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THE PROBLEM OF THERMAL-EXPANSION STRESSES

IN REINFORCED PLASTICS

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SUMMARY

Failure of adhesive bonds is attributed to boundary
stress concentrations. An analysis of the causes of in-
ternal-stress concentrations in rigid adhesive layers
leads to the conclusion that stress concentrations can be
eliminated in many cases by matching the coefficients of
thermal expansion of the component parts. A stress-equi-
librium formula for calculating the thermal-expansion co-
efficients of mixtures involves the density, modulus of
elasticity, coefficient of thermal expansion, and propor-
tion by weight of the ingredients. Illustrations of the
application of the formula derived include lead-antimony
and beryllium-aluminum mixtures, phenol-formaldehyde resin
and glass-fiber mixtures, and plastic plywoods. The ther-
mal-expansion coefficients of a number of pure and rein-
forced plastics are reported. Bonds obtained when thermal
coefficients are matched are stable over a wide tempera-
ture range.

I. MECHANICS OF ADHESIVES

This report describes a method of compounding a plas-
tic or other mixture or compositions to provide a material
having a predetermined desired coefficient of thermal ex-
pansion. In the preparation of plastics heretofore it has
been found practically impossible to produce a satisfactory
bond between a plastic and a metal facing or other metal
reinforcement. This is due for the most part to the dif-
ference in coefficients of expansion of the materials; the
plastics have relatively high coefficients of expansion as
compared with those of metals. Because of the differential
expansion, forces created upon changes in temperature have
been such as to prevent a satisfactory bond being obtained
between metals and plastics except where plastics of a

flexible rubber-like, or gummy type are used. Even in
the bonding of foils of tin, lead, aluminum, etc., to card-
board or paper for containers, gummy or tacky plastics
only have been used.

The problem of obtaining bonds between plastics or
other adhesives and various materials is considered as
being substantially the same problem as that of removing
or eliminating concentrated stresses at the boundaries.
If internal-stress concentrations can be removed, the full
strength of the adhesive can be developed to resist ex-
ternal loads.

Bonds produced by adhesives can be divided into two
general classes: the rubbery or yielding bond and the
rigid bond. In the first category are found most thermo-
plastic cements, rubber cements, and combinations of thin
rubber layers and cements. Adhesives of this class have
been found to provide durable bonds between dissimilar
materials at moderate temperatures. The rigid or high
modulus bond has generally been found unsatisfactory for
such applications. A possible exception is found in the
use of cold-setting cements of the phenol-formaldehyde
and urea-formaldehyde types. The advantages of the first
class over the second disappear at reduced temperatures
where the adhesive loses its ability to eliminate stress
concentrations by yielding with the dimensional changes
of the materials bonded. The rigid bond is superior for
many purposes to the yielding bond, if it can be obtained,
because it produces a stronger and less-yielding product.
For composite structural materials subjected to extreme
temperature changes a stable rigid bond is imperative.

In attempting to bond various materials together, it
has been found that materials having widely different co-
efficients of expansion cannot be bonded with any rigid
cement available. Certain thermoplastic adhesives pro-
duce satisfactory bonds at ordinary temperatures, but fail
at low temperatures when the bond becomes rigid and is no
longer able to yield to changes in dimension of the mate-
rials bonded. Certain rubber cements fall into the classi-
fication of bonds which are soft enough to yield with
changes in dimensions. These yielding bonds, however, do
not produce the rigidity required for structural applica-
tions and fail at low temperatures for the same reason
that rigid plastic bonds fail at ordinary temperatures;
namely, difference in rates of expansion and contraction
with changes in temperature.

These failures are caused by stresses resulting from differential expansion or contraction. These forces can be reduced by one or more of the following factors.

Effect of Various Factors on Bond Strengths

An analysis of the factors responsible for the production of stress concentrations in a rigid bond must include the following:

(1) The thickness of the materials bonded

(2) The thickness of the adhesive layer

(3) The modulus of elasticity of all components

(4) Changes in dimensions with changes in moisture content for all materials

(5) Changes in temperature to be encountered in service

(6) Coefficients of linear thermal expansion of all materials

Thickness of materials bonded.- It is evident that if the thickness of the materials bonded approaches zero, stresses set up by any other combination of factors must approach zero also. Accordingly, it has been found possible to bond thin metal foils to other materials. A method of eliminating stresses by this means would, however, have very limited practical application. This stress-reducing factor is utilized in the production of mechanical mixtures of materials of microscopic size or in the form of fine filaments, which are incompatible on a larger scale.

Thickness of adhesive.- In bonding two pieces of the same material the stresses set up in the bond as the result of restrained dimensional changes in the bonding material would be proportional to the thickness of the bond. It has long been recognized that thin adhesive layers produce stronger bonds than thicker ones.

Modulus of elasticity.- If the modulus of elasticity of any one of two adjacent materials is zero, the stresses set up between them must be zero. This is essentially

achieved by bonds which yield readily and offer little
resistance to static loads whether produced internally or
externally.

Moisture content.- The problem of bonding materials
having different dimensional stability with changes in
relative humidity can be reduced, if not eliminated, if
the surface of the combination is impervious to moisture.
At the time of bonding or at the end of the bonding op-
eration the material or materials sensitive to changes in
humidity can be made to contain the normal amount of water
present under average conditions. No completely satisfac-
tory solution to this aspect of bonding has been found.

Temperature.- Changes in temperature cannot be elim-
inated in any practical application. For cold-setting
phenol-formaldehyde and urea-formaldehyde cements the ef-
fect of temperature changes is minimized by bonding at
temperatures close to those encountered in service.

Thermal expansion.- From the standpoint of the ther-
mal stresses produced, the problem of bonding two differ-
ent materials becomes identical with the problem of bond-
ing two pieces of the same material provided the coeffi-
cients of thermal expansion of the two materials are the
same. A further reduction in stresses can be achieved if
the bonding agent has the same coefficient of thermal ex-
pansion as the materials bonded. A bond between materials
having different coefficients of expansion would have to
withstand the shear stresses produced by the differential
expansion or contraction experienced within the range of
temperatures encountered. Bonds can sometimes be main-
tained if the materials bonded are thin enough to permit
the relief of stresses by bending or warping, either of
which is undesirable. The bonding strength exhibited by
a particular adhesive is the additional load which, added
to the internal concentrated stresses, is sufficient to
disrupt the material. In some cases this additional load
is zero and the materials are said not to bond.

The logical conclusion to be drawn from the foregoing
discussion is that stable rigid bonds are possible over a
wide range of temperatures if the thermal-expansion coeffi-
cients of the component parts are matched. An example of
the results to be expected is furnished by the combination
of concrete and steel which individually have practically
equal coefficients of thermal expansion and contraction.

It is noted that certain proportions of cement, sand, and stone produce optimum results.

Various methods have been used in other fields to predetermine the thermal-expansion coefficients of mixtures, such as alloys, glasses, etc. Some of these methods appear to work satisfactorily in limited applications. Notable among these are weighted averages based on the thermal-expansion coefficients of the components and their proportions either by weight or by volume. These methods do not, however, give satisfactory results for plastic compositions.

II. DEVELOPMENT OF A FORMULA FOR CALCULATING

COEFFICIENTS OF THERMAL EXPANSION OF MIXTURES

If it is considered that an internal stress system exists in a mixture such that the stresses are nowhere sufficient to disrupt the material, the sum of the internal forces can be equated to zero and an expression for the thermal-expansion coefficient of the mixture is obtained. When small particles or fine filaments are incorporated into a mixture, the small dimensions appear to permit combinations of materials which would be incompatible on a larger scale.

The derivation of the resulting volume thermal coefficient of a mixture follows:

α coefficient of linear thermal expansion

β coefficient of cubical thermal expansion

K bulk modulus = 1/bulk compressibility

d density

P fraction or percent by weight

V volume

ΔT temperature difference

S stress

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Subscripts:

n   property of nth element

r   resulting property

    If it is assumed that each element in the mixture is constrained to change dimensions at the same rate as the aggregate, the stress set-up in the individual particles will be:

$$S_n = (\beta_r - \beta_n) \, \Delta T \, V_n K_n$$

since   S = strain per unit volume X volume X bulk modulus.

But

$$\Sigma(S_1 + S_2 + \ldots S_n) = 0 = (\beta_r - \beta_1) \, \Delta T \, (V_1 K_1)$$

$$+ (\beta_r - \beta_2) \, \Delta T \, (V_2 K_2)$$

$$+ \ldots (\beta_r - \beta_n) \, \Delta T \, (V_n K_n)$$

Since

$$\Sigma(V_1 + V_2 + \ldots V_n) = V_r, \quad V_n = \frac{P_n d_r V_r}{d_n}$$

which can be substituted for V_n in the above expression.

Also, since ΔT, d_r, and V_r are common factors, they can be eliminated from each term of the expression. Solving for β_r the following expression is obtained.

$$\beta_r = \frac{\dfrac{\beta_1 P_1 K_1}{d_1} + \dfrac{\beta_2 P_2 K_2}{d_2} + \ldots \dfrac{\beta_n P_n K_n}{d_n}}{\dfrac{P_1 K_1}{d_1} + \dfrac{P_2 K_2}{d_2} + \ldots \dfrac{P_n K_n}{d_n}}$$

Since the coefficient of linear thermal expansion is directly proportional to the cubical coefficient, α can be substituted wherever β appears with the following result:

$$\alpha_r = \frac{\dfrac{\alpha_1 P_1 K_1}{d_1} + \dfrac{\alpha_2 P_2 K_2}{d_2} + \ldots\ldots \dfrac{\alpha_n P_n K_n}{d_n}}{\dfrac{P_1 K_1}{d_1} + \dfrac{P_2 K_2}{d_2} + \ldots\ldots \dfrac{P_n K_n}{d_n}} \tag{1}$$

It is apparent by inspection that equation (1) based on stress equilibrium reduces to a percentage by volume calculation if the ingredients have the same bulk moduli. If the ingredients have the same modulus to weight ratios, the calculation amounts to a percentage by weight interpolation.

Equation (1) has been verified with experimental values of several metallic mixtures. The thermal coefficients calculated according to equation (1) for several mixtures of lead and antimony and of beryllium* and aluminum are compared with the measured values in figures 1 and 2.

III. APPLICATIONS TO PLASTIC COMPOSITIONS

In studies of the physical properties of reinforced plastics it has been found that the strongest materials were produced by oriented fibers in thermosetting resins.

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*Mixtures of Be and Al apparently form a mixture but no value for the bulk modulus or bulk compressibility was available. From the thermal coefficient, $17.8 \times 10^{-6}/{}^{\circ}C$, of a known mixture containing 32.7 percent Be and 66.3 percent Al, and with reported densities and thermal coefficients of the ingredients, the bulk modulus of Be was calculated from equation (1) to be 15.2×10^6 lb/sq in. Using this value the thermal coefficients of other mixtures of Be and Al were calculated with the results shown in fig. 3 in comparison with the reported values.

The material fabricated in this manner is essentially non-isotropic in all of its properties and has different co-efficients of expansion depending on the direction of the fibers in the test specimen. Materials having isotropic properties can be obtained by random distribution or by planned orientation. Solutions for any property must take into consideration the orientation of the filler as well as the percentage composition.

The derivation of the relationships involved follows the same line of reasoning used for the bulk determination. Consider a bar made of filaments of one or more types of material bound together by a resin binder. If this bar is heated, each of the elements would expand a certain amount if not constrained. Since the combination has its own rate of expansion different from that of any of the elements, a certain force would be required to deform each element to the equilibrium length of the composite material. This force in each case would depend on the cross-sectional area of the material, the distance it is deformed from its normal length, and its modulus of elasticity. The external resultant of the sum of these forces must be zero.

Letting A_n equal the area of the element in a plane normal to the axis of the bar with the other symbols representing the other quantities as in the bulk determination (equation (1)), except that Young's modulus (E) replaces the bulk modulus, it is then possible to write:

$$(\alpha_r - \alpha_1) \, \Delta T \, (E_1 A_1) + (\alpha_r - \alpha_2) \, \Delta T \, (E_2 A_2)$$

$$+ \cdots \cdots (\alpha_r - \alpha_n) \, \Delta T \, (E_n A_n) = 0$$

But

$$A_n = \frac{A_r P_n d_r}{d_n}$$

Therefore the expression for the linear thermal coefficient of the mixture under stress-equilibrium conditions is obtained:

$$\alpha_T = \frac{\dfrac{\alpha_1 P_1 E_1}{d_1} + \dfrac{\alpha_2 P_2 E_2}{d_2} + \ldots \ldots \dfrac{\alpha_n P_n E_n}{d_n}}{\dfrac{P_1 E_1}{d_1} + \dfrac{P_2 E_2}{d_2} + \ldots \ldots \dfrac{P_n E_n}{d_n}} \qquad (2)$$

The use of Young's modulus is necessary for calculating the coefficients of nonisotropic mixtures. The result obtained may be somewhat erroneous because the lateral deformation is neglected.

Application to a Mixture of Polystyrene

and Aluminum Oxide

The applicability of the formula is illustrated by the behavior of brass inserts in a mixture of styrene resin with fused aluminum-oxide powder. Brass inserts in ordinary polystyrene cause the polystyrene to crack because of the different coefficients of thermal expansion. The coefficient of linear thermal expansion of polystyrene is approximately $70 \times 10^{-6}/^{\circ}C$, that of brass is approximately $17 \times 10^{-6}/^{\circ}C$.

Fused aluminum oxide was chosen for use in the mixture because it has a low coefficient of linear thermal expansion ($8.7 \times 10^{-6}/^{\circ}C$) and a high modulus of elasticity compared to its density. Its choice for use with polystyrene was also determined in part by its desirable electrical properties. There was no appreciable change in the excellent electrical resistance of polystyrene when the aluminum-oxide filler was added. The data in table I for the coefficients of linear thermal expansion of mixtures of polystyrene and fused aluminum oxide, calculated according to the stress-equilibrium formula, show that approximately 90 percent of polystyrene and 10 percent of aluminum oxide would be required to match the coefficient of linear thermal expansion of brass. Since the coefficient of the particular brass used was not accurately known, and since it was thought better to err on the low side, 11 percent of aluminum oxide was used.

In figure 3, curve F represents the values of the coefficient of linear thermal expansion of mixtures of polystyrene and fused aluminum oxide calculated on a percentage by volume basis; curve G, on a percentage by weight

basis; and curve H, by the stress-equilibrium formula
(equation (2)). While the thermal coefficient of a mix-
ture of 89 percent of polystyrene and 11 percent of fused
aluminum oxide has not been measured, pieces molded with
brass inserts show a radical difference between the be-
havior of pure polystyrene and the filled material. Anal-
ysis with polarized light indicates that there are stresses
in the pure polystyrene concentrated at the boundaries be-
tween the brass and polystyrene, and these are sufficient
to rupture the polystyrene. With 11 percent of fused
aluminum-oxide filler no such stress concentrations occur
and there is no evidence that the filled styrene has frac-
tured. The brass was sufficiently well bonded to the
polystyrene mixture to permit sawing and machining of the
composite material.

The conventional methods of calculation would yield
for this composition a value of $63 \times 10^{-6}/°C$ for the co-
efficient of linear thermal expansion on a percentage by
weight basis, which would indicate that the material
should behave very nearly the same as the pure poly-
styrene. The behavior of the material, however, indicates
that its coefficient is close to that of brass, which
value was used to predetermine the composition by the use
of the stress-equilibrium formula.

Application to Compositions for Filling

Rivet Depressions

Rivet fillers for aluminum, used to cover depressions
caused by riveting, have been tested by exposure to
Washington weather for 1 year. An enigma developed when
it was found that the composition having the best general
weathering characteristics did not stand up the best in
this application. The calculated values for coefficients
of linear thermal expansion of the various compositions
are as follows:

Material	Calculated coefficient
(1) Cellulose nitrate + 25 percent aluminum pigment	$44.2 \times 10^{-6}/°C$
(2) Cellulose acetate butyrate + 25 percent aluminum pigment	$45.2 \times 10^{-6}/°C$
(3) Vinylite A + 30 percent aluminum pigment	$30.6 \times 10^{-6}/°C$

Since the coefficient of linear thermal expansion of aluminum is $24 \times 10^{-6}/^{\circ}C$, the results are easily explained on the basis that composition (3), which happened to come closest to the coefficient of aluminum, gave the best bond.

Inasmuch as the lowest coefficient obtainable with aluminum pigment is $24 \times 10^{-6}/^{\circ}C$ for 100-percent pigment, it becomes necessary to add another ingredient with a coefficient below aluminum to the plastic in order to obtain matched thermal coefficients. The following proportions were calculated for cellulose-plastic compositions to reasonably match aluminum:

Cellulose nitrate or cellulose acetate butyrate	66 percent
Aluminum pigment	20 percent
Fused aluminum oxide	14 percent

Similarly, the following proportions were calculated for a vinyl-acetate resin composition to match its coefficient of linear thermal expansion with that of aluminum:

Vinylite A resin	74.6 percent
Aluminum pigment	20.0 percent
Fused aluminum oxide	5.4 percent

Application to Mixtures of Phenol-Formaldehyde

Resin and Glass Fibers

Approximate values for the properties of glass and phenol-formaldehyde resin required for use in the stress-equilibrium formula are as follows:

Young's modulus of elasticity

For glass	11×10^{6} lb/sq in.
For phenolic resin	1×10^{6} lb/sq in.

Coefficient of linear thermal expansion

For glass	$7.44 \times 10^{-6}/^{\circ}C$
For phenolic resin	$59 \times 10^{-6}/^{\circ}C$

Density (g/cc)

For glass	2.56
For phenolic resin	1.30

In order to simplify the calculation of the coefficients
of linear thermal expansion of mixtures of these materials,
equation (2) can be written in a form consolidating the
physical constants:

$$\alpha_r = \frac{a_1 P_1 + a_2 P_2 \cdots\cdots + a_n P_n}{b_1 P_1 + b_2 P_2 \cdots\cdots + b_n P_n} \qquad (3)$$

where a and b are constants for specific materials for
a specific temperature range. The approximate values for
these constants for the phenol-formaldehyde resin and
glass calculated from the physical constants listed above
are:

	Glass	Phenol-formaldehyde resin
a	29.1	45.4
b × 10⁶	3.91	.77

   In figure 4, curve I represents a percentage by
weight interpolation for the glass-resin mixtures; curve
J is calculated by the stress-equilibrium formula. Meas-
ured values of the coefficients of linear thermal expan-
sion of two compositions shown in table II are plotted
according to the percentage of the resin in the mixture.
These samples contained approximately 4 percent of starch
which was neglected in calculating curve J. The theoret-
ical coefficients for the compositions containing starch
were not calculated because the required physical con-
stants are not known. The experimental points fall much
closer to the curve J calculated by the formula than to
curve I. The curve on a percentage by weight basis would
be similar to curve F in figure 3 and would be still fur-
ther from predicting the actual result.

   The addition of metal faces to reinforced plastics
may be desired in order to take advantage of the high-mod-
ulus properties of metals, as in an I beam, or to obtain
a facing impermeable to moisture. To do this effectively
it would be necessary to have matched thermal-expansion
coefficients in order to insure satisfactory bonds. To
calculate the mixture of glass fiber and phenolic resin
required to match aluminum alloy 24S, whose coefficient

of linear thermal expansion is $23 \times 10^{-6}/°C$, let α_r in equation (3) equal this latter value and solve for the percentage of glass; thus

$$23 \times 10^{-6} = \frac{29.1P_g + 45.4\ (100-P_g)}{3.91P_g + 0.77\ (100-P_g)} \times 10^{-6}$$

The required percentage of glass is found to be 31.3.

The indicated glass content is seen to be a little higher than was present in the panels prepared with glass-fiber mat, phenolic resin, and starch, whose thermal-expansion coefficients are reported in table IV. These panels were fabricated between aluminum-alloy-24S faces. It was found possible to remove the metal face without seriously damaging it or the core material. The metal faces could not be removed from several other panels, having compositions closer to that calculated, without tearing the metal, shearing the metal at the bond, or rupturing the core.

The starch was added to these compositions in order to absorb the water present in the ingredients or released by the resin during curing. It has been found difficult or impossible to produce plastic compositions with phenolic-thermosetting resins at low pressures unless some water-absorbent material is present. Some of these glass-fiber panels were bonded at pressures as low as 50 pounds per square inch.

IV. DETERMINATION OF COEFFICIENTS OF
THERMAL EXPANSION OF PLASTICS

In the early stages of the investigation an estimate of the coefficient of thermal expansion of the resin-bonded materials was obtained by the following method. Composite strips of one layer of metal and one of a fibrous material impregnated with the resin in varying proportions was pressed flat and cured at $150°$ C. The strips were then permitted to cool to room temperature. If the composite strip remained straight when cooled, it

was considered that the thermal expansion of the plastic
composition matched the metal. As the investigation pro-
ceeded, quantitative data for the coefficients of linear
expansion of the resins were required.

The equipment used for this purpose consisted of two
telescoping fused-quartz tubes, the inner tube being
shorter than the outer and resting on the specimen. The
expansion was measured by a dial gage, graduated to 0.0001
inch, and fastened to the outer quartz tube with the meas-
uring foot resting on the inner quartz tube which in turn
rested on the specimen. The temperature of the specimen
was varied by immersing the quartz tubes containing the
specimen in a water or an oil bath, heated with a hot
plate, so that the rate of temperature rise of the bath
was approximately 1° C per minute. The temperature of the
specimen was measured by means of a potentiometer con-
nected with a copper-constantan thermocouple, which was
attached to the center of the specimen. Simultaneous
measurements of temperature and extension were obtained by
setting the potentiometer at predetermined points and re-
cording the extension when no deflection was produced by
opening or closing the circuit. The coefficient of linear
expansion of the specimen was calculated from the tempera-
ture-extension curves. The results thus obtained were cor-
rected for the expansion of the fused-quartz tubes by
adding the coefficient of linear thermal expansion of
fused quartz, $0.5 \times 10^{-6}/^\circ$C. While this relatively rapid
method does not insure a uniform temperature throughout
the specimen, it presents a better picture of the changes
taking place in the specimen which might be masked by
changes in water content and by plastic flow at elevated
temperatures, both of which would appreciably affect the
results if the time of heating the specimen was prolonged.
The stress on the specimen applied by the inner quartz
tube and the micrometer foot did not exceed 10 pounds per
square inch.

The specimen used for thermal-coefficient measure-
ments was a bar $6\frac{1}{2}$ to $7\frac{1}{2}$ inches long and about 1/2 inch
wide. The thickness was that of the sheet from which the
specimen was cut. Specimens for determination of the
properties of both pure phenolic resin (Durez 120) and
compositions of this resin containing filler were molded
in the laboratory at 150° C and 1000-pounds-per-square-
inch pressure. The length of the specimen was measured
at room temperature to the nearest 0.01 inch with a steel
scale. The specimens were rounded on the ends in order

to obtain definite contact between the specimen and the apparatus over a small area. The position of the speci- men with respect to the quartz tubes was maintained by washers near the ends of the specimen which came in con- tact with the sides of the tubes but offered no appreci- iable resistance to vertical motion of the specimen.

Measurements of the coefficient of linear expansion of an alloy using the method described above are compared in table III with precision measurements on a duplicate sample. The results are not strictly comparable since the coefficient of linear expansion of the sample changes slightly with the heat treatment occurring during measure- ment. Because the time required to make the measurements differs in the two methods, the amount of annealing that has occurred between measurements is different. The re- sults, however, are essentially the same and indicate that the method employed for the experimental work de- scribed in this paper is quite reliable.

Factors Affecting Thermal-Coefficient

Measurements of Plastics

Before considering the actual measurements, some of the factors peculiarly affecting the thermal expansion and related properties of plastics should be discussed. Organic plastic compositions, or water-absorbent mate- rials, in general, in addition to the basic constituents, contain a certain amount of water which apparently acts the same as an additional solid in the composition. A great deal of the variation in the reported values for the linear thermal expansion of wood is undoubtedly re- lated to differences in the water content of the wood at the time of testing. In order to minimize such effects all specimens tested in this investigation were initially conditioned at 25° C and 50-percent relative humidity, which is representative of normal conditions.

The modulus of plastics varies considerably with change in temperature, particularly near the softening point. The range of temperature to which the reported values apply was chosen in each case to avoid large changes in water content and to avoid softening points. Each of these effects is indicated by breaks in tempera- ture-extension and extension-time curves. Near the softening point of pure plastics the molding strains are

relieved and dimensional changes occur which depend on the method of manufacture. These changes correspond to the dimensional changes encountered on aging. Reinforced or laminated materials also show changes in dimensions involving the relief of the thermal stresses set up by the differential coefficients of expansion of the resin and reinforcing medium. Prolonged heating at elevated temperatures causes shrinkage by the removal of water from the mixture. The relief of molding stresses seems to be permanent, the removal of water reversible.

Results of Thermal-Expansion

Measurements for Plastics

Representative measurements of thermal-expansion coefficients of plastic materials for various temperature ranges are presented in table IV. A typical thermal-expansion curve for pure molded phenolic resin is shown in figure 5.

Micronex or carbon black is frequently added to plastic compositions as a filler. It is therefore interesting to note that the addition of 10 percent of this material to phenol-formaldehyde resin reduced the thermal coefficient of the mixture approximately 20 percent. (See table IV.) From published values for the density and thermal-expansion coefficient of carbon black together with the measured properties of the pure phenolic resin, the bulk modulus of carbon black was calculated to be approximately 3×10^6 pounds per square inch.

Lignin resin is used in a number of applications in conjunction with phenolic resins. Here it is treated as a filler. Two effects are to be noted; first, that the product does not become stable until it has been heated a considerable length of time beyond the time required to cure the phenolic resin; and second, that the lignin initially increases the coefficient of the mixture but after heating finally decreases it by a small amount.

The effect of the walnut-shell flour is similar to that of the lignin resin. The manufacturers of this material state that it contains a large proportion of lignin. One of the uses of this material is as an extender for plywood adhesives.

The behavior of filled phenol-formaldehyde resin containing 25 percent of glass fiber, 71 percent of phenolic resin, and 4 percent of starch, is illustrated by the curves for mixtures of glass fibers and phenolic resin shown in figure 6. Curves L and O are for pure phenol-formaldehyde resin and glass fibers, respectively. Curve N was obtained on the first heating cycle. The form of the curve above 70° C is affected by plastic flow, relief of molding strains, and further curing of the resin. The weight of the inner fused-quartz tube and the pressure of the micrometer foot contribute some of the force producing plastic flow. The shrinkage indicated at 100° C on curve N took place over a period of 5 hours, during which time the temperature was maintained constant. The rate of shrinkage was initially rapid but reached a steady value after about 4 hours. After cooling the sample slowly and then reheating to 100° C the same steady rate of shrinkage was resumed for 4 additional hours, after which the specimen was slowly cooled to room temperature. The total shrinkage amounted to 0.5 percent. Curve M of figure 6 is the thermal-expansion curve for this annealed specimen.

The transparent materials for which data are given in table IV have been used or proposed for use as airplane windshields. The temperature-deflection curves in each case varied from a smooth curve on the first heating cycle between 50° and 100° C. The curve for the Columbia Resin 39 sample (fig. 7, curve P) showed a decrease in expansion in this range followed by a resumption of the upward trend. No such break occurred in the cooling curve (fig. 7, curve Q) or in the curve obtained when the sample was heated a second time (fig. 7, curve R), although the temperature was raised above 110° C. The sample was permanently shortened during the first heating to the extent of 0.5 percent. The specimen at the same time increased in thickness. The curve for methyl-methacrylate resin (fig. 8, curve S) for the range 50° to 100° C showed an increase in expansion followed by a decrease. Again the break did not occur in the cooling curve (fig. 8, curve T). The changes were too small to be measured significantly with a steel scale so a check was run on smaller specimens which were heated in an over at 80° C for 18 hours. The indicated change was verified by an increase in dimensions in the plane of the sheet and a decrease in thickness. This is in agreement with observed dimensional changes on aging. Methyl-methacrylate resin

is one of the best available materials from the standpoint of freedom from crazing, unless subjected to strain, and dimensional stability. The surfaces of both materials appeared to be unaffected by the treatment.

The Pregwood samples listed in table IV were submitted by the Formica Insulation Company and were cut from the same sheets as the test specimens reported upon in NACA Advance Restricted Report of July 1941, entitled "Properties of Reinforced Plastics and Plastic Plywoods." The modulus data reported at that time for parallel-ply material may be used with the measured thermal coefficients to calculate the thermal coefficients of the cross-ply material. The modulus of the cross-ply material may also be calculated as a composite column using the data for the parallel-ply materials. It is assumed, perhaps erroneously, that the "high" and "low" resin designations indicate definite resin contents. The calculated and observed values for the several properties are shown in table V.

CONCLUSIONS

The implications of the concept and methods of analysis touched briefly in the preceding pages are too numerous to be adequately treated in so short a space. Special applications have been mentioned throughout the paper. Some general conclusions are presented in the following paragraphs.

Stable bonds are possible between large sections if the thermal coefficients of the component parts are matched. The bond under such conditions is not affected by extreme temperature changes.

The method of computing the thermal coefficients of mixtures is applicable to mixtures in general and particularly applicable to problems in reinforced plastics.

Since the magnitude of the stresses distributed throughout the mixture are proportional to the size of the elements, the ultimate strength of the material and its fatigue limits should be raised by reducing particle size. Specifically, the strength of plywood should be increased by the use of thin veneers. At the temperature of fabrication the effect of particle size should reach a minimum.

It is possible to formulate pigmented protective coatings which will have improved adhesion to the coated materials by the use of the thermal-coefficient formula. The thermal-coefficient method described in this paper offers a rapid and reliable means of obtaining the basic physical data needed for use in the calculations. With such information the proper combination of materials can be calculated to yield a film matching the base material with respect to coefficient of thermal expansion.

National Bureau of Standards,
    Washington, D. C.

TABLE I

CALCULATED COEFFICIENTS OF LINEAR THERMAL EXPANSION OF

MIXTURES OF POLYSTYRENE AND FUSED ALUMINUM OXIDE

Composition of mixture		Calculated coefficient of linear thermal expansion	
Fused aluminum oxide (Al_2O_3) (percent)	Polystyrene (percent)	By stress equilibrium formula (equation (2)) ($\times 10^{-6}/°C$)	By rule of mixtures on percentage by volume basis ($\times 10^{-6}/°C$)
100	0	8.7	8.7
75	25	9.0	41.7
50	50	9.6	56.3
25	75	11.7	64.7
20	80	12.5	65.9
9.7	90.3	17	68.2
5	95	23.2	69.1
0	100	70	70

TABLE II

COEFFICIENTS OF LINEAR THERMAL EXPANSION OF MIXTURES

OF GLASS FIBERS, PHENOLIC RESIN, AND STARCH

Composition of mixture			Coefficient of linear thermal expansion	
Glass fiber (percent)	Phenol-formaldehyde resin (Bakelite XC-11749) (percent)	Starch (percent)	Calculated by stress equilibrium formula (equation (2)) ($\times 10^{-6}/°C$)	Measured ($\times 10^{-6}/°C$)
100	0	---------	7.44	---------
50	50	---------	14.2	---------
25.2	70.8	4	---------------	26.0
25	75	---------	23.6	---------
22.2	73.8	4	---------------	29.9
10	90	---------	37.4	---------
0	100	---------	60	---------

TABLE III

COMPARISON OF PRECISION METHOD AND RAPID METHOD OF
MEASURING COEFFICIENTS OF LINEAR THERMAL EXPANSION

Temperature range (°C)	Average coefficients of linear thermal expansion			
	Precision method[a]		Rapid method	
	First test ($\times 10^{-6}$/°C)	Repeat test ($\times 10^{-6}$/°C)	First test ($\times 10^{-6}$/°C)	Repeat test ($\times 10^{-6}$/°C)
20 to 60	17.7	17.8	17.5	17.2
60 to 100	18.6	18.3	17.9	18.7
100 to 150	18.3	18.5	18.4	19.0
150 to 200	-----------	18.7	19.0	19.3
20 to 100	18.1	18.0	17.7	17.9
20 to 150	18.2	18.2	18.0	18.3
20 to 200	-----------	18.4	18.3	18.6

[a]Data supplied by Division II-6. The cooperation of P. Hidnert in supplying this information and other data represented graphically in figs. 1 and 2 is gratefully acknowledged.

TABLE IV

MEASURED COEFFICIENTS OF LINEAR THERMAL

EXPANSION FOR VARIOUS PLASTICS

Material[a]	Range (°C)	Linear thermal expansion coefficient ($\times 10^{-6}/°C$)
Pure phenolic resin (Durez No. 120) . .	20-100	58.5 - 58.9
	20- 50	49.7
	20- 30	50.2
Durez No. 120, 10% Micronex carbon . .	20-100	45.7 - 47.4
	20-100	44.9
Durez No. 120, 41% reagent-quality aluminum oxide	20- 50	34.7
Durez No. 120, 10% lignin resin (First heating)	20- 53	47.9
	53-100	78.8
	20-100	62.8
Durez No. 120, 10% lignin resin (Second heating)	20-100	54.7
Durez No. 120, 10% lignin resin (Third heating)	20-100	54.1
	20- 53	47.2
	53-100	59.9
Durez No. 120, 10% walnut-shell-flour filler (First heating)	20- 49	43.8
	49-100	68.0
	20-100	59.2
Durez No. 120, 10% walnut-shell-flour filler (Second heating)	20- 49	45.7
	49-100	58.8
	20-100	54.1
Glass Mat 25%, Bakelite XC-11749 phenolic resin 71%, starch 4%		
(First heating)	20- 65	29.9
(Third heating)	20- 65	29.3
Glass Mat 28%, Bakelite XC-11749 68%, starch 4%	20- 70	26.0
Glass Cloth 44%, Durez No. 120 39%, starch 17%	20- 70	17.8
Columbia resin No. 39		
(First heating)	10- 50	103.3
(Second heating)	20- 50	105.8
Do.----do.----	20-100	124.7
Methyl-methacrylate resin	20- 50	71.5

TABLE IV (Continued)

Material[a]	Range (°C)	Linear thermal expansion coefficient ($\times 10^{-6}$/°C)
Pregwood P-5, parallel-ply maple,[b] low resin content		
Parallel to grain	20- 50	4.7
Perpendicular to grain	20- 50	63.5
Pregwood P-1, parallel-ply maple, high resin content		
Parallel to grain	20- 50	5.9
Perpendicular to grain	20- 50	68.7
Pregwood P-7, 7-ply maple, plies alternately crossed, low resin content		
Four-ply direction	20- 50	13.5
Three-ply direction	20- 50	19.8
Pregwood P-3, 7-ply maple, plies alternately crossed, high resin content		
Four-ply direction . . . . ; .	20- 50	16.7
Three-ply direction	20- 50	21.0
8-ply 0.01-inch-thick birch, symmetrical cross-ply construction, 39.5%		
Amberlite PR-14	20- 30	15.4

[a]Percentage figures are based on the weight of the total composition.

[b]These Pregwood materials (P-1 to P-8, inclusive) were erroneously reported to have been prepared with birch veneers in the NACA advance restricted report of July 1941, entitled "Properties of Reinforced Plastics and Plastic Plywoods."

TABLE V

MEASURED AND CALCULATED VALUES FOR COEFFICIENTS OF LINEAR THERMAL EXPANSION

AND MODULUS OF ELASTICITY OF PREGWOODS

Material	Measured values[a]		Calculated values	
	Modulus of elasticity in tension $(10^6$ lb/sq in.)	Coefficient of linear thermal expansion for the range $20°$ to $50°$ C $(10^{-6}/°C)$	Modulus of elasticity in tension $(10^6$ lb/sq in.)	Coefficient of linear thermal expansion for the range $20°$ to $50°$ C $(10^{-6}/°C)$
I. HIGH RESIN CONTENT				
Parallel-Ply Material (P-1)				
Parallel to grain	3.70	5.9	------------	----------------
Perpendicular to grain	.84	68.7	------------	----------------
Cross-Ply Material, 7 Ply (P-3)				
Parallel to 3-ply direction	2.04	21.0	2.07	20.5
Do.------ 4-ply----do.---	2.29	16.7	2.47	15.0
II. LOW RESIN CONTENT				
Parallel-Ply Material (P-5)				
Parallel to grain	3.97	4.7	------------	----------------
Perpendicular to grain	.68	63.5	------------	----------------
Cross-Ply Material, 7 Ply (P-7)				
Parallel to 3-ply direction	2.17	19.8	2.09	15.6
Do.------ 4-ply----do.---	2.52	13.5	2.56	11.4

[a]The values given for the coefficient of linear thermal expansion are those obtained on the first heating cycle.
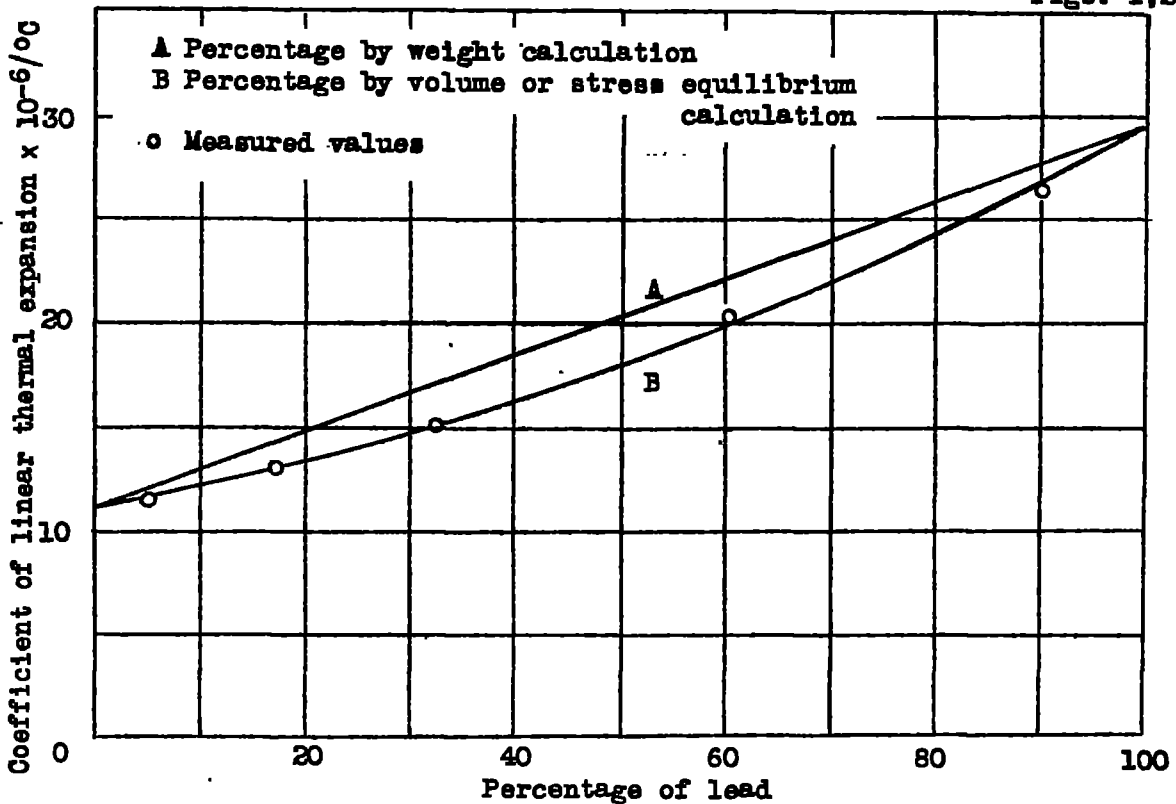
A Percentage by weight calculation
B Percentage by volume or stress equilibrium
                                        calculation
·o Measured values

Coefficient of linear thermal expansion x 10^{-6}/°C

Percentage of lead

Figure 1.- Thermal expansion coefficients of lead-antimony mixtures.

C Percentage by weight calculation
D Percentage by volume calculation
E Stress equilibrium calculation
o   Measured values

Coefficient of linear thermal expansion x 10^{-6}/°C

Percentage of beryllium
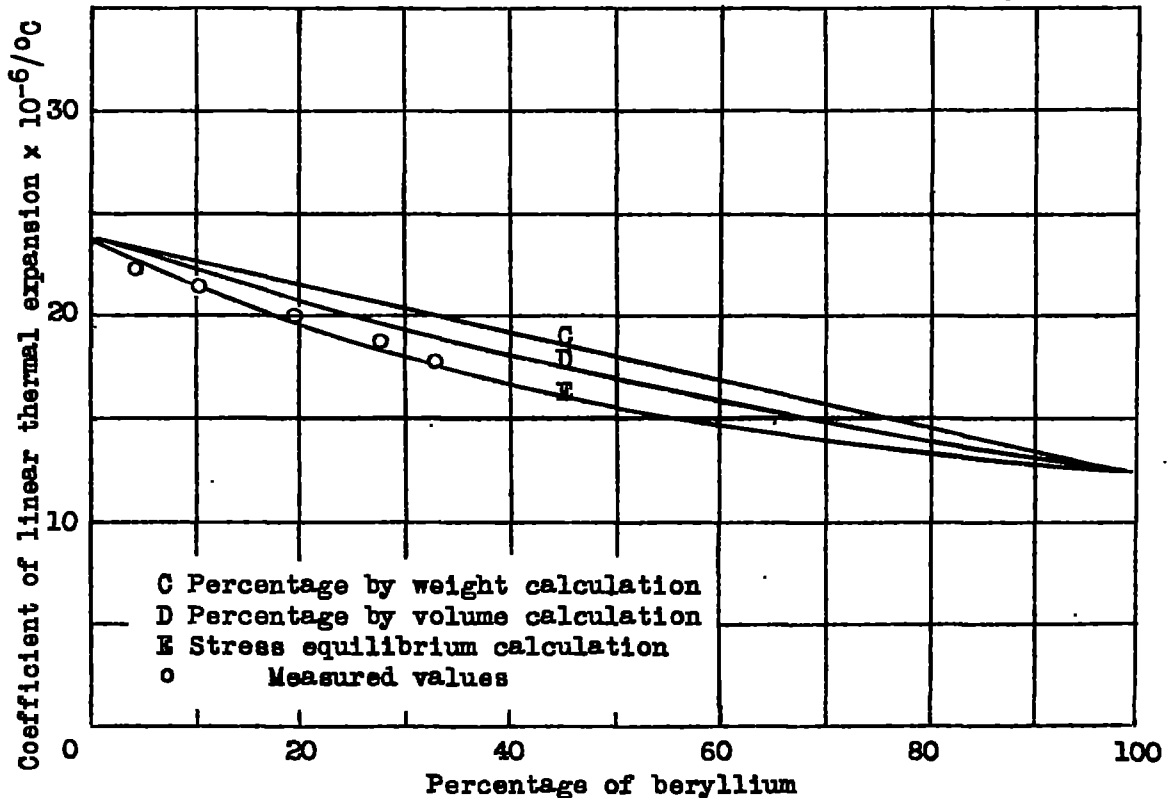
Figure 2.- Thermal expansion coefficients of beryllium-aluminum alloys.
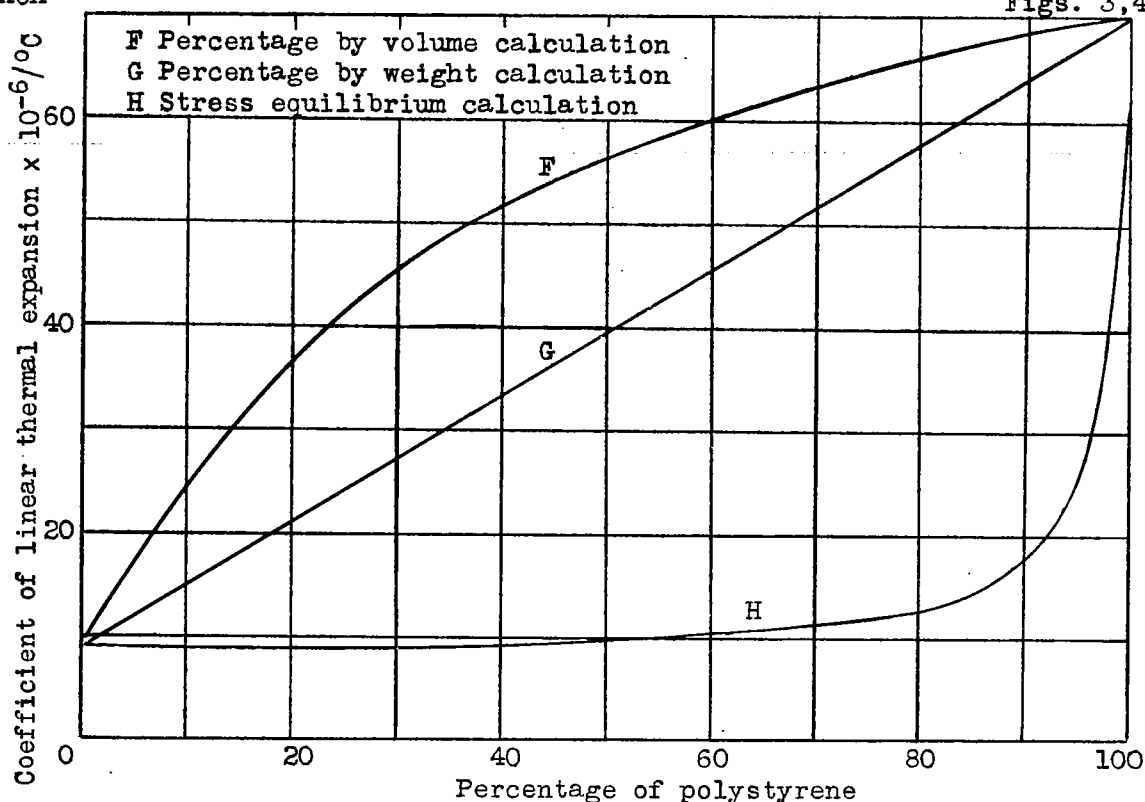
Figure 3.- Thermal expansion coefficients of polystyrene and fused aluminum oxide mixtures.
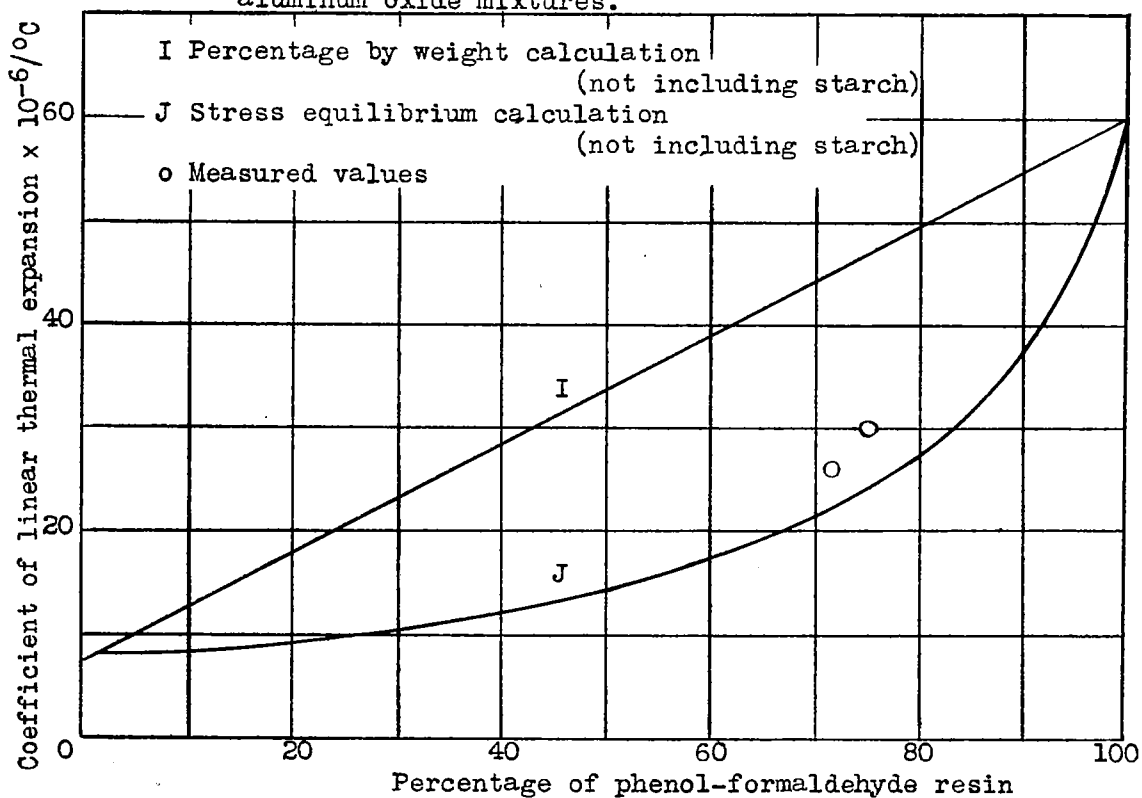
Figure 4.- Thermal expansion coefficients of phenol-formaldehyde resin and glass fiber mixtures containing approximately 4 percent of starch.
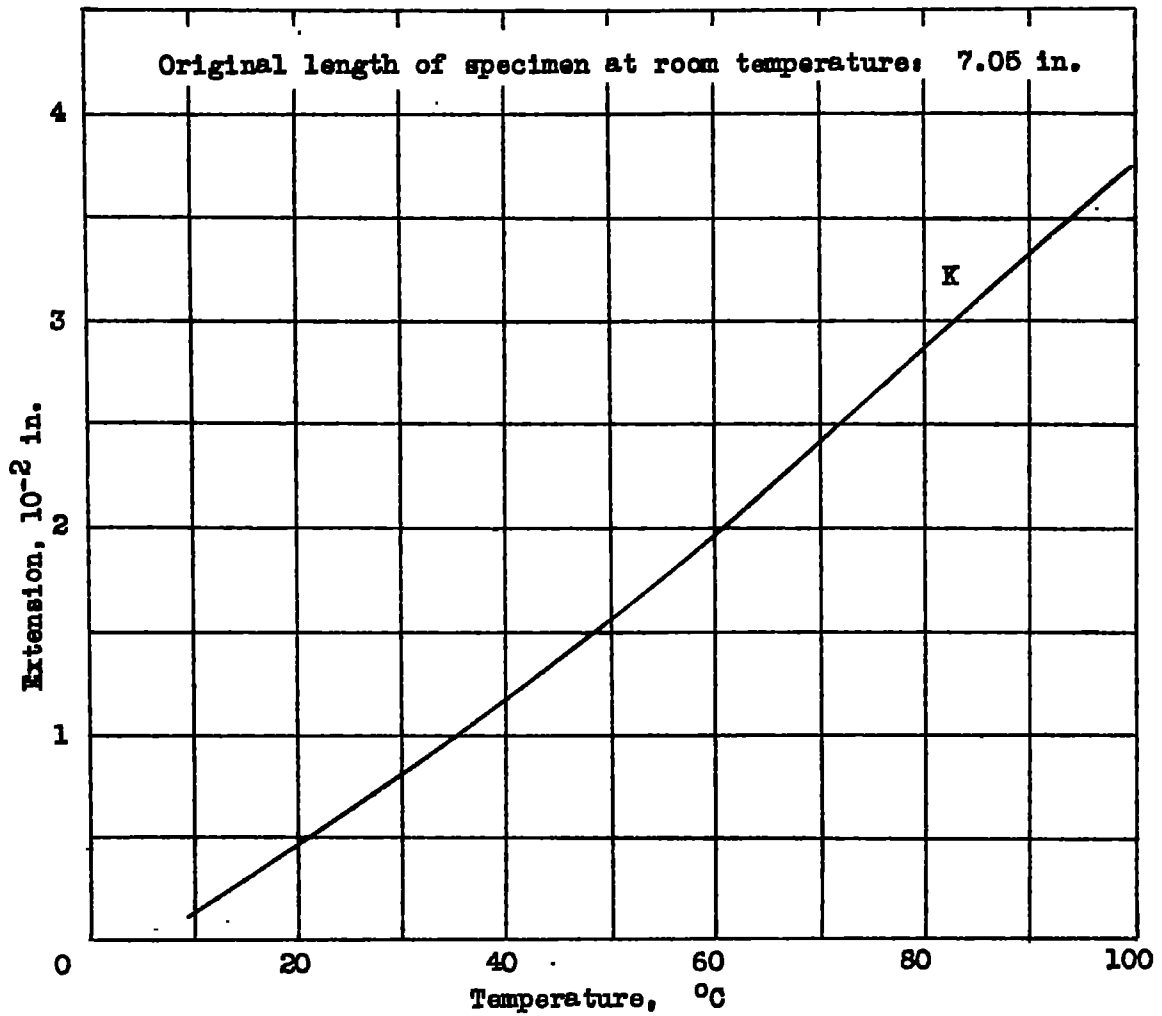
Original length of specimen at room temperature: 7.05 in.

Figure 5.- Thermal expansion curve for pure molded phenolic resin
           (Durez 120).
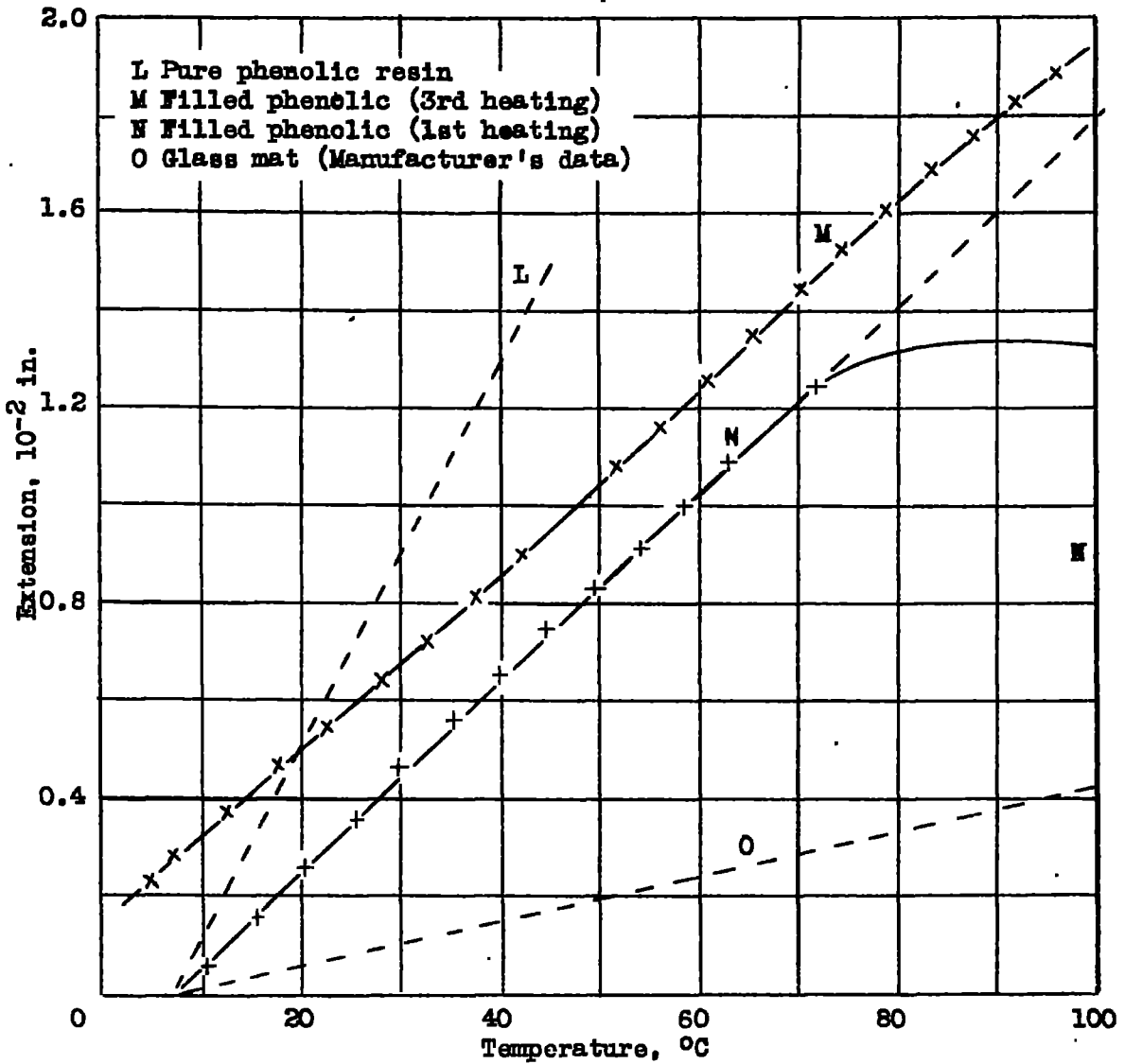
Figure 6.— Thermal expansion curves for phenolic resin and glass fiber
mixtures.

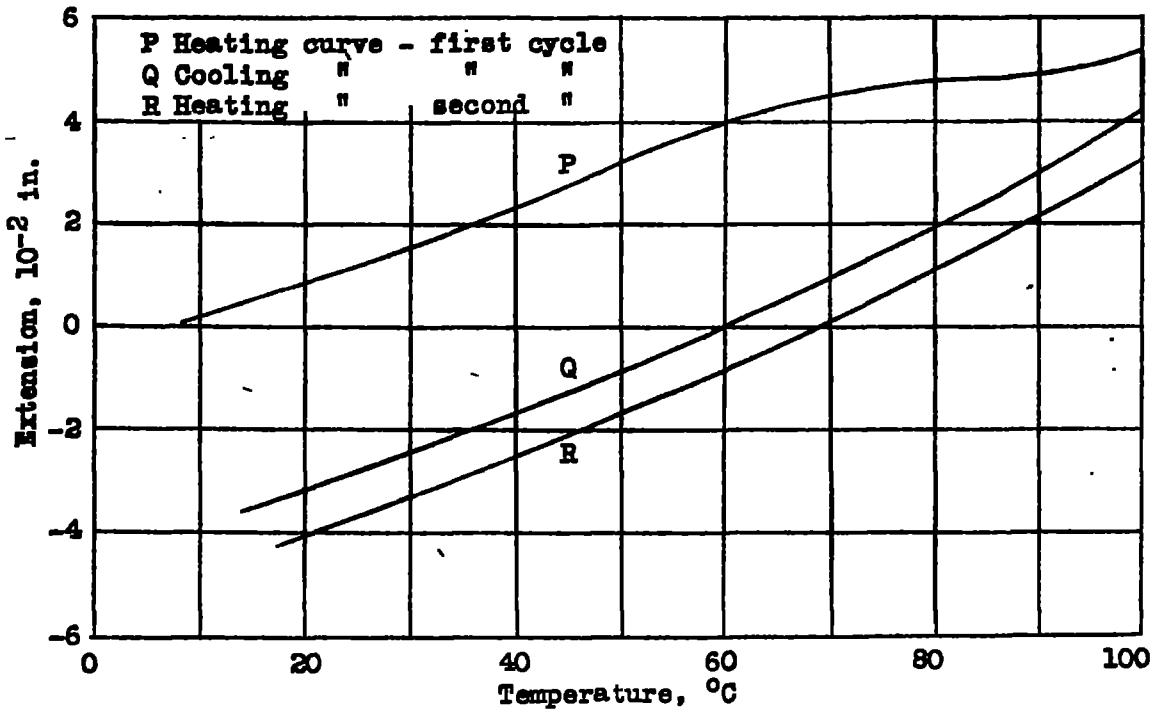Original length at 25° C: 6.57 in.
Final length at 25° C: 6.54 in.

Figure 7.- Thermal expansion curves for Columbia Resin No. 39.
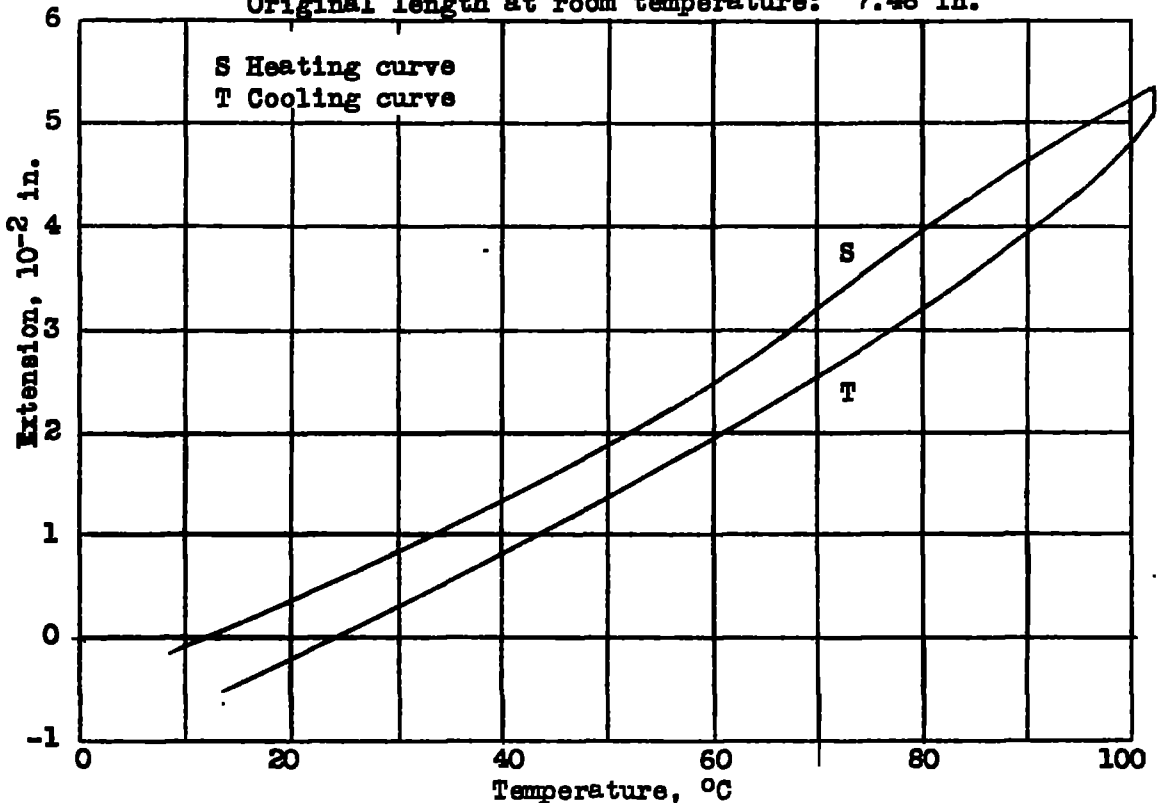Original length at room temperature: 7.48 in.

Figure 8.- Thermal expansion curves for cast methyl methacrylate resin.
Original length at 25° C: 7.04 in.