: Factors A[illegible] Adhesive Bond Formation

By H[illegible] and E. W. Merrill[2]

s long been the aim eld of adhesion to predicting not only what, but for pre- of the resultant here is to consider s involved in such

le at the outset to ion of an adhesive. pioneered in this hat there are two onds: mechanical anical joints form r dovetailing of the us surfaces, while hich can occur on s rough surfaces, om intermolecular ttractions between ad. Probably both sent to some degree cBain then further id which wets both a can be solidified bond and is there- He apparently con- bond to form if the nd a tensile stress however small.

ttributes three es- sive: it must be a t, and it must be ation. Equally in- it not stipulated, weight, composition, ties like coefficients reover, no specifica- dherend surfaces are ce for this definition e and quantitative ng as both adherends rge number of ma- a and low molecular g a substantial range physical properties. dhesive was applied achieved usually by olvents were some-

ion implies that wet- te to bond formation stion of what is not tting has no uni-

[illegible] definition but is related to the contact liquid and the solid will be remembered regarded as the angle of a droplet by the and the solid surface droplet rests and is in the liquid. One considers wetting to angle is less than wetting if it exceeds group considers com- occur if the contact that wetting is in- as the angle in- materials, when contact angles with glass and the cases McBain fall largely

whether combinations high contact angles for specific adhesion, experiments were molecular weight materials Palmer (4) and Wood- evaluate the possible factors other than con- combinations were also large and small dif- points, polarities, of expansion, etc. small amount of ad- was placed upon the and the combination enough to keep tempera- uniform throughout the C. above the adhes- ion. The system was about 10 C. below this whereupon formation of a relatively investigated by droplet with a spatula room temperature. The rials were tested, in- combinations in which had a higher melting hesive.

vaseline, benzene, cellulose glass, ice, paraffin, poly-

silicon nitrate, potassium nitrate, sodium chloride, zinc chloride; lead stearate; *n*-octadecanol; oleic and stearic acids; phthalate; dibutyl phthal- benzophenone, nitrobenzene; hexane, diphenyl, naph- phenanthrene; glass,

unmistakably in all cases. Of course, the bonds so formed could be destroyed by cooling to 100 C. below the adhesive's melting temperature, due to stresses resulting from unequal coefficients of expansion. The successful bonds formed by mercury are particularly interesting, since this material forms some of the largest known contact angles with ice, glass, styrene, etc. Bonds therefore formed here regardless of the magnitude of the contact angles involved.

In these tests, no extensive control of adherend surfaces was attempted, though they were as fresh, clean and smooth as possible. Despite all reasonable precautions, adsorbed layers of gases and water vapor, and probably traces of grease, were undoubtedly present, since no high vacuum tests were undertaken. Similarly, surface characteristics are influenced not only by age but by methods of preparation, a familiar example being the differences in metal surfaces depending upon whether they were prepared by grinding, milling, polishing, etc. Indeed, tests were deliberately undertaken on a given system in which different kinds of surfaces were prepared, and in which surface contamination as by oxidation was permitted. In all of these cases, bonds formed. As further evidence, the every extensive search made among others by Loughborough and Haas (8) to find solid surfaces to which water will not stick upon freezing deserves mention. This is of critical importance in de-icing of airplane wings during flight. No case of nonadhesion is reported in spite of the great number of materials tested.

While the evidence is not, of course, complete, the foregoing suggests that an adhesive bond will form if a low molecular weight material at a temperature above its melting point is brought into contact with a solid surface and is then allowed to freeze in place.

High Polymers as Adhesives

The capacity of thermoplastic high polymers to stick to solid surfaces when molten and then cooled to solidification is well known, and in this respect their behavior closely parallels that of low molecular weight materials. The tackiness often exhibited by molten polymers reflects this capacity to stick, as well as the reluctance of these polymers to flow resulting from their high viscosity.

Since a polymer usually does not show a well-defined melting tempera-

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or of Chemical Engr. te of Technology, Cam-

Dewey & Almy Chemical formerly with Massachu- nology.

bers in parentheses refer ded to this paper.

will store from 6 to 10 months, as will melamine resin treated materials.

Laminating pressures recommended for the chemical glues when they were first introduced were in the 25 psi. range as compared to 100 to 250 psi. for the low-pressure phenolic resins. However, it has been established that a marked improvement in properties is noted when the chemical glues are processed at 100 psi. and excellent properties are obtained when molded at 1500 psi. The previous statement is not intended to be facetious but is based on established facts and constitutes the basis of the author's reference to these materials as chemical glues when added in excess in the resin-filler ratio and processed at low pressures.

On molding or laminating the phenolic-treated materials, the treated sheets are placed between corrosion-resistant steel sheets to produce a flat laminate, or the die-cut pieces are loaded into the mold cavity. In some cases, the die-cut parts are stapled together for ease in handling and loading the mold cavity. Because the treated material is dry and the material essentially self-lubricating, a minimum of make-ready is required which tends to offset the longer curing time noted above when compared with the chemical glues. Molds are either of the metal-to-metal type or metal with an expandable bag or pressure membrane on the other side. The mold is usually heated by steam, direct gas flame, or electricity. After molding, the finishing operations include sawing, grinding, drilling, punching, painting or any other required operation.

The chemical glue treated material is processed in much the same manner except that lubrication of the mold by special lubricants is quite often required, and the customary use of an air-excluding membrane requires additional time for assembly. In view of the fact that the sticky material requires more time for lay-up assembly, this additional make-ready time tends to offset the advantage of faster cure of this type of resin. Molds for this resin may be made of plaster, wood, cast plastic, metal or any combination of these materials. Heating of the treated material may be accomplished by infrared lamps, heated ovens, steam, or electricity. Finishing operations are similar to those noted above.

During the war period, the contact pressure type of resin was employed almost exclusively with fillers of the inorganic type. This type of filler was wetted readily by the resin, and, because of the properties of the filler, moldings having exceptionally high strength values were produced and served very satisfactorily in a wide variety of end uses. Full data on the physical properties of this type of molding or laminate are available from a variety of sources.

Because of the types of molds employed, tooling costs were exceptionally low, and changes in the molds could be made rapidly and at low cost. This had a decided advantage in the war effort because of the many changes which were made in design of such items as plane parts as combat experience indicated a weakness in a structure or as engineering developments dictated a change.

As a result of the acceptance of parts molded in this manner during the war period, it was predicted that a large peacetime industry would be established based on production of products using the same materials and techniques as employed under war conditions. This prediction failed to take into consideration that the costs of the war program were underwritten by the United States Government and that the high material costs for resin and inorganic filler were generally disregarded as long as satisfactory performance was obtained. Temporarily, at least, the usual economic yardstick was discarded and end-use performance became the only criterion of value. When the normal economic laws once again became part of our business life, the high material costs could not be disregarded. In addition, the inexpensive molds did not stand up under long production runs, and as a result of a combination of these factors, the expected volume in this field failed to materialize, and as a result production has been confined to prototypes, models, and a few specialty uses. Apparently the engineering and tooling ability of proponents of this type of production did not match their enthusiasm and optimistic outlook which failed to include some very important and pertinent economic considerations.

Some effort has been devoted to attempts to employ cellulosic fillers and inorganic fiber mats to offset the high cost of woven inorganic filler. In the case of cellulosic fibers, the molecular weight of the chemical glues does not permit fiber penetration, with the result that low dimensional stability results. In the case of mat materials, the technique of handling is to load the dry filler into the mold and then to add the resin as a pour charge over the dry mat, after which a film of cellophane or other material is placed over the cavity charge and heat and pressure applied. Because of the excessive make-ready time required and in view of the fact that an excess of resin must be added to allow for good filling out of the mat, this PP and PM technique of molding appears to have serious economic disadvantages. A new technique of injecting the resin into the dry filler while it is in a closed and heated mold appears to have certain advantages which may provide a solution to the problem.

A very interesting technique of processing the chemical glue type of resin is that of continuous lamination. In this process a series of webs of paper, cloth, or fiberglas fabric are individually resin treated from separate treating pans and then laminated into a single ply by passing them simultaneously through squeeze rolls. At the squeeze rolls, a layer of cellophane is imposed on the top of the ply and another on the bottom and the composite web is passed into a heating oven. Longitudinal pressure is produced on the web—while in the oven—by differential speeds on squeeze rolls at opposite ends of the oven. Lateral pressure is produced by contraction of the cellophane, while held under tension by tenter frames, from the oven heat. The cellophane acts as supporting web, pressure pad, and, in addition, imparts a high finish to the laminate during the curing operation. This process has several advantages over the more conventional manner of laminating individual sheets in a hydraulic press, but recently disclosed figures indicate that the more modern hydraulic presses, when operated efficiently, produce laminated material at twice the footage per unit time compared to a continuous laminating machine. When a paper-polyester resin laminate of the type produced in this manner is compared to a melamine-surfaced phenolic laminate, it is found to be lower in surface hardness, less stain-resistant, and lower in abrasion resistance. The resins usually employed have lower heat-distortion points and because the molecular size does not permit good fiber penetration the dimensional stability of the laminates is rather low when compared to the melamine-phenolic type of material. This type of laminate, because it can be produced in any desired length, may possibly find application in wall panels and similar applications.

As new materials are developed and improvements in processing techniques are worked out for presently available materials, the field of low-pressure laminates and molding materials will undoubtedly find its proper place in the plastics industry.

ture, the question arises as to whether a minimum temperature exists below which sticking becomes impossible. To explore this point, Judge (6) brought together various combinations of plastics and adherend surfaces at controlled temperatures. This was done by pressing together in a tightly fitting mold a thin foil of the adherend upon the flat face of a disk of the plastic under test, approximately $\frac{15}{16}$ in. in diameter and 0.2 in. thick. The entire apparatus was located in a thermostatic bath whose temperature was controlled to ±0.2 C. The system was of course first brought to temperature before pressure was applied, whereupon constant temperature was maintained throughout the test. Occurrence of sticking was determined qualitatively by pulling the foil from the disk. If sticking developed at a given temperature, the run was repeated at a new temperature approximately 2 C. lower until a minimum temperature was discovered at which sticking occurred but below which it did not occur. Table I presents the results using tin as an adherend. The evidence indicates that each polymer tested shows a unique temperature above which sticking develops but below which it rapidly becomes difficult and impossible to form a bond. For polystyrene, this temperature lies in the neighborhood of 80 C. and is evidently little affected by pressure. Above this temperature, the capacity for sticking develops rapidly, and indeed polystyrene becomes noticeably tacky to a light touch with a spatula at 110 C. Below 80 C., however, polystyrene quickly loses its capacity to stick even at prolonged exposure at high pressure to an adherend surface. Other plastics were found to behave in a fashion analogous to polystyrene. While Table I reports only results for tin as an adherend, entirely similar results were obtained for aluminum, cellulose, and styrene foil as adherends, whose minimum temperatures of bond formation were found to lie within 2 C. of that of tin.

Further inspection of Table I shows that the minimum sticking temperature for these polymers appears to coincide with their second order transition temperatures. It will be remembered that the second order transition temperature, a term coined by Ehrenfest (5), is defined as the temperature at which curves of primary thermodynamic properties like volume and enthalpy plotted against temperature show a discontinuity in slope. The values reported in Table I were determined on the materials tested by the use of a dilatometer designed according to Jenckel and Ueberreiter (7), with 20 min. allowed for each observation point.

TABLE I.—MINIMUM TEMPERATURES OF ADHESION TO TIN.

Adhesive	Second Order Transition, deg. Cent.	Time of Pressure Application	Pressure Applied, psi.	Minimum Temperature of Bond Formation, deg. Cent.
Polystyrene[a]	81	7½ hr.	10 000	75.5
		1 hr.	10 000	80
		5 min.	10 000	82
		10 hr.	50	80
		1 hr.	50	85
Polyvinyl butyral[b]	45	2 hr.	10 000	40
		10 min.	10 000	45
Polymethyl methacrylate[c]	53	1 hr.	5 000	50
		10 min.	5 000	65
Polyvinyl alcohol[d]	58	1 hr.	5 000	55
		5 min.	5 000	65

[a] Dow Styron, R-1-K27, GA type.
[b] duPont, V. F. 7100.
[c] duPont Lucite, SED 3633.
[d] duPont 52–22, Type A.

The curve for the polystyrene used here is shown in Fig. 1 and is typical.

These transitions have been very extensively studied, among others, by Boyer and Spencer (2), and are considered due to a rapid increase in rotational and vibrational freedom of the molecular chain segments at these temperatures. Thermoplastic polymers often (but not always) exhibit second order rather than first order transitions. A polymer's second order transition temperature is relatively unaffected by pressure but is lowered by solvent or plasticizer addition; this temperature rises with increasing molecular weight, but soon reaches a maximum constant value which is then independent of further molecular weight increases, providing no cross-linking occurs. Boyer and Spencer (3) showed that these second order transitions are not equilibrium effects, since the discontinuity in the curve of Fig. 1 disappears if 60 hr. instead of 20 min. are allowed for each observation point.

The coincidence of the minimum adhesion temperature and the transition temperature appears consistent with these facts. Adhesion undoubtedly requires a sufficient mobility of the atoms and molecular segments in the adhesive surface so that their force fields can key into the companion force fields of the adherend surface. Without such mobility and orientation, no perceptible bond formation can occur. Mobility increases as the temperature rises above the transition temperature but is rapidly lost below it, which explains why polystyrene shows a rapidly declining capacity to stick below 80 C. (see Table I). If mobility at a lower temperature is required, then this can be attained by reducing the polymer's transition temperature through solvent addition. Thus a nitrocellulose lacquer can be made to stick to metal surfaces far below the transition temperature of dry nitrocellulose, since the orientation required for bonding occurs before the solvent evaporates completely. On the other hand, mobility can be destroyed by raising the transition temperature through cross-linking. Thus, thermosetting resins used as adhesives are usually applied in partly polymerized form and then "set up" in place by heating, oxidation, etc. When applied in molten or solution form, orientation can clearly occur before extensive cross-linking destroys mobility. When applied as a dry powder or film, the polymer is usually made to melt before setting-up, and so again has an opportunity to orient. In all these cases, of course, a poor bond results if a film of low cohesive strength separates the

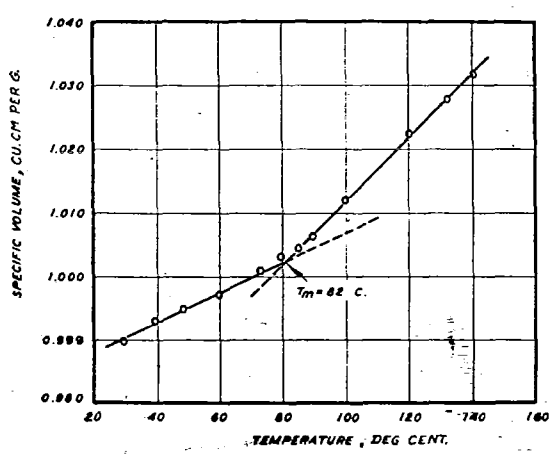

Fig. 1.—Specific Volume *Versus* Temperature for Polystyrene (11).

adherend and adhesive, such as the mold lubricants and parting agents used in molding.

The foregoing, therefore, suggests that a liquid will bond to a solid surface with which it is brought isothermally into contact if the combination is then cooled to below the transition temperature (either first or second order) of the liquid. A bond will of course also form if the liquid's transition temperature is increased above the system's temperature, as by cross-linking or solvent evaporation.

Bond Strength

While it has been suggested here that any liquid can be made to bond to any solid surface, the strength of the bonds so formed has not yet been considered. A great many factors have been recognized as affecting bond strength, and a few deserve brief discussion. It has, for example, been proposed that strong joints cannot be made to polar adherents with nonpolar adhesives, and *vice versa*. The experimental evidence for this generalization is not entirely satisfactory. Table II presents the test results of Loughborough and Haas (8), showing the shearing force needed to cause a button of ice to break loose from the indicated adherends, as determined in a centrifugal testing machine. Tables III and IV show Woodruff's findings (13) on the force required to shear off a button of the indicated adhesive 0.3 in. thick and 1.0 in. in diameter from a single adherend surface, by application of force parallel to this surface by means of a yoke which fits snugly around the adhesive button. The rate of loading was approximately 50 psi. per min. Results should be regarded as of comparative value only. The findings are evidently not consistent with the polarity criterion; for example, Table II shows ice, which is highly polar, to stick as well to polyethylene as to glass, which are respectively nonpolar and polar. The equal strengths for Wood's metal bonds to stainless steel and bakelite in Table III or for naphthalene and water to stainless steel in Table IV are again exceptions to the polarity rule. It is worth mentioning in passing that these bond strengths correlate no better with contact angles than with polarity.

TABLE II.—ADHESION OF ICE-FILM TO MISCELLANEOUS MATERIALS, −25 C. TESTS BY LOUGHBOROUGH AND HASS, BY CENTRIFUGAL TECHNIQUE.

Adherend	Shear Strength, psi.
Polished steel	185
Polished copper	124
24 ST aluminum	220
Glass (96% silica)	158
Microscope slide	122
Polyethylene	160
Rubber	170

It is not intended to imply here that the polarity rule is necessarily incorrect. These examples are cited to show that bond strength does not appear to depend solely upon one factor. Variables like coefficients of expansion and other physical properties must also be considered, since these may cause stress concentrations which weaken an otherwise strong bond, as discussed below.

Effect of Bond Thickness:

It has been known for a long time that bond rupture strength varies inversely and widely with thickness. A typical curve is shown in Fig. 2, showing results for a polymethyl methacrylate bond between two steel cylinders $\frac{15}{16}$ in. in diameter, stuck together end to end, and tested in tension at a loading rate of about 6500 psi. per sec. Each of the data points is the average of three tests. The bonds were formed isothermally at the various temperatures shown, by inserting a layer of molten polymer between the cylinders placed end to end, after which the bonds were cooled to room temperature for test. All care was exercised to keep the cylinders properly aligned while allowing the adhesive freedom to contract as it wished during cooling. The results show that bond strengths at room temperature appear independent of temperature of formation within the ranges investigated.

TABLE III.—ADHESION OF WOOD'S METAL (MP 62 C.) TO VARIOUS ADHERENDS, AT 50 C.

	Shear Strength, psi.
Glass	151
Lucite	84
Bakelite	46
Polystyrene	8
Stainless steel	37

Various explanations of this thickness-strength behavior have been proposed, and of these, four will be mentioned here. The first attributes this behavior to the development of stresses resulting from differences in thermal coefficients of expansion between adhesive and adherend. This theory was well restated recently by Turner (12), who proposed overcoming the difficulty by adjustment of the coefficient of the adhesive to correspond with that of the adherend by incorporation of suitable pigments and fillers. Figure 3 shows that unfilled polystyrene bonds thicker than 0.10 in. actually break spontaneously upon cooling, even though good bonds form initially, due evidently to the development of high stresses upon cooling. Filling the styrene with asbestine brings the coefficients of expansion of adhesive and adherend more closely into line, and so improves the thickness-strength behavior of the bond. The dips in the curves at small bond thicknesses are presumably due to "starvation" or to stresses resulting from compression of the particles of filler.

TABLE IV.—ADHESION OF VARIOUS MATERIALS TO STAINLESS STEEL.

	Melting Point, deg. Cent.	Test Temperature, deg. Cent.	Shear Strength, psi.
Naphthalene	80	55	90
Water	0	−20	78
β - Methyl naphthalene	35	14	63
Silver nitrate	212	190	48
Wood's metal	62	50	37
α - Methyl naphthalene	−22	−40 (?)	32
Lead stearate	116	62	30
Stearic acid	69	43	12
Paraffin	47	29	7
n-Octadecane	28	10	2

Further evidence indicating the influence of thermal stresses upon bond strength is presented in Fig. 4. Here is shown a typical curve of bond strength *versus* temperature of test at constant bond thickness for a thermoplastic polymer, in this case, polymethyl methacrylate. These tests, as before, were on metal cylinders stuck together end to end and tested in tension at a load rate of 6500 psi. per sec. The coefficient of expansion of the adhesive is roughly ten-fold that of the metal in this case. As the temperature falls, inspection shows that bond rupture strength increases until the second order temperature is reached. Here the rupture strength decreases abruptly, possibly because the material is no longer capable of rapid flow to remove strain inequalities. The strength again rises, reaches a maximum, and then falls off to zero as the internal thermal stresses become more and more important. Many cases of bond failure may be attributed to the development of such stresses. Figure 5 presents the same test data for unfilled and filled polystyrene. The benefits to be derived from adjustment of coefficients are evident.

A second explanation for the thickness-strength curves as in Fig. 2 attributes this behavior to differences in moduli, Poisson's ratio, etc., of adhesive and adherend. It appears that, even when thermal expansion coefficients are perfectly matched, unequal moduli of adhesive and adherend would still result in a curve qualitatively similar to Fig. 2. It will be noted that the curve for filled polystyrene in Fig. 3 still shows some variation of strength with thickness, and this may be due to differences either in the thermal coefficients or the moduli.

The so-called theory of flaws is a

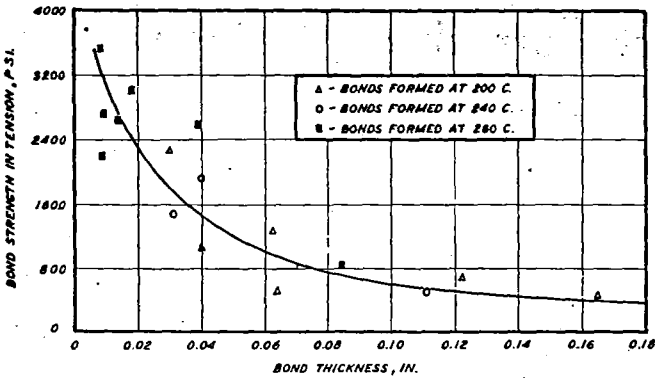

Fig. 2.—Bond Strength at 25 C. *Versus* Thickness (11).
Adhesive: polymethyl methylcrylate. Adherend: lathe-turned steel.

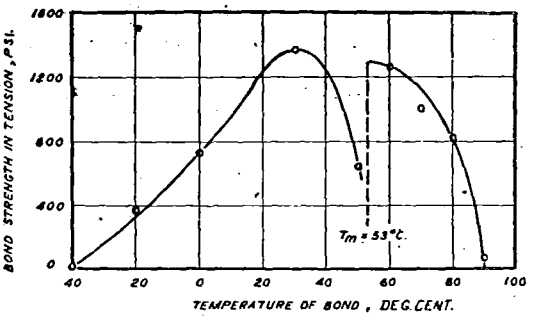

Fig. 4.—Bond Strength *Versus* Temperature (11).
Adhesive: polymethyl methacrylate. Adherend: emery-ground steel. These bonds were formed at 240 C., and were all 0.1 in. thick.

third possible explanation of the thickness-strength behavior of adhesives. This attributes the higher average strength of thin adhesive sections to the fact that these necessarily contain fewer structural flaws than thicker sections. Bikerman's (1) ingenious analysis of tests of paraffin wax bonds between metal blocks showed that this theory goes a long way toward explaining his experimental findings.

The fourth possible explanation of this thickness-strength behavior, proposed by McBain and Alexander (9), suggests that orientation occurs in adhesive films due to the influence of near-by solid adherend surfaces. McBain's X-ray study of glue films used as wood adhesive, however, uncovered no supporting evidence.

It will be noticed that these four possible explanations of thickness-strength behavior are not necessarily mutually exclusive, that is, all four may simultaneously affect bond strength. Only the last two theories mentioned offer a reasonable explanation for the fact that the strength of thin bonds may far exceed the cohesive strength of the adhesive material in bulk. The desirability of further work to establish the reasons for thickness-strength behavior is clear, since corrective measures can be taken only after causes are known.

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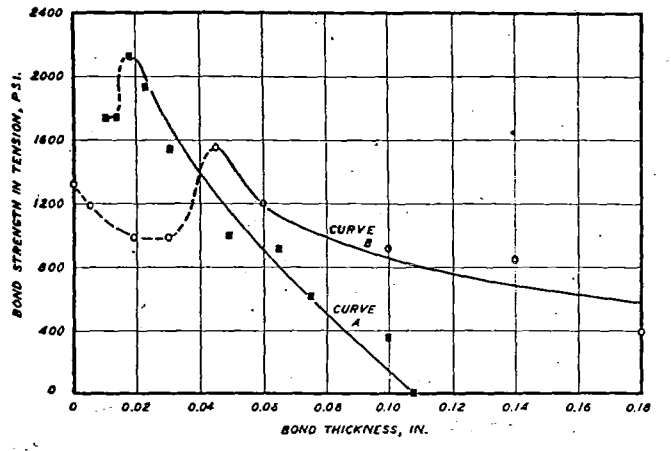

Fig. 3.—Bond Strength at 25 C. *Versus* Thickness (11).
Curve *A*: polystyrene without filler (cubical coefficient of expansion: 240 × 10^{-6} reciprocal degrees centigrade) bonded to lathe-turned steel surfaces (cubical coefficient: 33 × 10^{-6}).
Curve *B*: polystyrene filled with 60 per cent by weight of asbestine (cubic coefficient 114 × 10^{-6}) bonded to emery ground aluminum surfaces (cubic coefficient 75 × 10^{-6}).

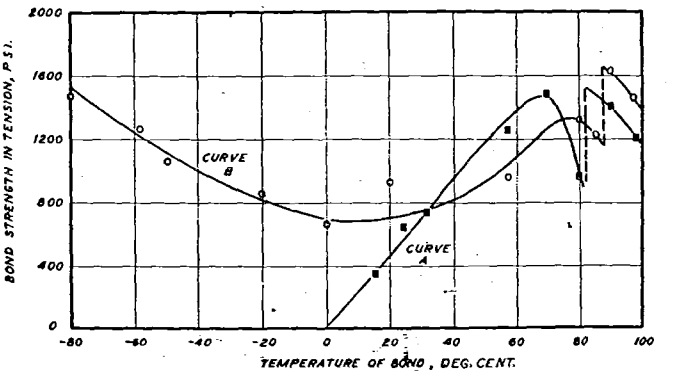

Fig. 5.—Bond Strength *Versus* Temperature (11).
Curve *A*: polystyrene without filler (cubic coefficient 240 × 10^{-6}), bonded to emergy-ground aluminum surfaces (cubic coefficient 75 × 10^{-6}).
Curve *B*: polystyrene filled with 60 per cent by weight of asbestine (cubic coefficient 114 × 10^{-6}), bonded to emery-ground aluminum (cubic coefficient 75 × 10^{-6}). All bonds were formed at 220 C., and were 0.1 in. thick.