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# Thermal Expansion of Photomechanical Materials*

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## Synopsis

A quartz thermal expansion apparatus was developed to measure the thermal expansion of photomechanical plastics. Three different methods of motion measurement correlated with a maximum error of ±1% for three different models of Hysol 4290 epoxy. The thermal expansion of a 30% plasticized epoxy was determined and was found to exhibit essentially the same characteristics as the 4290 epoxy except for a shift in the temperature scale.

## INTRODUCTION

Preliminary studies indicate significant changes in expansion between the glassy and rubbery states of a viscoelastic material. Consequently it is necessary to obtain careful measurements of expansion over a large range of temperatures to a relatively high degree of accuracy to obtain reliable expansion data for these materials. This phase of a general exploratory program in photomechanics was devoted to the development and application of apparatus to perform that function.

This report contains a description of the development of the thermal expansion measuring equipment and includes data for both elastic and viscoelastic materials. As preliminary background, a brief review is presented of thermal expansion apparatus employed by other investigators.

## BRIEF REVIEW OF THERMAL EXPANSION APPARATUS

This review of thermal expansion measurement methods is based upon the report by Hidnert and Souder.[1]

In the precision micrometric method a specimen is supported horizontally in a furnace by wires. Two traveling microscopes are used to measure the separation between the wires as the model changes length. This method is not adaptable to low modulus materials such as plastics because of the problem of model sag due to its own weight.

The interference method described is for small length specimens and crystals. The specimen is set between two flat ($^1/_5$ wavelength) quartz plates oriented at 20 minutes of arc with each other. Normal illumination

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by monochromatic light produces interference fringes. As the specimen expands the fringes move past a fiducial point on the quartz plate. The number of fringes times the wavelength is equal to the expansion of the model plus an atmosphere correction. When done in a vacuum this method yields results to 1% at 300°C. and less at higher temperatures. This method may be satisfactory for plastics. However it necessitates a vacuum oven and a very small specimen since the expansion coefficients for plastics are so high. The small specimen size could lead to high percentage errors along with the requirement of acute operator vigilance.

The fused quartz tube dial indicator method is similar to the apparatus described in this report. The difference is that the quartz tube encloses the specimen in the National Bureau of Standards method whereas the specimen is left exposed for better heat transfer in the method used in this report. The accuracy reported by the N.B.S. is 2%.

The autographic optical lever method involves the expansion of a known material to rotate a mirror about a vertical axis for the temperature scale. It uses the unknown material to rotate the mirror about a horizontal axis to obtain the length change scale. A beam of light is reflected from the mirror onto a piece of film to give the "temperature" versus expansion plot. This method is accurate to 6% in the range of 20–100°C., and 3% from 20 to 500°C. It is not applicable to materials that soften upon heating as most plastics do.

The liquid-micrometer method requires that the specimen exert a force to move a diaphragm which changes a liquid level. The specimen is also under pressure. Therefore, mechanical deformations are possible ruling out its use for plastics. It is reported that, with a 2-in. sample, it is possible to record changes of the order of $10^{-6}$ in., although neither the sensitivity nor the accuracy is normally as high as this.

The induction furnace and dial indicator method of measuring thermal expansion is similar in principle to that explained in this report except that the motion transfer bar uses different materials along its length and the support legs for the dial indicator are of quartz. Therefore calibration is necessary and is accurate only when the tests are run starting with the equipment at room temperature in every case. The dial indicator has its disadvantages which are to be discussed later in the report.

The capacitance method uses the expansion of the specimen to move the plates of a small capacitor which changes the plate current of a vacuum tube. This is an infinite resolution device and can be used in an autographic recording system. A well isolated oscillator circuit is required for this method.

The x-ray method of measuring thermal expansion is used to obtain coefficients for crystals. The coefficient of expansion can be obtained using very small samples. This method may not be suitable for plastics unless the effect of the radiation on specimen properties is known.

## EQUIPMENT DEVELOPMENT

The development of the apparatus to be described in subsequent sections involved division of the general problem into specific problem areas, each of which was investigated separately, and then was reinvestigated as a component of the completed apparatus. It was necessary to design a model which would permit accurate, continuous recording of temperature and elongation. A method was required for transmitting the model motion from inside the oven to sensing equipment mounted outside the oven. Finally it was necessary to record the data during each run.

Details of the approaches used to solve these problems appear in the following paragraphs of this section.

### Specimen Design

The load applied by the measuring apparatus, the measurement method, the specimen thermal inertia, and the desired gage length dictate the specimen design.

The load applied by the measuring equipment must induce a low stress level. Since plastics at elevated temperatures exhibit low moduli or are viscoelastic, this requires either a specimen with a large cross-sectional area, or a light load on a small cross-section area specimen.

The thermal inertia of the model must be small, or the heating rate must be slow, to avoid transients in the model which could lead to thermal stresses and erroneous strain information.

In preliminary tests models were cut from plate stock. They were rectangular in cross section (1 in. by 1/2 in.) with a 5/16 in. diameter hole down the length in the center of the section to accommodate the measuring rod. Preliminary tests indicated the necessity for a slow heat input rate and thermal stability at each data point for thick-walled models. This led to long test times and required constant vigilance by the operator.

Various approaches were utilized to circumvent these problems. The final model was a thin walled cylinder with forced air circulation. This was further improved by perforating the thin cylinder. The new design minimized thermal transients and, as a result, radial gradients. It also allowed a relatively fast heating rate thereby permitting continuous recording of model expansion since it was not necessary to stabilize the temperature at each data point. Figure 1 shows the details of the specimen finally selected for expansion studies of photoviscoelastic plastics.

### Motion Transfer

The measurement of the specimen expansion involved transferring the expansion motion out of the temperature chamber to equipment mounted on top of the oven.

For maximum efficiency in using this procedure, fused quartz was chosen as the material for the transfer rods. The coefficient of expansion for the fused quartz is $0.5 \times 10^{-6}$ in./in./°F.[2] while the coefficients for

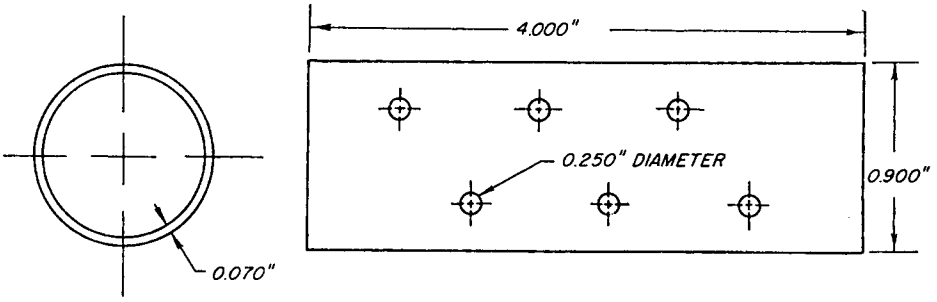


Fig. 1. Specimen dimensions. Five thermocouples, two on inside surface, two on outside surface, one imbedded within the model. Air circulation holes arranged to prevent large cross-sectional area decrease and buckling.

plastics range from about $30 \times 10^{-6}$ to over $100 \times 10^{-6}$ in./in./°F. Consequently there is approximately a 1.6% correction involved at the most.

The configuration that was used consists of a quartz rod within a quartz tube (Fig. 2). A 1-in. diameter slotted quartz plate is attached perpendicular to the rod at the model end. The tube has a similar plate welded to it which is drilled out to permit the quartz rod to pass through. The specimen is held between these two plates with the rod passing through the specimen and tube.

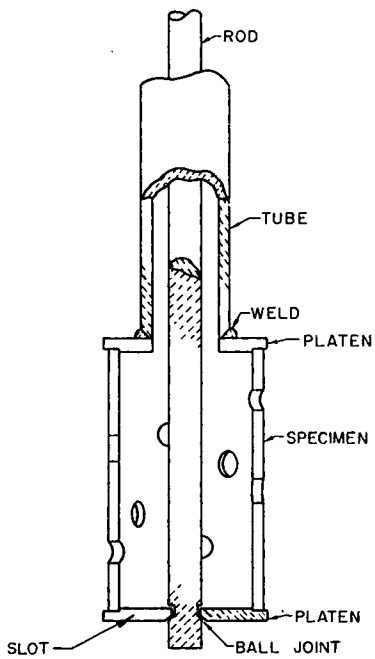


Fig. 2. Specimen in place in extensometer. All components fused quartz except specimen.

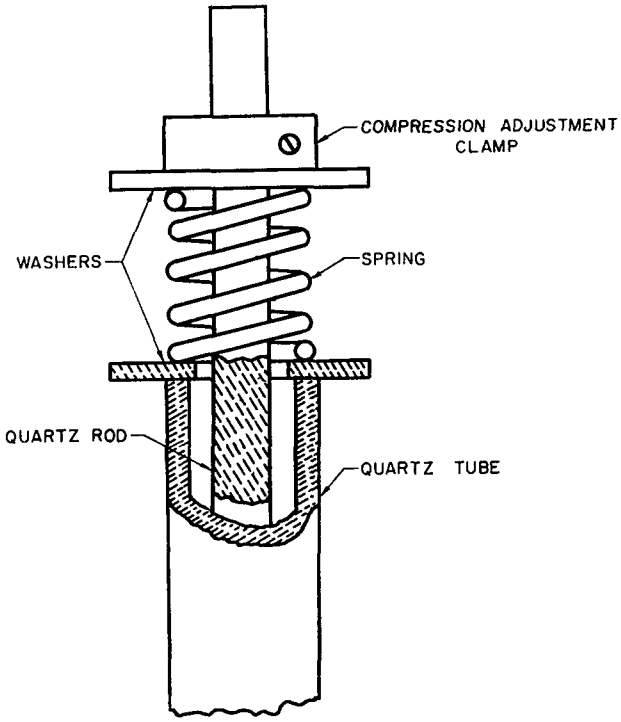


Fig. 3. Detail of spring region.

Assembly of the system is completed by clamping the tube to a quartz plate outside the temperature chamber with the axis of the tube vertical. To prevent the quartz rod from falling, a spring is attached to the rod and bears on the tube. This permits light load contact with the model for positive motion pickup. It can be seen schematically in Figure 3. A photograph of the assembly appears in Figure 4.

A check was made to determine whether temperature gradients existed

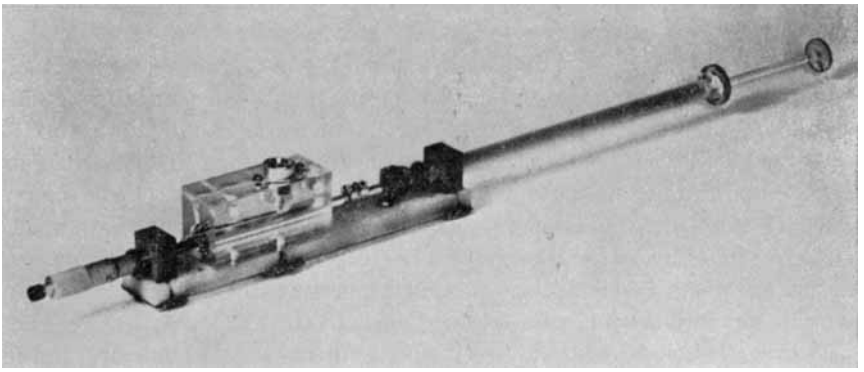

Fig. 4. Assembled extensometer with LVDT and calibration micrometer in place.

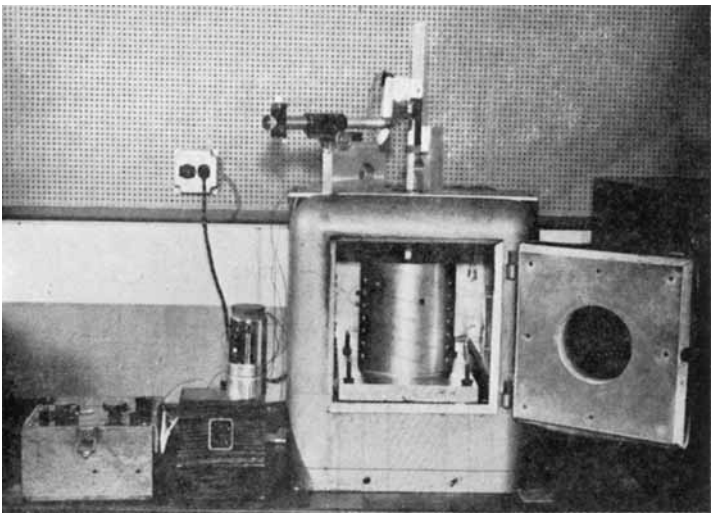

Fig. 5. General experiment arrangement for optical data recording.

between the quartz tube and rod. A quartz specimen was used for this purpose. No significant motion was observed in the temperature range from 70 to 350°F., thus indicating negligible gradients.

## Motion Recording Methods

Four methods were utilized to record model motion. All but one yielded reliable results. However, all are described in the succeeding paragraphs.

**Method 1—Optical.** A long focal length objective microscope with a filar micrometer eyepiece was used to measure the relative displacement between two fiducial marks, one on the tube and one in the rod, both of which were simultaneously in the image field of the eyepiece. This difference measurement minimized effects caused by motion of the microscope base and mounting.

This was the most precise method employed to record displacement data, and was the first used in this program. It was also the reference against which all other methods were tested. It had the disadvantage of requiring long times for temperature stabilization before displacement readings could be made. The optical arrangement for this method is shown in Figure 5.

**Method 2—Dial Gage.** A dial indicator direct reading to 0.0001 in. was mounted on the quartz plate with the anvil fastened to the central quartz rod. The difficulty inherent in this method is the fact that the plunger tends to "hang up" when the motion is away from the plunger point. A motion reversing mechanism is needed when a model is cycling between two temperature methods.

Erratic results were obtained even when utilizing the dial indicator in the proper fashion. Furthermore, as tests with Johanssen gages showed, the

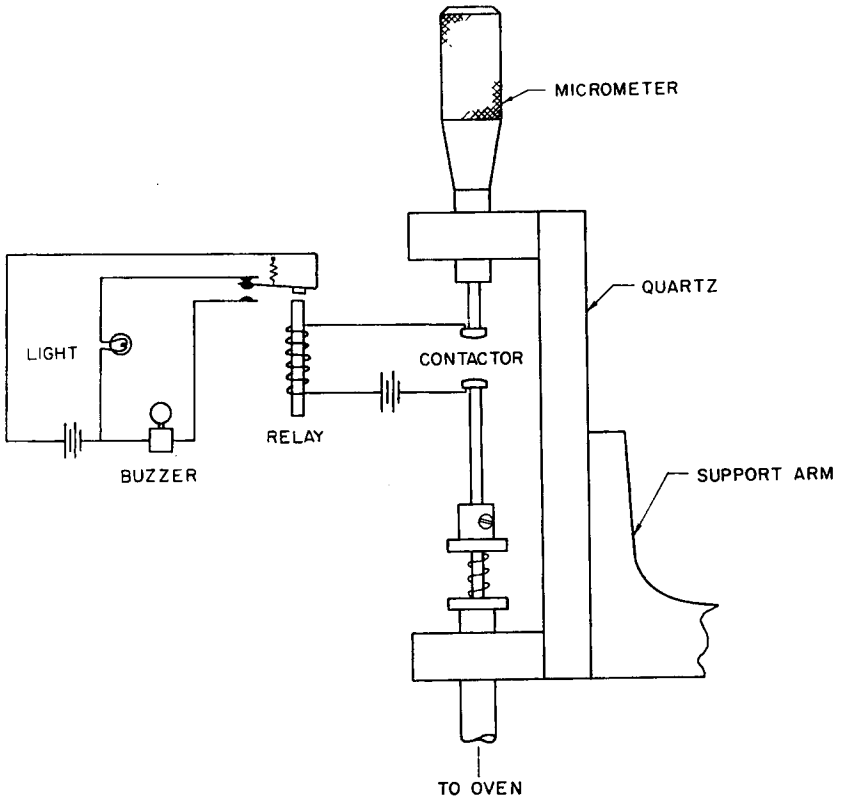


Fig 6. Contactor configuration.

dial scale indications required correction. As a result this method was abandoned.

**Method 3—Contactor.** A simple make-and-break electric contact arrangement was designed. One contact point was placed on the central quartz rod and the other was placed upon the micrometer anvil. These controls were connected electrically to a relay which would energize either a buzzer or light depending on whether it was on or off.

The micrometer anvil could be moved a given amount either into contact with the quartz rod or away from it. A schematic arrangement of the equipment is shown in Figure 6. It has the disadvantage of intermittent recording of elongation data and the presence of an operator who is summoned to activate the temperature chart to indicate the time at which a reading is made. In addition, it is necessary to keep track of the chosen elongation intervals which are preset on the microscope barrel.

**Method 4—LVDT.** A linear variable differential transformer was used to sense continuously the elongation of the specimen so that the complete test could be recorded on a single sheet of graph paper, with motion along one orthogonal axis and temperature along the other. This was accom-

plished by feeding the transformer output through a rectifier to one channel of an X–Y recorder.

The transformer was mounted on a quartz plate to which the quartz tube was fastened. The transformer core was mounted on the quartz rod. In this manner the expansion of the quartz required a small correction to be made to the data. For epoxy this was of the order of 1%.

Calibration was achieved by mounting a micrometer barrel above the transformer. The barrel pushed against a nylon rod which was attached to the core of the transformer. In this manner it was possible to calibrate the transformer immediately before and after each test to minimize correc-

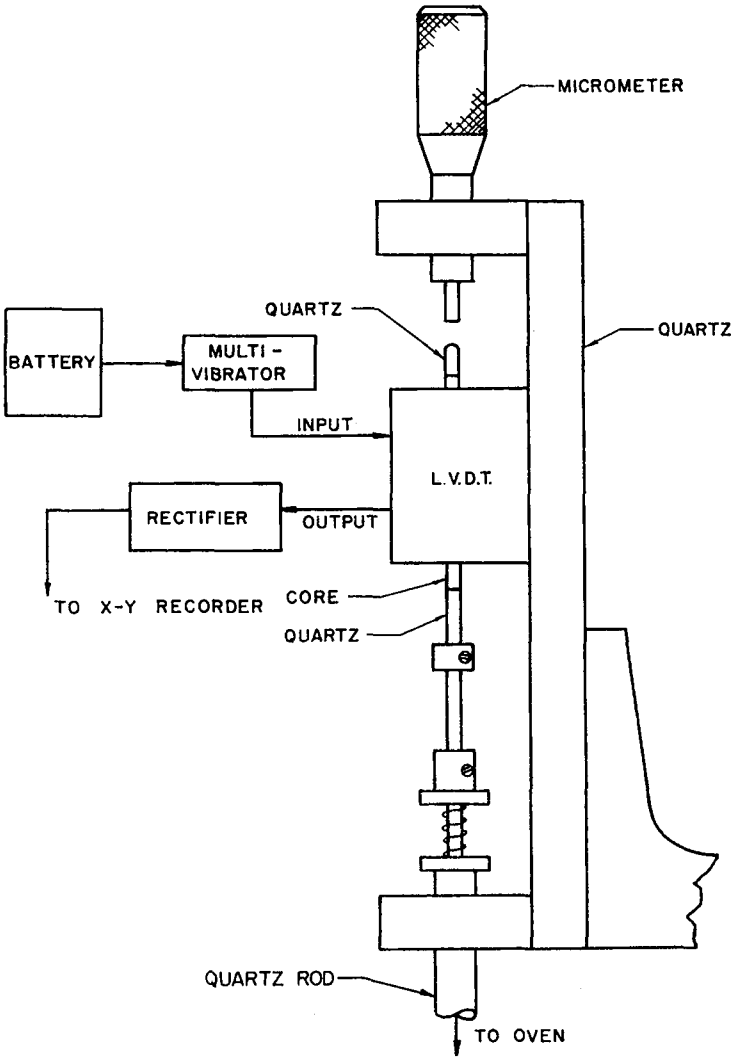


Fig. 7. LVDT configuration.

tions which might occur after long times as a result of possible signal drift. During the test the micrometer was raised well above the model. The measuring head is shown in place in Figure 7.

A battery was used to supply power to the system, and a transistor multivibrator was constructed to supply the linear transformer.

### Temperature Measurement

The thermocouples were formed from copper–constantan B and S size 36 solid wire. Each wire was coated with teflon and the pair sheathed in fiberglass. The thermocouple wires were electric welded to form the bead.

The five thermocouples were placed on the model as shown in Figure 1. They were connected in series, with the cold junctions in an ice water bath. The output was connected to the X–Y recorder with a scale of 5 mv./in. However the scale was read as 1 mv./in. to obtain the average of the five thermocouple outputs. The usual calibration checks were made before testing each model.

### Data Recording

The thermocouple output was connected to the X-axis of a Moseley Autograf X–Y recorder. The recorder was always used for the temperature information whether the expansion strain was read visually or automatically.

When using one of the visual recording techniques to obtain the strain (i.e., optical or dial indicator method) the recorder pen was dropped momentarily to place a dot on the graph paper at the instant the strain was read.

The linear transformer has infinite resolution. Therefore its output was rectified by a full wave diode bridge and put into the Y-axis of the X–Y recorder.

Calibration for all methods was done with the micrometer head which could be read to 0.0001 in.

## EXPERIMENTAL RESULTS

### Data

The curves of $\Delta L/L$ as a function of temperature for Hysol 4290 epoxy and Hysol XCP5-C467 30% plasticized epoxy are shown in Figures 8 and 9, respectively.

It is particularly interesting to observe the agreement of methods 1, 3, and 4 as shown in Figure 8. In order to avoid obscuring the data from the optical and contactor methods, the LVDT data were plotted as points instead of as a continuous curve.

The unplasticized and plasticized epoxy yielded similar expansion curves. The principal difference appears to be a shift in the temperature scale. The general character of the curves, in which a large change in $\alpha$ occurs near

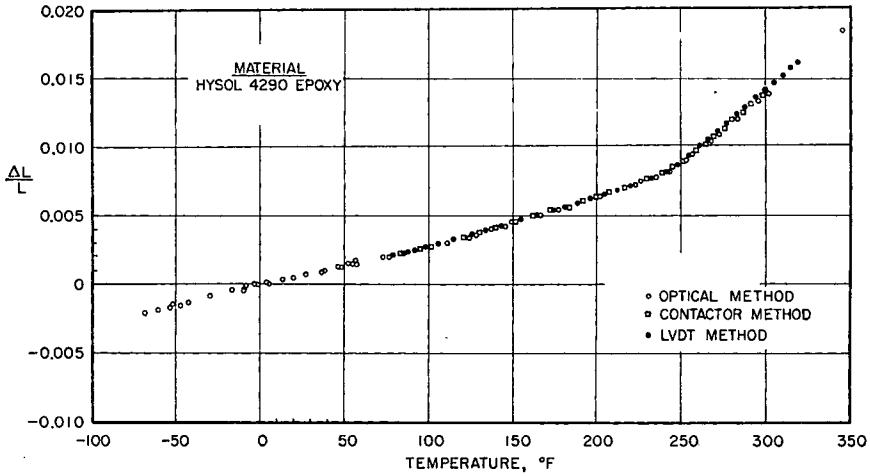


Fig. 8. Comparison of expansion data obtained on epoxy by three different methods.

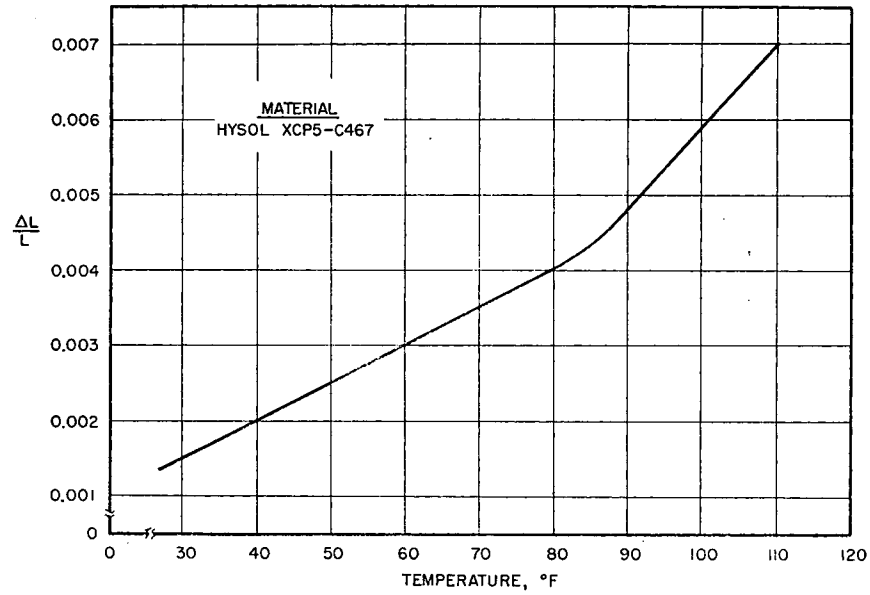


Fig. 9. Expansion data for viscoelastic material.

the glass temperature, is also typical of rocket grain materials. Curves of $\alpha = d(\Delta L/L)/dt$ for the two epoxies appear in Figure 10.

## Experimental Errors

In Table I are listed the experimental errors associated with the measuring and recording equipment.

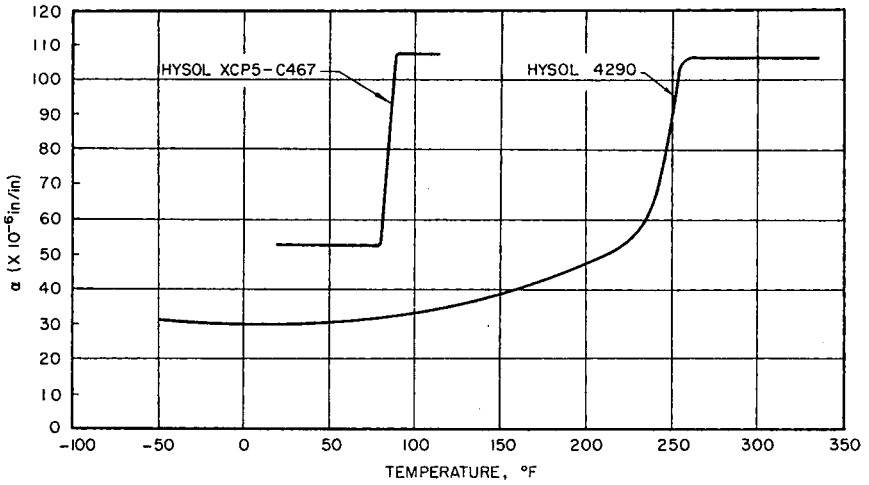


Fig. 10. Thermal expansion coefficient for two plastics.

TABLE I
Experimental Errors

| Item | Maximum error | Minimum error |
|---|---|---|
| Thermocouple | 1/4% | 0.1% |
| Model length | 0.00002 in. | — |
| Optical microscope | 0.00005 in. | — |
| Dial indicator | 0.0001 | — |
| X–Y recorder | 1/4% | |
| Contactor | 0.0005 in. | 0.0001 in. |
| Micrometer | 0.0002 in. | 0.0001 in. |
| Linear trans. | Infinite resolution | |

The thermocouple output was checked against boiling water and powdered Dry Ice. In both cases the accuracy was better than 1/4%. The recorder has a long time drift accuracy of 1/4% as reported by the manufacturer. The calibration accuracy is a function of the least count of the micrometer and is variable. If the overall expansion is considered it is 1/2%. Using the contactor the error for the same range is almost 1%. However, these errors for the micrometer and contactor are random errors that could possibly occur at each reading and not necessarily always in one direction. Thus the actual cumulative error could be less than that obtained for any one reading.

## References

1. Hidnert, P., and W. Souder, *Thermal Expansion of Solids, Precision Measurement and Calibration Handbook*, **77**, Vol. 3, National Bureau of Standards, Washington, D. C.,
2. *Handbook of Chemistry and Physics*, 42nd Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1960–61.

## Résumé

On construit un appareil à expansion thermique en quartz par la mesure de l'expansion thermique des plastiques photomécaniqes. On met en corrélation trois différentes méthodes de mesure de mouvement avec une erreur maximale de ±1% en utilisant trois différents modèles de Hysol-époxy 4290. On détermine l'expansion thermique d'un époxy plastifié à 30% et on trouve qu'il montre des caractéristiques essentiellement semblables à un époxy 4290, excepté le déplacement de l'échelle de température.

## Zusammenfassung

Zur Messung der thermischen Ausdehnung von photomechanischen plastischen Massen wurde eine Quarzapparatur entwickelt. Mit drei verschiedenen Hysol-4290-Epoxy-Modellen wurde eine Korrelation dreier verschiedener Methoden zur Bewegungsmessung mit einem maximalen Fehler von ±1 Prozent erreicht. Die thermische Ausdehnung eines 30% weichgemachten Epoxyharzes wurde bestimmt und zeigte, abgesehen von einer Verschiebung der Temperaturskala, im wesentlichen die gleiche Charakteristik wie das 4290-Epoxyharz.

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