
8
10
12
14
16

FIGURE 2.


LEGEND
○ 225000
● 147000
◒ 77000
◑ 54000
(2)
8000
6000
4000
2000
0
0
2
4
6
8
10
12
14
FILM THICKNESS (MILS)
EFFECTIVE ADHESION (P.S.I.)

aluminum and regenerated cellulose. In Figure 3 a comparison of the adhesion data obtained in this for 25 and 250 microns film thicknesses is plotted along with McLaren's data versus intrinsic viscosity. Both sets of data indicate a critical molecular weight, that corresponding to $[\eta] = 0.50$ despite the fact that the two methods of measuring adhesion are entirely different and the substrates are different. In addition, Wiley and Brauer[60] have shown that the second order transition point for polyvinyl acetate is approximately constant above $[\eta] = 0.50$ indicating little change in cohesive properties above this molecular weight.

In Figure 4 the <u>effective adhesion extrapolated to zero film thickness</u> is shown <u>versus temperature</u> for all four molecular weight fractions. If the "Shear-stress" theory as presented on pages 10 and 11 represents the mechanism of failure, "zero-thickness" films should represent the bulk polymer behavior since the theory suggests that such failures are cohesive. Data in Figure 4 show a decrease in strength with temperature (a quite rapid decrease for the higher molecular weight films) and a merging of curves in range of 40° C. - 50° C. At this temperature there is no significant difference in the data. Misch and Picken[69] in an investigation of elastic properties of polyvinyl acetate report that above 50° C. no change in the temperature dependency of the force required to maintain a sample in a given isothermal extension was observed; below 50° C. such dependency was

FIGURE 3.

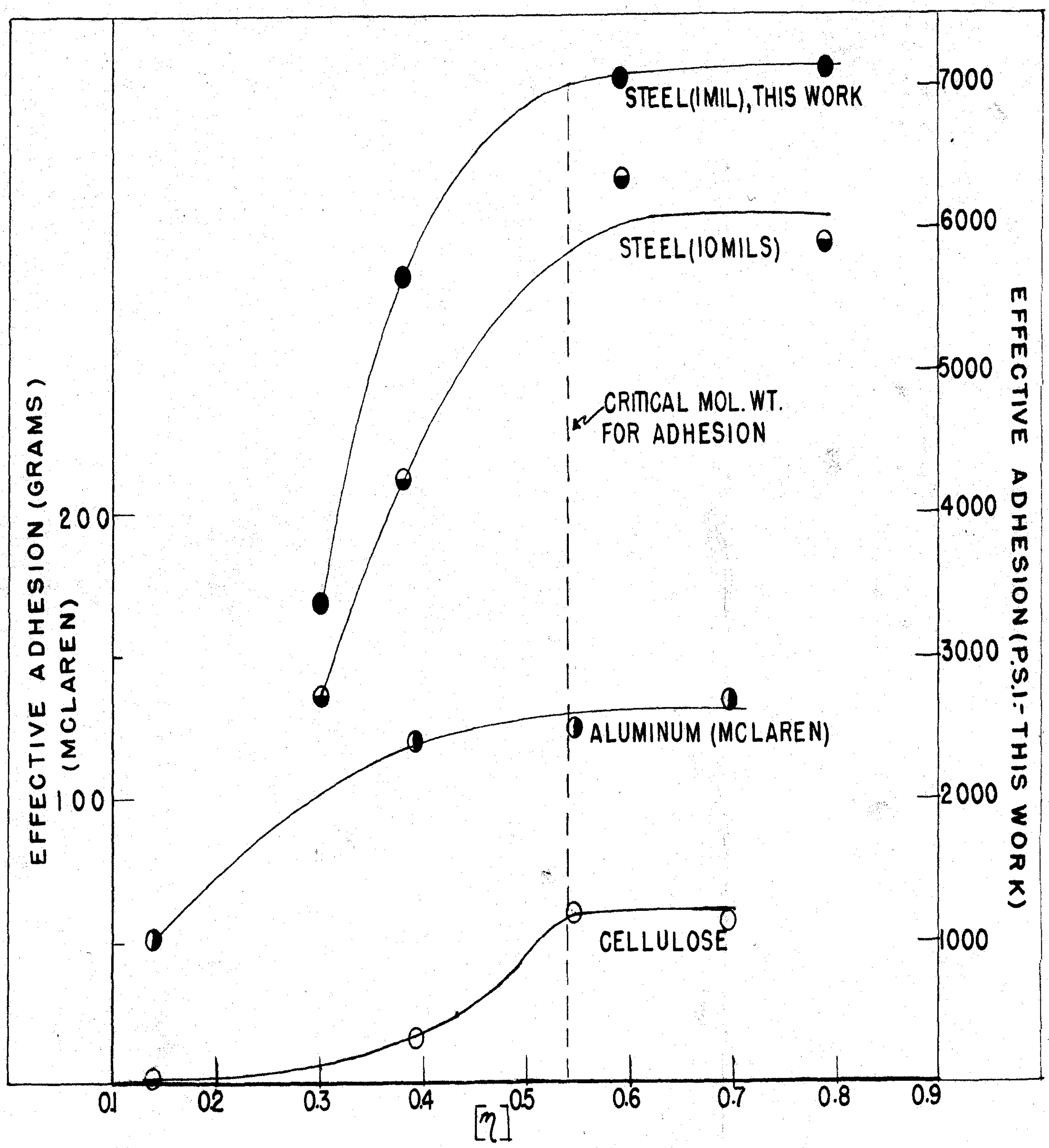
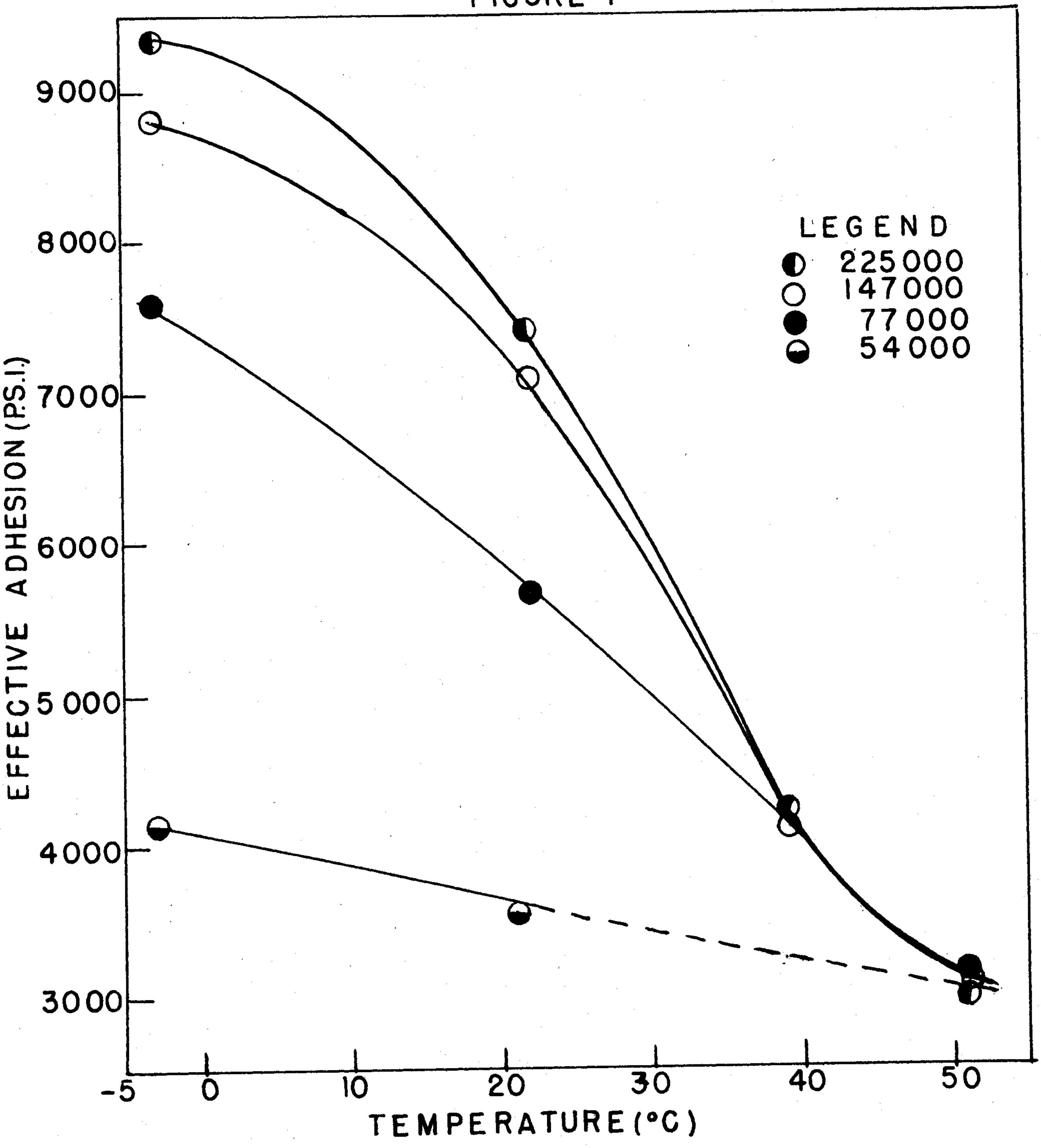

EFFECTIVE ADHESION (GRAMS) (MCLAREN)
200
100
EFFECTIVE ADHESION (P.S.I.-THIS WORK)
7000
6000
5000
4000
3000
2000
1000
STEEL(1MIL),THIS WORK
STEEL(10MILS)
CRITICAL MOL. WT. FOR ADHESION
ALUMINUM (MCLAREN)
CELLULOSE
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
[η]

FIGURE 4·



LEGEND
◐ 225000
○ 147000
● 77000
◒ 54000
EFFECTIVE ADHESION (P.S.I.)
9000
8000
7000
6000
5 000
4000
3000
-5
0
10
20
30
40
50
TEMPERATURE (°C)

observed to undergo values from plus to minus. This would indicate a change in elastic properties at about 50° C. Tuckett[70] reports an elastic temperature range for polyvinyl acetate as 35°C.-45° C. Such a characteristic temperature may be identified with the "brittle-temperature" or "freezing-temperature" of Clash and Berg[71] reported for other polymers and rubbers. In all cases, it represents the temperature at which, upon approach from above, there is a transition from an elastic to a brittle state; this is evidenced by a rapid increase in modulus. Although there is no detailed data on molecular and tensile strength dependence of polyvinyl acetate in the literature, it is interesting to view such data of Carswell, Hayes, and Nason[72] for polystyrene. Their data show the same but less pronounced behavior (at an unspecified rate of testing) with a merging at about 105° C., about 24 C° above its recognized second-order transition point. Interestingly, the data show this same behavior at 50° C. for polyvinyl acetate whose second-order transition temperature is 24° C.-28° C.[73,74] — a 24 C° difference. Indeed, it is surprising that the difference in both cases (24 C°) is the same because brittle points vary with the rate of testing. However, it should be pointed out that both polystyrene and polyvinyl acetate are similar in the respect that they are linear polymers which do not crystallize and do display elastic properties similar to rubber above its transition range.

In order to establish the relation between effective adhesion and evidences of molecular weight distribution two blends were prepared as follows:

Blend A: Equal weight fractions of $M = 225,000$ and $M = 54,000$. The viscosity average molecular weight for blend was 148,000.

Blend B: Equal weight fractions of $M = 225,000$ and $M = 147,000$. $M_{\text{blend}} = 180,000$.

Although the average molecular weight for both blends is larger than the "critical molecular weight" for adhesion, the results (Figure 5) show blend A to have an effective adhesion definitely lower (about 15%) than a sharp fraction of $M = 147,000$. On the other hand, blending of two fractions both of which exceed the critical molecular weight has no significant effect. This behavior of lowering effective adhesion by low molecular weight materials also parallels the behavior found to Mark[75] for the tensile strength of cellulose acetate filaments.

The effect of a plasticizer on adhesion is illustrated in Figure 6. The curves are not necessarily parallel; in fact, similar plots for 5° C. do not exhibit this parallelism but instead show a decrease in slope with increasing plasticizer content (Figure 7). The presence of a plasticizer could produce several effects. One adhesional effect

FIGURE 5.

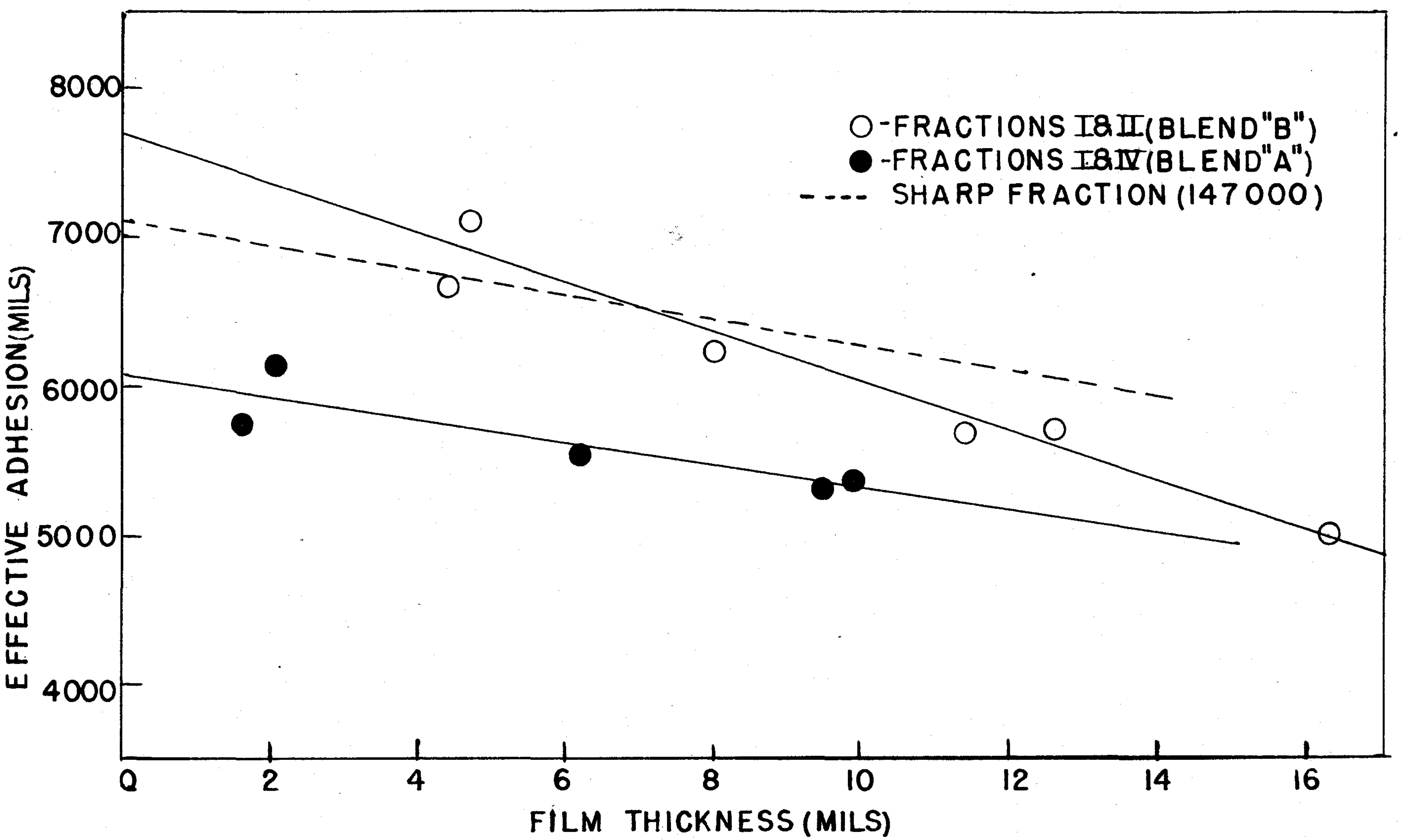
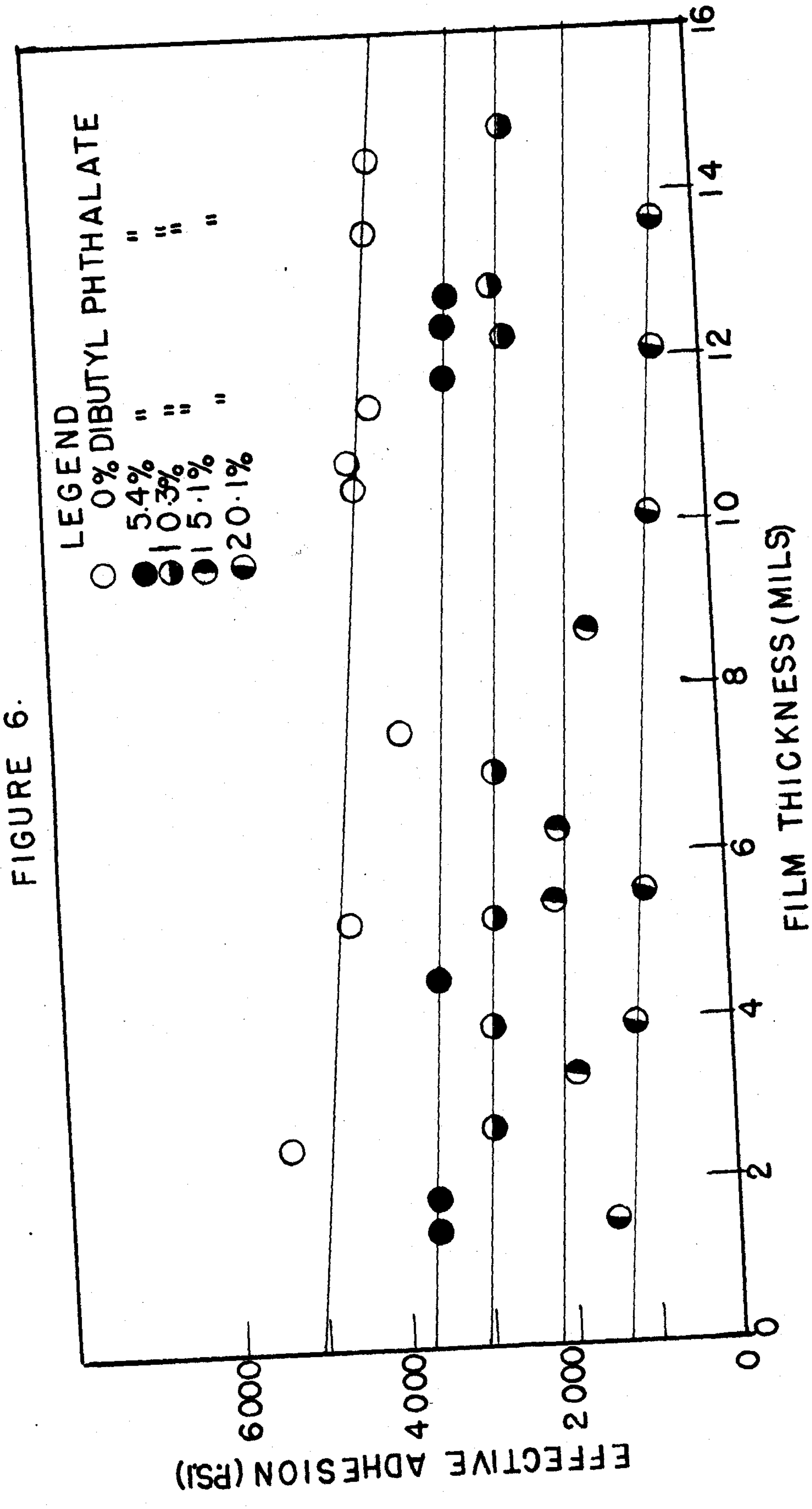

○ -FRACTIONS I&II (BLEND "B")
● -FRACTIONS I&IV (BLEND "A")
---- SHARP FRACTION (147000)
EFFECTIVE ADHESION (MILS)
8000
7000
6000
5000
4000
0
2
4
6
8
10
12
14
16
FILM THICKNESS (MILS)

FIGURE 6.


LEGEND
○ 0% DIBUTYL PHTHALATE
● 5.4% " "
◐ 10.3% " "
◐ 15.1% " "
◐ 20.1% " "
EFFECTIVE ADHESION (PSI)
6000
4000
2000
0
FILM THICKNESS (MILS)
0
2
4
6
8
10
12
14
16

is that the decrease of effective adhesion versus film thickness is less marked for plasticized specimens which could be attributed to the internal softening and the consequent ability to relieve stresses. This is illustrated particularly by the data at 5° C. (Figure 7). It is also shown that effective adhesion is considerably reduced as the weight percent of the plasticizer is increased, the largest decrease occurring in the initial increment of plasticizer. If adsorption occurs at the interface this behavior is to be anticipated. If no adsorption occurred at the interface one would expect a parallelism between "zero-thickness-films" and bulk tensile properties of polymers. Boyer[66] gives the following relation between tensile strength and plasticizer content:

$$T.S. = a - \frac{b}{\bar{M}_2} - \frac{w_1}{M_1} \qquad (10)$$

where w_1 is weight concentration of plasticizer of molecular weight M_1 and $\bar{M}_2$ is the number average molecular weight. For M_2 and M_1 constant, it reduces simply to:

$$T.S. = A - Bw_1 \qquad (11)$$

Figure 8 illustrates the agreement of zero-thickness-films with this equation at both temperatures.

The parallelism between thin film specimens and bulk polymer may be extended further to include the time

FIGURE 7

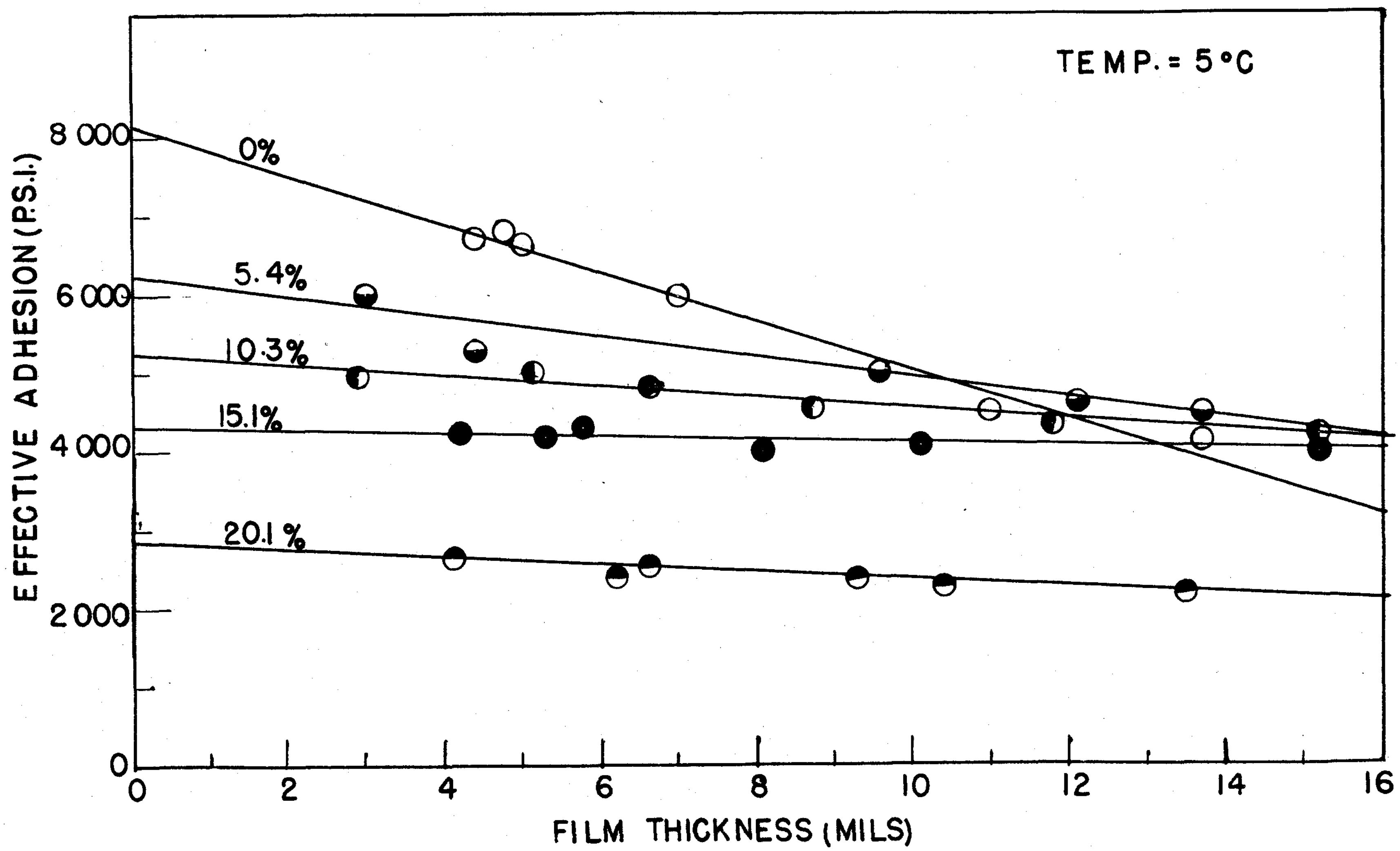
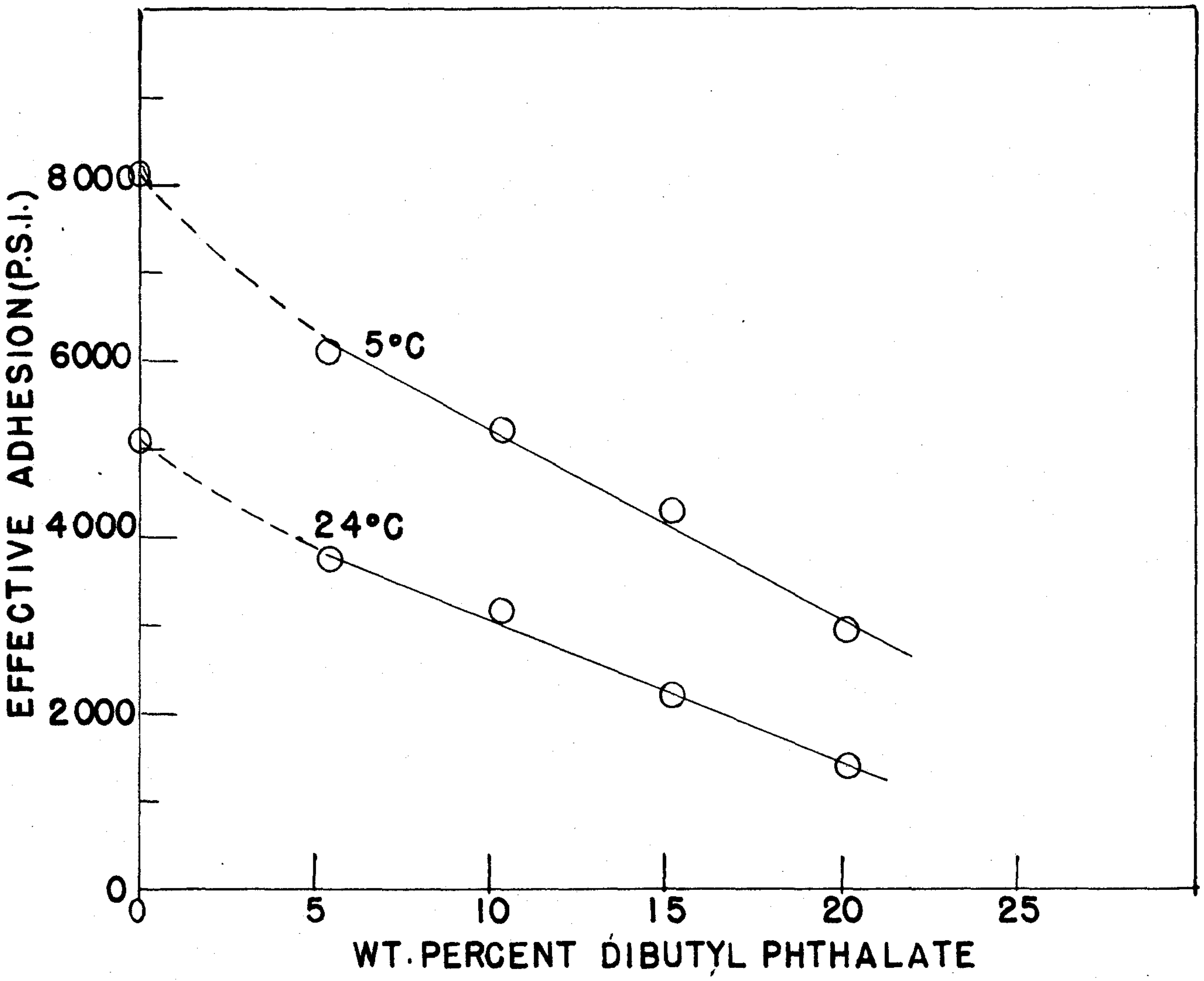

TEMP. = 5 °C
0%
5.4%
10.3%
15.1%
20.1 %
EFFECTIVE ADHESION (P.S.I.)
8 000
6 000
4 000
2 000
0
0
2
4
6
8
10
12
14
16
FILM THICKNESS (MILS)

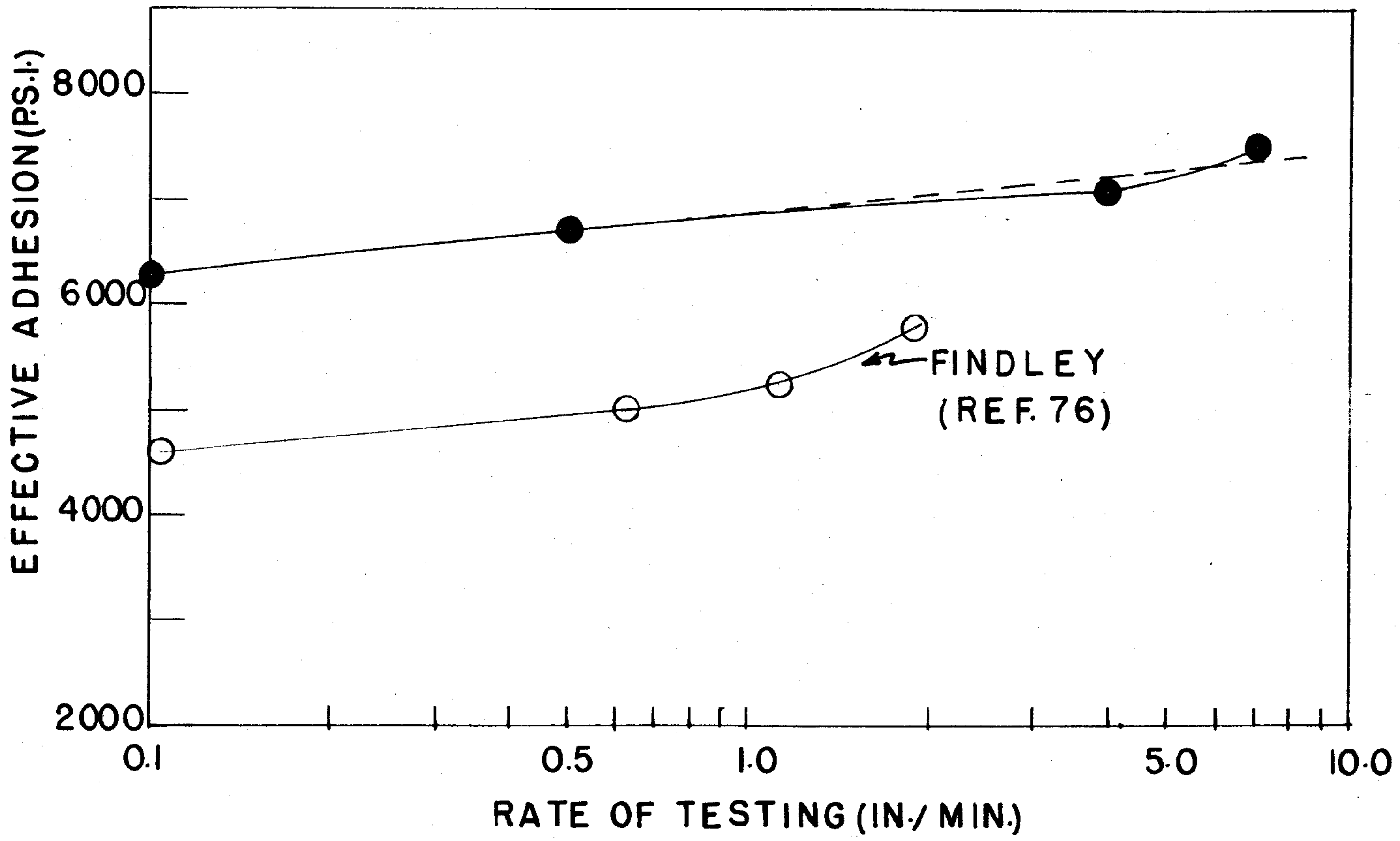
FIGURE 8.


5°C
24°C
EFFECTIVE ADHESION (P.S.I.)
8000
6000
4000
2000
0
0
5
10
15
20
25
WT. PERCENT DIBUTYL PHTHALATE

dependence. Figure 9 illustrates data obtained for "zero-thickness" films over a rate of stress application range of approximately two orders of magnitude. The data represent a linear relation between tensile strength and logarithm of the rate of loading and evidences of 10% increase in strength for each order of magnitude increase in rate of stress application. In the same figure, the author has also presented the data of Findley[76] to illustrate the behavior of cellulose acetate. Other workers[77] have shown a similar increase of 10% in strength for an order of magnitude increase in rate of stress.

Thus far, all evidence presented points to a cohesive mechanism of failure for thin films; for thicker films, undoubtedly, both adhesive and cohesive mechanisms take place. It has been observed that for thicker films ($>$ 100 microns) that a peripheral ring of bare metal, increasing in width as the film thickness is increased, becomes evident; also, such a peripheral ring occurs more readily when failure occurs at lower temperatures. Apparently, at low temperatures the polymer is not able to relieve stresses as well, which is consistent with polymer behavior. Such a failure is represented by a number of small islands of polymer surrounded by a peripheral ring of apparently bare metal - a picture consistent with the observations of others, notably Meissner and Baldauf[48]. The appearance of these peripheral rings may be considered as good evidence of, at

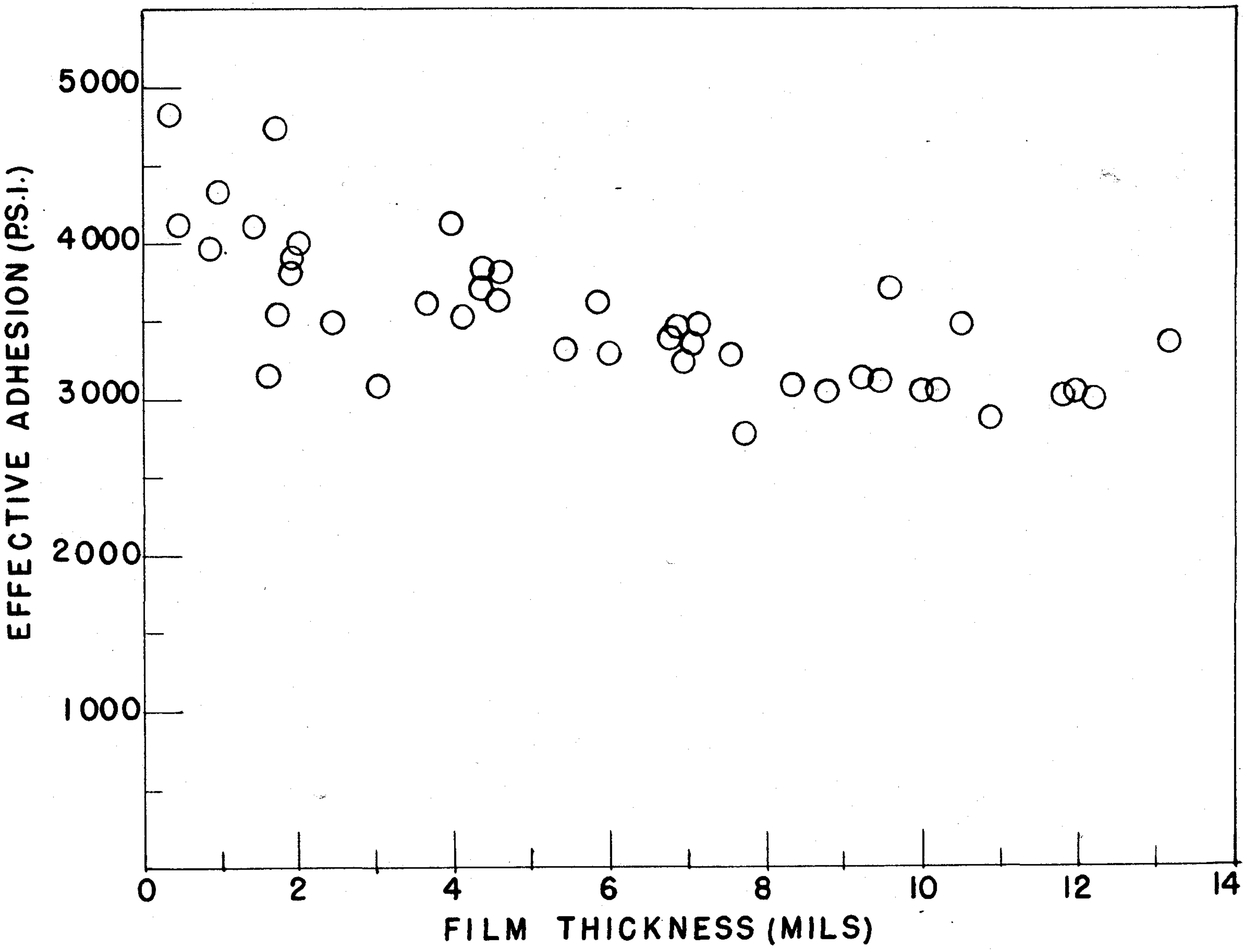
FIGURE 9.


EFFECTIVE ADHESION (P.S.I.)
8000
6000
4000
2000
0.1
0.5
1.0
5.0
10.0
RATE OF TESTING (IN./MIN.)
FINDLEY
(REF. 76)

least, initiation of failure in shear. Since the shear strength of adhesive joints approximates their adhesion tensile strength[78], it is quite possible that the shear component developed in the tensile test must have a considerable value. A theoretical stress analysis of the tensile adhesion test would represent an important contribution to our understanding of adhesion in general; however, no such quantitative treatment has been worked out to date. In addition, since the ultimate strength is beyond the ordinary theory of elasticity for polymers, prospects for an early solution of this problem seem poor.

It must be emphasized, at this point, that all experiments in this work were performed with carefully purified and fractionated polymers and that the high effective adhesion values are a direct consequence of this procedure. Figure 10 shows the results obtained with unpurified parent polymer used in the fractionation. The adhesion values are the same as for the lowest (and smallest) molecular weight fractions and exhibit considerably more scatter The mean tensile adhesion strength compares closely (3520 p.s.i.) with the value of 3600 p.s.i. reported for polyvinyl acetate - stainless steel by DeLollis and others[78]. The much lower strength of the unpurified polymer suggests strongly that impurities are adsorbed at the interface, adversely affecting the adhesion. Such adsorbed impurities

FIGURE 10.


EFFECTIVE ADHESION (P.S.I.)
5000
4000
3000
2000
1000
0
2
4
6
8
10
12
14
FILM THICKNESS (MILS)

depending on their concentration, size, and location would cause a wide distribution of results. The most unfavorable location would, of course, be near the periphery of the adherend surface where the stress concentration is the greatest. As a preliminary test of the effect of the adsorption of impurities at the surface, decanoic acid traces were adsorbed from n-heptane on <u>one</u> surface only. In every case failure at a much lower value was observed to take place and always at that particular surface for these specimens.

A more thorough investigation of the effects of a preadsorbed film is shown in Figure 11. Decanoic acid was preadsorbed from n-heptane solutions onto the surfaces at different coverages indicated as fractions of a monolayer calculated on the basis of the geometrical surface area and the cross-sectional area of decanoic acid as 20 square angstroms[79]. The results are striking in that the effective adhesion is decreased markedly with only traces of decanoic acid on the surface. An unusual behavior of effective tensile adhesion versus film thickness is also evident with the increase of adhesion with film thickness. It should be noted that the molding time for the data in Figure 11 is listed as one hour. A variation in effective adhesion versus thickness at different molding times is illustrated by Figure 12 in which the data represent approximately 6 monolayers preadsorbed. For a given film thickness and coverage,

FIGURE 11.

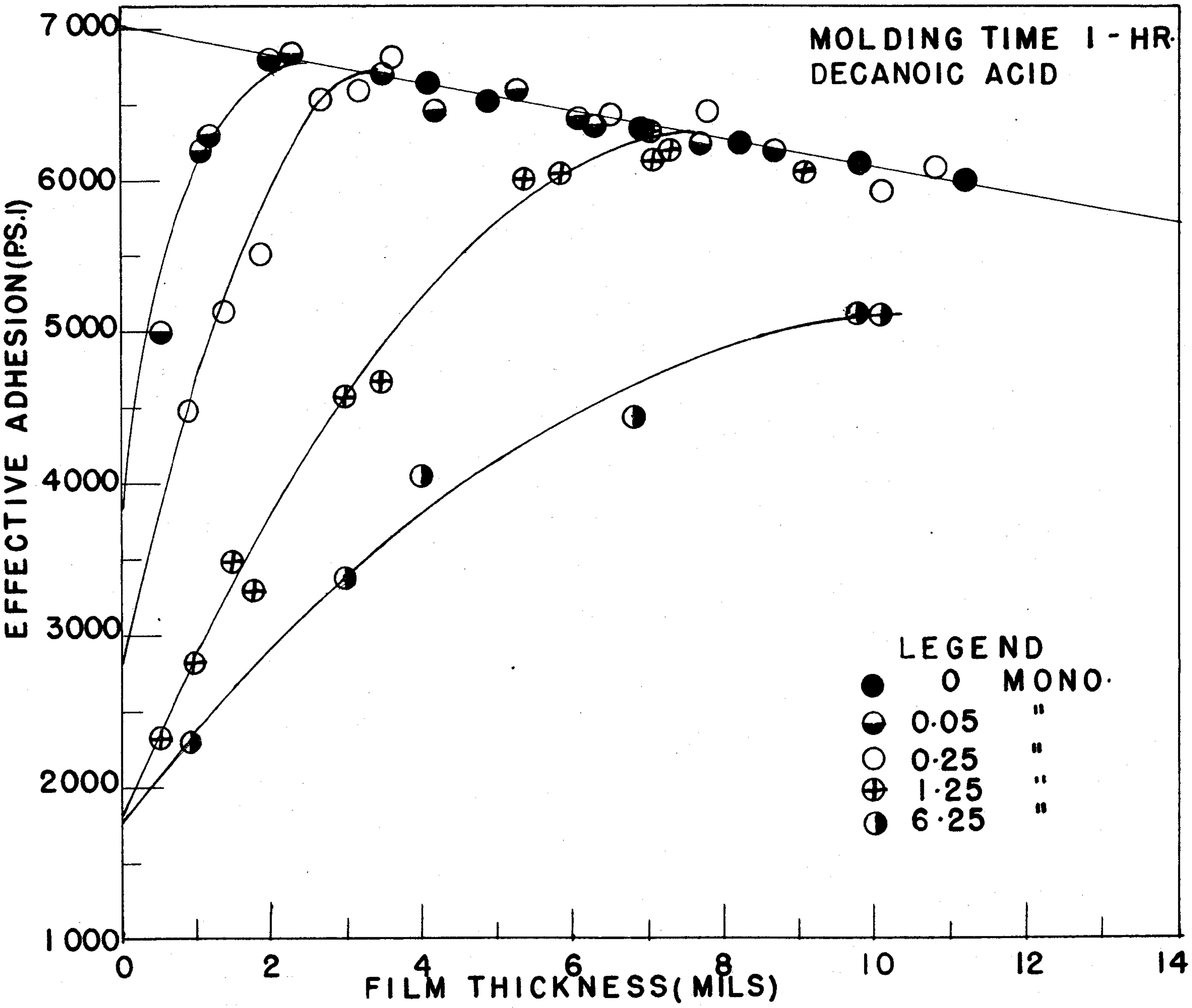
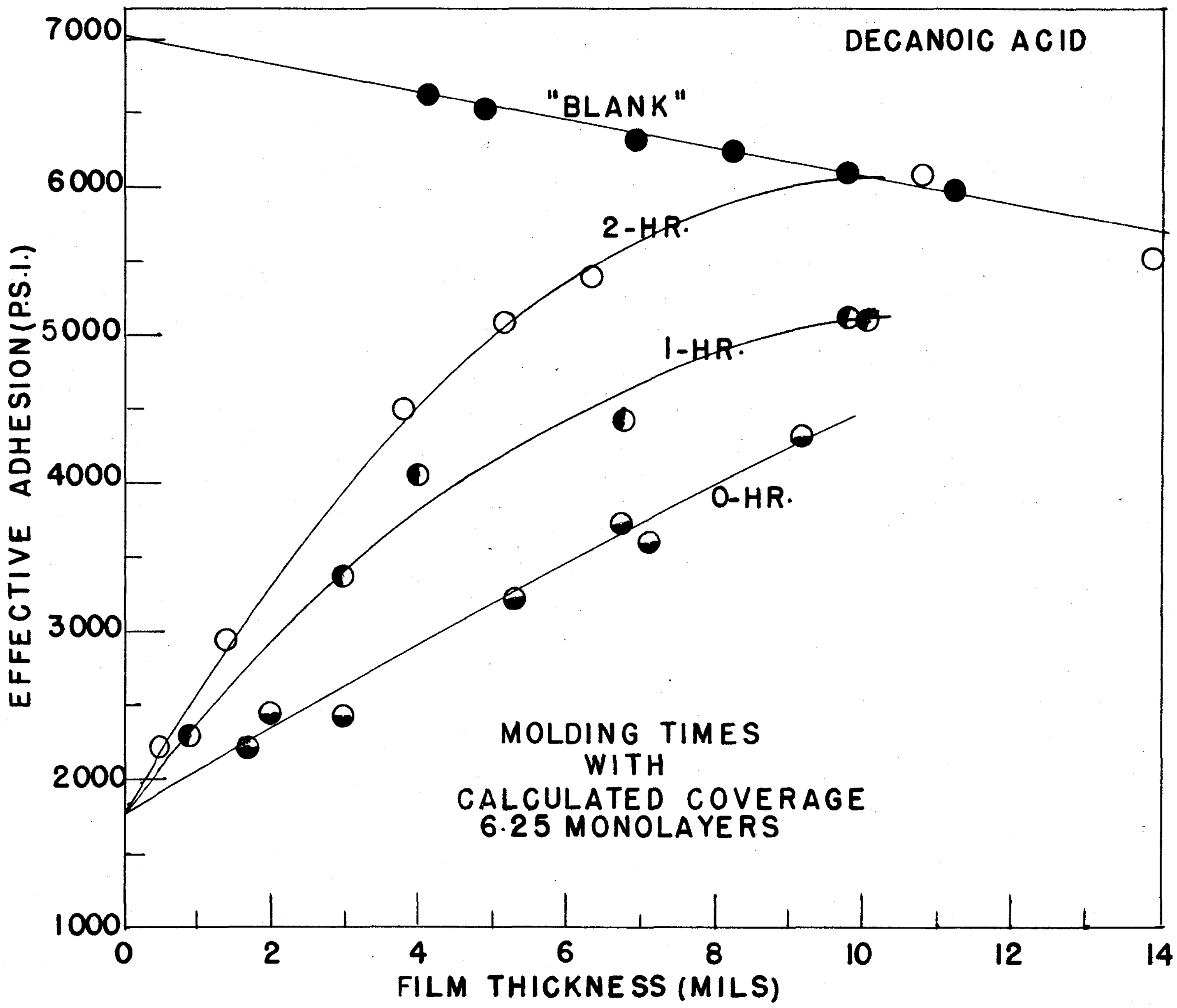

MOLDING TIME 1 - HR.
DECANOIC ACID
EFFECTIVE ADHESION (P.S.I)
7000
6000
5000
4000
3000
2000
1000
0
2
4
6
8
10
12
14
FILM THICKNESS (MILS)
LEGEND
● 0 MONO.
◒ 0.05 "
○ 0.25 "
⊕ 1.25 "
◑ 6.25 "

FIGURE 12.


DECANOIC ACID
"BLANK"
2-HR.
1-HR.
0-HR.
MOLDING TIMES
WITH
CALCULATED COVERAGE
6.25 MONOLAYERS
EFFECTIVE ADHESION (P.S.I.)
7000
6000
5000
4000
3000
2000
1000
0
2
4
6
8
10
12
14
FILM THICKNESS (MILS)

the adhesion increases with molding time. In fact, depending on coverage, the adhesion increases with time and becomes identical with the blank run (no preadsorption) at some definite film thickness. Also, one should emphasize that tests made with only solvent on the surface resulted in the same curve as the "blank" for a molding time of one hour.

Before discussing the above results, it is appropriate to introduce also results with perfluorodecanoic acid preadsorbed films. The cross-sectional area is assumed to be about 28 square angstroms. The effective adhesion versus film thickness at various coverages for a molding time of one hours is shown by Figure 13; for a given coverage of 3.6 monolayers the effect of molding time is shown in Figure 14.

Preceding the discussion of these results it should be emphasized that the test specimens are in every mechanical and chemical sense the same except that the metal surface has been replaced totally or partially by a non-polar surface. In adsorption of a non-polar acid, as in the adsorption investigations of Greenhill[81], Daniels[80], and others of long chain polar compounds on metals, the carboxyl group is attached to the surface presumably by hydrogen bonding and the non-polar end of the molecule is standing up and, in this case, in contact with the polymer. The effect is essentially that of replacing a metal surface of high surface free energy by a surface of low surface free energy. It will be recalled

FIGURE 13.

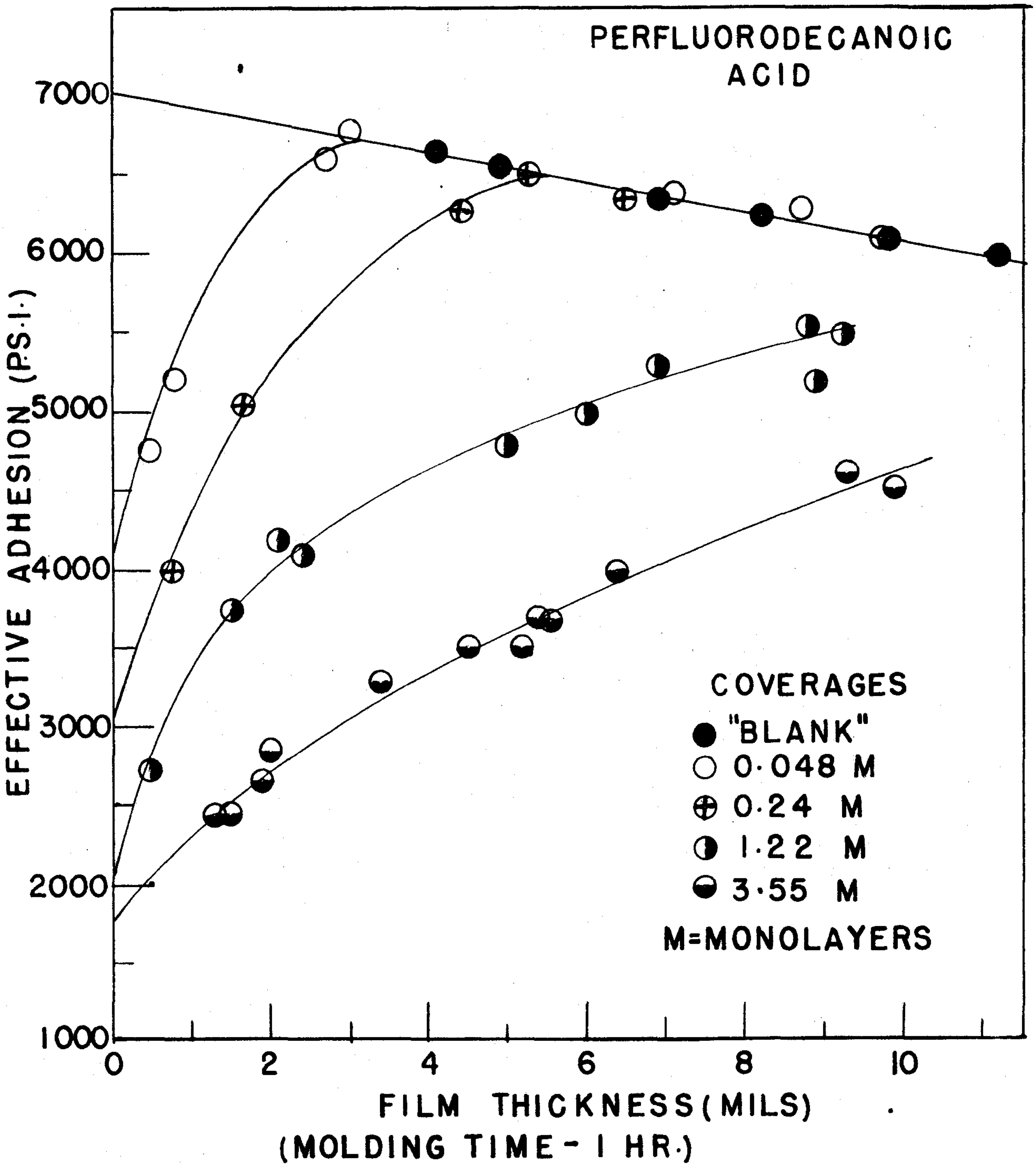
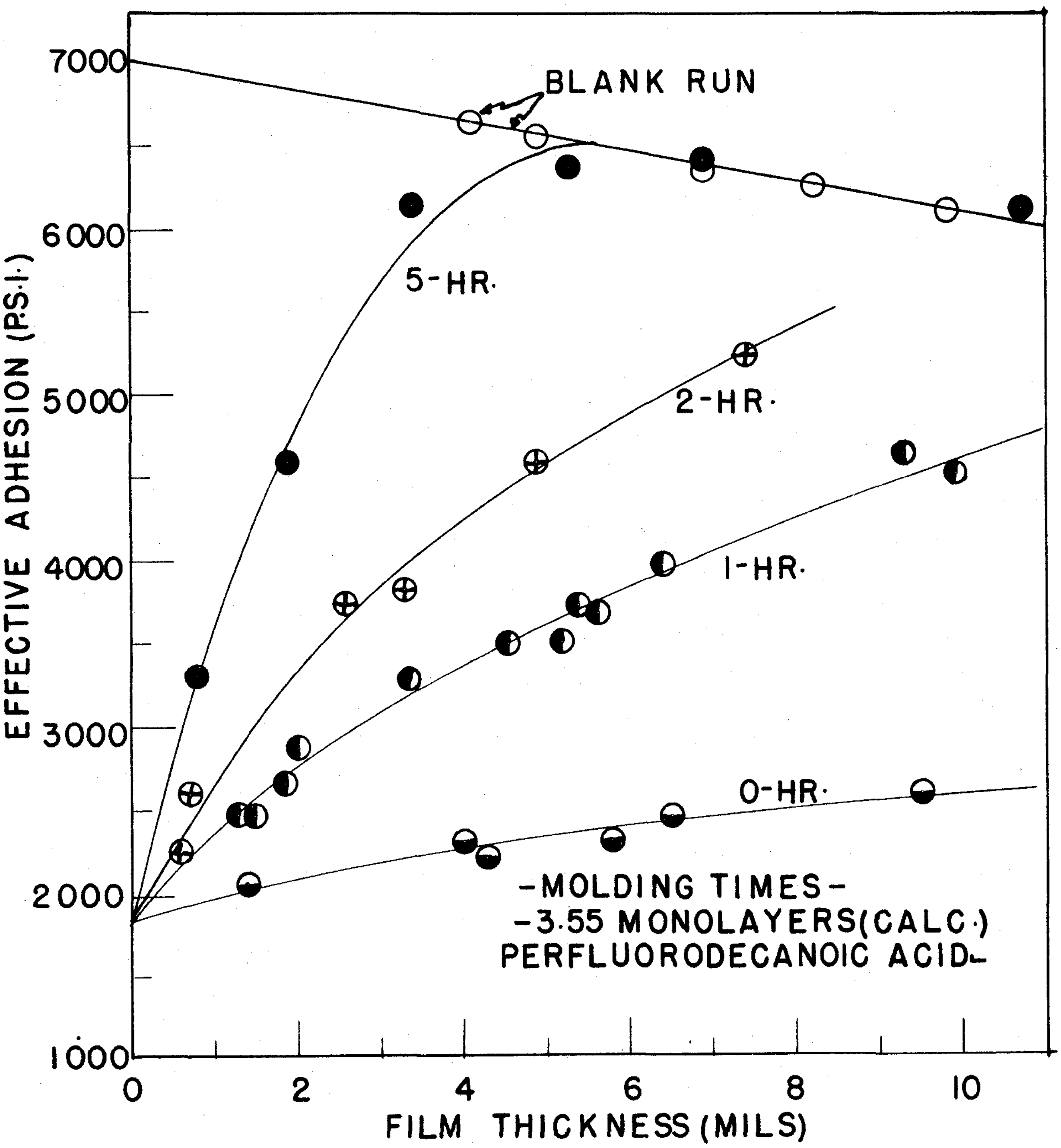

PERFLUORODECANOIC ACID
EFFECTIVE ADHESION (P.S.I.)
7000
6000
5000
4000
3000
2000
1000
0
2
4
6
8
10
FILM THICKNESS (MILS)
(MOLDING TIME - 1 HR.)
COVERAGES
● "BLANK"
○ 0·048 M
⊕ 0·24 M
◐ 1·22 M
◒ 3·55 M
M=MONOLAYERS

FIGURE 14.


BLANK RUN
5-HR.
2-HR.
1-HR.
0-HR.
-MOLDING TIMES-
-3.55 MONOLAYERS(CALC.)
PERFLUORODECANOIC ACID-
EFFECTIVE ADHESION (P.S.I.)
7000
6000
5000
4000
3000
2000
1000
0
2
4
6
8
10
FILM THICKNESS (MILS)

that thin films bonded to a metal surface have been shown to fail in cohesion indicating the adhesive strength to be rather high. Thermodynamically, an adhesive failure requires

$$\gamma_P > \gamma_M - \gamma_{P/M}$$

However, with a preadsorbed film the criterion for failure in adhesion

$$\gamma_P > \gamma_{sf} - \gamma_{P/f}$$

which is more easily satisfied since γ_{sf} is quite low. Consequently, one might expect adhesive failure for preadsorbed films. The data obtained supports this qualitative picture and <u>visual</u> observations of the specimen after fracture did show apparently bare metal spots over the surface. In fact, with polyethylene as the polymer, the films at about one monolayer coverage seemed to fail at both interfaces almost simultaneously with the metal surfaces being completely bare of polymer and the polymer film almost completely disjoined. The results with this polymer will be discussed later.

The phenomena of increasing adhesion with increasing film thickness may be ascribed to diffusion of the preadsorbed acids into the polymer film. As the film thickness is increased the concentration of a given amount of acid in the film is less and the driving force (concentration on surface - concentration in bulk) is greater. Therefore, for a given molding time and coverage one would have less "acid" on the surface and a consequent increase in adhesion for thicker films. This presumes that the adhesion is a function of the surface not covered with the preadsorbed acids. Substantiation of this mechanism is given by Figures 12 and 14 in which, for a given coverage, all curves for various molding times extrapolate to the same values at zero-film-thickness.

From the above, it becomes clear that zero-film-thicknesses for various coverages are unique in that they represent pure tensile adhesion since shear stresses and diffusional effects are extrapolated out. To illustrate the decrease of adhesion of zero-thickness-films with increasing coverages, Figure 15 is shown with the data for both decanoic and perfluorodecanoic acid. It is evident that both sets of data may be represented by a single curve. This figure suggests several conclusions:

(1) The surface roughness factor is approximately 1.5 since the curve tends to level out about that calculated coverage.

(2) The surface energies of the two different preadsorbed films are approximately the same since both curves are the same, particularly at $\phi = 1$, where $\phi = \frac{\theta}{1.5}$.

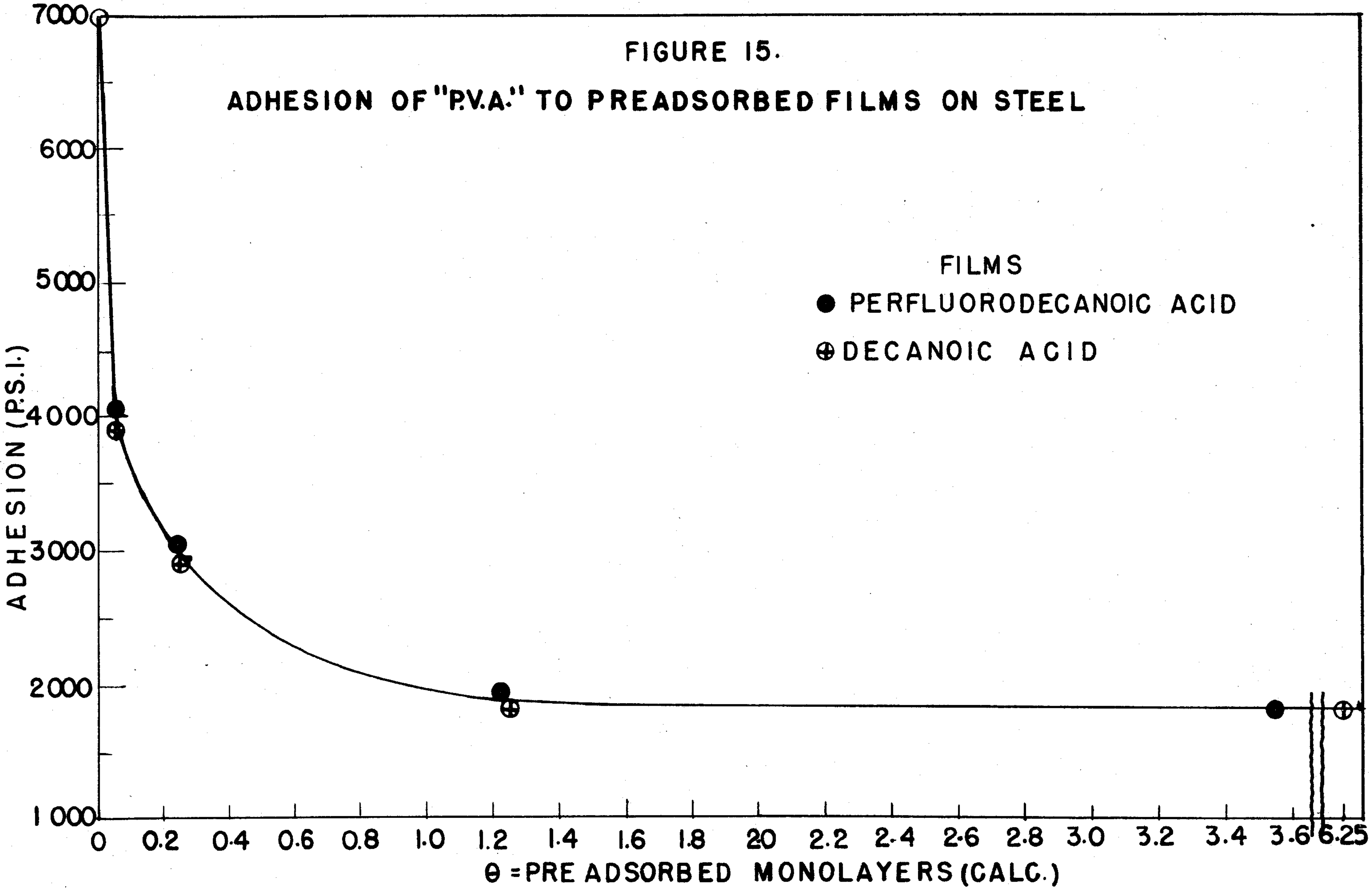


FIGURE 15.

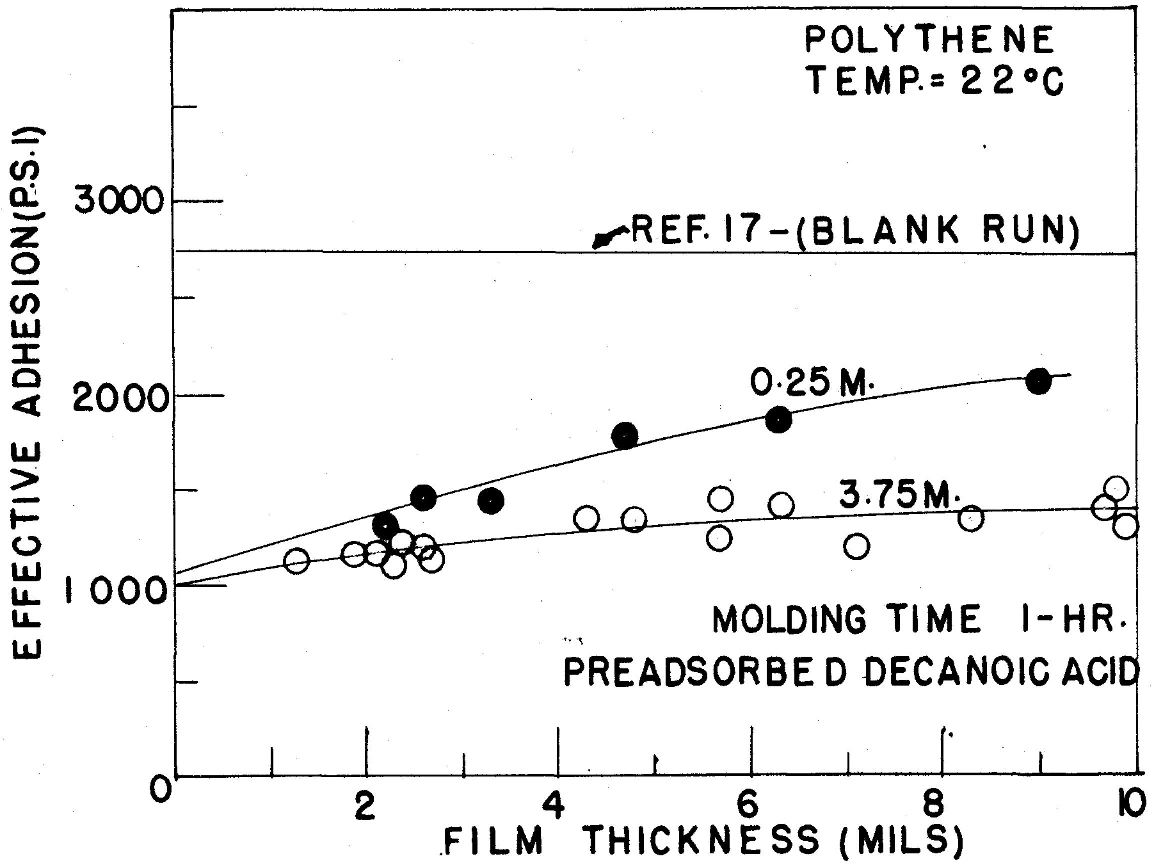
ADHESION OF "P.V.A." TO PREADSORBED FILMS ON STEEL

(3) The surface is heterogeneous since the tensile adhesion being a function of coverage or $(1 - \phi)$ might be expected to decrease linearly down to $\phi = 1$ if the surface were homogeneous.

The first inference is certainly logical qualitatively since the surfaces were ground and do exhibit peaks and valleys. The second conclusion has been verified by heats of wetting of powdered solids covered by stearic and perfluorodecanoic acids[88] to various coverages up to $\theta = 1$. The heats of wetting at full monolayer coverages exhibit practically no difference; small differences in surface energies would certainly be beyond the range of sensitivity of this mechanical type of testing. The third conclusion of surface heterogeneity is not unlikely; a number of investigators[82-87] in the field of adsorption have attributed their results to surface heterogeneity. Halsey[83], in particular, has succeeded in deriving theoretical adsorption isotherms assuming an exponential distribution of surface energies. Also, it should be mentioned that heats of wetting of water on powdered solids covered with stearic acid and perfluorodecanoic acid films[88] show a decrease of heats of wetting with coverage similar to the decrease of tensile adhesion. Although the heats (differential) of adsorption versus coverage for gases on solids have been known for a long time to exhibit this sharp decrease at small coverages, the data of Rhodin[85] and Beebe and Stevens (Hill[89]) for adsorption of N_2 on polycrystalline copper and iron, respectively, are particularly informative. Rhodin showed that the differential heats of adsorption were greater at small coverages than a simple sum of the differential heats of adsorption on the [110], [100], and [111] crystal faces of copper. In view of this, the author suggests the possibility of adhesion being a function of the energy distribution over a surface, in particular the number and the energy of active sites above the average surface energy. This would be consistent with Figure 15 when one considers that the greatest percentage decrease in adhesion ($\sim$60%) occurs when $\phi \cong 0.07$. After $\phi = 0.07$, the tensile adhesion decreases much less rapidly with increasing coverage.

As mentioned previously, there are two methods of testing the effect of surface free energy on adhesion with preadsorbed films: (1) change the preadsorbed film for a given polymer, the results with this method have been discussed; (2) change the polymer and compare the behavior of two polymers with the same preadsorbed film. In the latter case, the natural selection of a polymer was polyethylene since it is non-polar and offers a comparison with polar polyvinylacetate. Figure 16 shows the results obtained with a calculated coverage of 3.75 monolayers or an actual coverage (assuming surface roughness factor = 1.5) of 2.5 mono-

FIGURE 16.


POLYTHENE
TEMP.= 22°C
REF. 17-(BLANK RUN)
0.25 M.
3.75 M.
MOLDING TIME 1-HR.
PREADSORBED DECANOIC ACID
EFFECTIVE ADHESION (P.S.I.)
0
1 000
2000
3000
2
4
6
8
10
FILM THICKNESS (MILS)

layers. The zero-film thickness effective adhesion is seen to be 1000 p.s.i.; this value, as mentioned previously, should represent true tensile adhesion with diffusional and shear stresses extrapolated out. The effect of polarity then is clearly reflected in the comparison with polyvinyl acetate whose effective adhesion under the same conditions is 1750 p.s.i. At the same time there can be no doubt whatsoever that the failures in this instance are adhesional; the polymers in cohesion are readily capable of sustaining much higher loads under the same stress-distribution. This is clear when one considers the zero film thickness effective adhesion of the blank runs - 2750 p.s.i. and 7000 p.s.i. - for polyethylene and polyvinyl acetate respectively.

SUMMARY

The thin-film effective tensile adhesion of a polymer-metal adhesive-adherend system has been identified with bulk properties of polymers. This establishes a cohesive mechanism of failure for thin films less than 25 microns in thickness. With the visual observations, after fracture, of peripheral rings increasing in width with thickness of the film, this identification verifies the "Shear-Stress Theory" of failure.

The identification of thin-film adhesion with bulk properties has been demonstrated with molecular weight, temperature, brittle point, molecular weight distribution, rate of loading, and plasticizer content.

The preadsorption of a film effecting a change from a high surface free energy surface to one of low surface free energy has been shown to decrease the effective adhesion 60 to 75% of its original value. The decrease was greatest for polar polyvinyl acetate (75%) and less for non-polar polyethylene (60%). However, the adhesion of the more polar polymer to a non-polar surface was greater than that of a non-polar polymer to a non-polar surface.

The decrease of adhesion with fractional coverage of the surface by decanoic acid and perfluorodecanoic acid was shown to be the same. However, the relation of adhesion versus coverage was not linear but instead an exponential

type relation similar to the variation of heats of wetting on powdered solids versus coverage and to the variation of the differential heats of adsorption of gases on polycrystalline materials versus coverage. The explanation of the latter has been based on, and shown to be due to, surface heterogeneity. Similarly, the rapid decrease in effective adhesion versus coverage may be attributed to surface heterogeneity. It should be noted that this decrease in adhesion is much more rapid than that of the heats of adsorption versus coverage. Such a rapid decrease also was noted with the heats of wetting data. The suggestion is that the small percent of "active centers" on a metallic surface contribute greatly to the overall adhesion and adsorption takes place initially at these centers rendering these the least active with respect to adhesion.

EXPERIMENTAL

Fractionation of Polyvinyl Acetate.

The technique employed in the fractionation was essentially that of Wagner[67]. Seventy-five grams of duPont's "Elvacet 40-15" was dissolved in 1200 ml. of acetone at approximately 30° C. The solution was filtered through a fritted glass suction filter to remove dirt, lint, and extraneous impurities. The resulting solution was allowed to stand overnight in a constant temperature bath (30° C.). The procedure consisted of adding the precipitant, (1:1 or 1:2) water-methanol, to the solution very slowly and with constant stirring until a moderate opalescence was observed. At this point the addition was discontinued and the solution heated about 3°-4° C. causing the solution to be clear. The solution was allowed to cool to bath temperature with constant stirring and then allowed to stand overnight, ca twenty hours. After this period the insoluble fraction settled out as a gel phase. This gel phase was completely separated by decanting most of the supernatant solution and centrifuging the gel plus a small amount of remaining solution. Further controlled additions of precipitant produced other fractions. The fractions prepared were redissolved in acetone and reprecipitated totally in a large amount of water. The polymer fractions were then dried to constant weight under 3 mm. pressure and 40°-50° C. (about 3-4 weeks).

The molecular weight of each individual fraction was determined by the viscosity method using an Ostwald-Cannon-Fenske type viscometer. Determinations of viscosities were made at at least three concentrations; actually the specific viscosity was calculated directly. Since the viscosity, with kinetic energy corrections, is represented by

$$\eta = Adt - Bd/t$$

A, B = viscometer constants
d = density
t = time of flow

and the specific viscosity is defined by,

$$\eta_{sp} = \frac{\eta}{\eta_o} - 1 \qquad \text{where } \eta_o = \text{viscosity of solvent}$$

the specific viscosity, assuming additive volumes of polymer and solvent, is readily obtained. Using the values $\frac{\eta_{sp}}{C}$ at three concentrations and extrapolating to zero concentration the intrinsic viscosity $[\eta]$ is obtained which for polyvinyl acetate is related to the molecular weight by

$$[\eta] = 1.88 \times 10^{-4} M^{0.68}$$

The data obtained are given in Table I.

Table I

Fraction	Intrinsic Viscosity	Molecular Weight M
A-1	0.79	225,000
A-2	0.59	147,000
A-3	0.38	77,000
A-4	0.30	54,000
P-2,3,4	0.55	130,000
F-2	0.61	150,000

All other fractions for subsequent investigations were prepared and molecular weights determined similarly.

Preadsorption of Films.

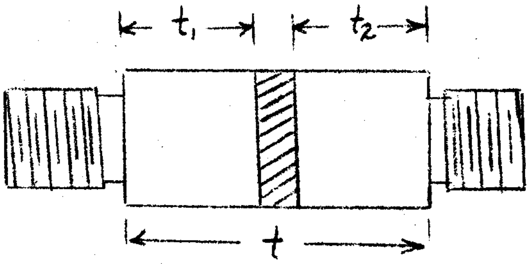
Films of long chain acids, decanoic (A.R.) and perfluorodecanoic acids (M.M.M. Co.), were adsorbed on the metal surfaces by pipetting a predetermined amount of solution onto the surfaces from a serological pipette graduated in 0.001 ml. divisions and allowing the solvent to evaporate. The solutions were prepared by weighing the solute with a semi-micro analytical balance to the nearest hundredth of a milligram and dissolving this in n-heptane (Phillips Petroleum - Pure Grade, minimum 99% mol percent purity). Solutions of desired concentration were then prepared by successive dilutions so that a given volume gave the desired adsorption coverage. The cross-sectional areas of the molecules were assumed to be 20 and 28 square Ångstroms for decanoic and perfluorodecanoic acids respectively in the calculation of coverages based on the geometrical area of the surface.

Preparation of Test Specimens.

Cylindrical plugs, 0.7500 inches in diameter and 0.500 inches in length, were ground on a surface grinder yielding a surface of about 14 micro-inches - which is the r.m.s. average height of the peaks. Other surface roughness values were obtained by varying the size and type of wheel. All data reported are for a surface roughness of 14 micro-inches except the data for preadsorbed films; the surfaces in these experiments were 5 micro-inches as determined by a profilometer.

After grinding, the surface was covered with a film of polymer by applying a one percent polymer solution (acetone as solvent) with a camel hair brush. When films were preadsorbed this step was replaced by the preadsorbing step. Specimens covered with a polymer film were dried "in vacuo" at 30° C. for a period of one to two hours.

The plugs were assembled in a mold[89] and molded with additional polymer powder giving rise to a polymer film between two plugs viz:



The molding temperature was 260°-275° C. for polyvinyl acetate and 300° F. for polyethylene specimens. The specimens prepared were tested in a universal Olsen testing machine of 10,000 pounds capacity. To insure pure tensile application of load the set-up contained two needle-bearing universal joints, one on each end of the specimen. A Buick engine mount consisting of a rubber pad cemented to two metal plates was pulled in series with the specimen to provide a cushion effect after fracture of the specimen.

After fracture, the polymer was dissolved from the plugs with an appropriate solvent. By measuring the thicknesses, t_1 and t_2, of the plugs after dissolving the polymer and measuring t before fracture, the polymer film was calculated as $t - (t_1 + t_2)$.

For high temperature testing, the test specimen was surrounded by a split and hinged brass cylinder whose inner surface was painted a mottle black and an infra-red lamp was directed towards the split. By varying the voltage with a rheostat and adjusting the distance from the split, temperatures as high as 80° C. could be attained conveniently. Low temperatures were accomplished by use of a copper sleeve which fitted about the sample and had a reservoir for coolant. With solid CO_2 in the reservoir temperatures as low as -60° C. could be attained.

All testing was done at a rate of travel of the crossheads of 4.0 inches per minute except as otherwise noted.

Plasticization of Polymer.

The plasticizer, dibutyl phthalate, C.P., was redistilled and precalculated amounts were introduced into a series of glass tubes containing polyvinyl acetate. The tubes were evacuated overnight and sealed off. They were subsequently placed in an oven at 150° C. for 18 hours. After this time diffusion was found to be complete in all cases and the plasticized polymer could be obtained as a homogeneous mass.

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