

T H E U N I V E R S I T Y O F M I C H I G A N

COLLEGE OF ENGINEERING  
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LOW-TEMPERATURE PROPERTIES OF ASPHALTS  
USED IN MICHIGAN PAVEMENTS

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## SYNOPSIS

The literature indicates that low-temperature cracking of bituminous concrete pavements may be at least partly influenced by so-called glass transition temperature of the asphalt used.

This study included design and construction of equipment and measurement of glass transition temperature ( $T_g$ ) of 38 asphalts used in Michigan. A workable method has been established and variability of results has been determined.

Six of the asphalts tested were about 19 years old and came from the Michigan Test Road, US-10, Flint-Pontiac area.

The glass transition data was also applied to predict low-temperature viscosities using the Williams-Landel-Ferry equation.





## INTRODUCTION

There is an increased concern over cracking of bituminous pavements. A typical example of such undesirable cracking can be observed on Interstate I-75 in Michigan and similar phenomena have been reported also by other states. <sup>(5,6,10,11)\*</sup> Such cracks in relatively new pavements are not only unsightly, but they also destroy the structural continuity and soundness of the pavement. The discontinuities in the pavement caused by cracking will be a long-range nuisance requiring maintenance and diminishing the life of the original pavement, by causing reflecting cracks in a overlay which is applied when the original surface becomes rough. Therefore, reduction in frequency and size of cracks is a rewarding goal to pursue.

The general causes of cracking may be: traffic loading, material properties, pavement component thickness, environmental conditions, and construction procedures. One of the factors which has been increasingly discussed is the behavior of asphalt in a bituminous mix at low temperatures. It has been especially noted that in the northern regions often quite evenly spaced transverse cracks appear which tend to fit the category of nonload thermal type of cracking. <sup>(5,6)</sup> Such cracks often contribute to rapid losses in riding quality of the pavement when water penetrates through the cracks and causes the swelling of the subgrade.

The physical properties of pavement asphalts are usually measured and

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\*Raised numbers in parentheses indicate references in the bibliography.

specified at 77 F or higher temperatures. Sometimes a penetration test may be run at 32 F. Is this sufficient to characterize the behavior of a given asphalt at low temperatures? It has been suggested that cracking may be correlated with temperatures at which asphalt becomes brittle. This temperature is often called the "glass transition temperature" and will be further discussed in this paper.

## PURPOSE AND SCOPE

The main purpose of this investigation was to find a workable method for measuring the brittle point for asphalts used for Michigan highways. The work included:

- (1) Establishment of a test procedure for measuring the glass transition temperatures of asphalt cements.
- (2) Measurements of glass transition temperatures on asphalt cements from various sources in Michigan as received in the MDSH Testing Laboratory.
- (3) Limited work on field correlation of cracking with  $T_g$ .
- (4) Attempted predictions of low temperature viscosity using the Williams-Landel-Ferry (WLF) equation.

## LITERATURE REVIEW

A brief review of literature on glass transition temperature is given in this section. The review includes discussion of glass transition temperature, measurement, and practical significance.

### NATURE OF GLASS TRANSITION TEMPERATURE

All materials have temperatures at which the material changes its physical and thermodynamic properties. At the melting point of a crystalline solid or the boiling point of a liquid, a change in volume takes place at constant temperature, producing a discontinuity in the volume-temperature curve. Phase changes caused by such discontinuities in density, enthalpy, and other primary physical properties are termed first-order transitions.<sup>(1)</sup> There are also so-called second-order transition temperatures where the primary physical properties of the material do not change sharply at the point.

As the temperature of an asphalt is lowered, the soft rubber-like properties are gradually lost, the material hardens, and finally changes to a glass-like material. The temperature at which such change takes place is known as the glass transition temperature (the brittle point). It is customary to identify this brittle temperature with the second-order transition temperature.

The glass transition temperature ( $T_g$ ) varies with the molecular weight of a material as illustrated in Table I. It is also known that  $T_g$  is markedly influenced by small amounts of residual solvent or other diluent.<sup>(2)</sup> Jones, Darter, and Littlefield<sup>(3)</sup> have discussed the influence of chemical composition

of a material on  $T_g$  and the thermal coefficient of expansion as shown in Table II.

#### MEASUREMENT OF GLASS TRANSITION TEMPERATURE

The glass transition temperature can be measured by several experimental techniques. The measurements of penetration, linear expansion, or specific volume change over a wide range of temperatures are the examples. However, the method of finding the specific volume change by using a dilatometer is the most widely used. Schmidt and Santucci<sup>(4)</sup> investigated the  $T_g$  of 52 asphalts by using a dilatometer. The asphalt samples were supplied by the Bureau of Public Roads and represented a cross section of commercial production in the United States. They reported  $T_g$  values ranging from -34 F to 5 F, with approximate distribution as shown in Figure 1.

The value of the glass transition temperature of polymers depends also on the rate of temperature change. However, Schmidt and Santucci reported in the same paper that usable  $T_g$  values could be obtained by determining the specific volume of asphalt sample while the temperature is changed at a uniform rate of 2.0 C (3.6 F) per minute.

Doyle<sup>(9)</sup> measured a transition point of asphalt cement by measuring the thermal expansion of a specimen using a linear expansion measurement device. He defined the transition temperature as the temperature at and above which a specimen "softens" and stops expanding due to the relaxation of the specimen and the existence of friction between the specimen and underside support surface. It is understood that this transition point is closer to a softening

point rather than a glass transition point.

#### PREDICTION OF LOW-TEMPERATURE VISCOSITIES

By using the glass transition temperature the temperature dependence of viscosity in amorphous polymer can be expressed by a single empirical function.<sup>2</sup>

R. J. Schmidt and L. E. Santucci presented the use of the equation developed by M. L. Williams, R. F. Landel, and J. P. Ferry (WLF equation) in calculating low-temperature viscosity. The equation is expressed as follows:

$$\log \frac{N_1}{N_2} = \frac{C_1 (T_2 - T_g)}{C_2 + T_2 - T_g} - \frac{C_1 (T_1 - T_g)}{C_2 + T_1 - T_g}$$

$N_1$  = viscosity at temperature  $T_1$  (poises)

$N_2$  = viscosity at temperature  $T_2$  (poises)

$T_g$  = glass transition temperature (F)

$C_1$  = 17.44 (constant)

$C_2$  = 92.88 (constant)

By substituting experimentally determined values of  $T_g$  and  $N_2$ , the viscosity  $N_1$  at any low temperature  $T_1$  can be calculated. For paving asphalts it is often convenient to use viscosity at 140 F as the value for  $N_2$  because data at this temperature may be readily available.

#### LOW TEMPERATURE CRACKING

Schmidt in another paper showed an example taken from work by K. O. Anderson and B. P. Shields,<sup>(5,6)</sup> where one section of a pavement had 348 transverse cracks per mile and the recovered asphalt had a  $T_g = 13$  F while another similar section had no cracks and the recovered asphalt had a  $T_g = -11$  F.

Schmidt pointed out that a 24-degree difference in  $T_g$  was apparent between the "crack resistant" and "crack-prone" asphalts, and that the  $T_g$  of the asphalt may be a useful indication for non-load associated cracking of bituminous pavement layers.

## LABORATORY WORK

### APPARATUS

The apparatus for measuring glass transition temperatures of asphalts consisted of three main parts:

- (1) Dilatometer.
- (2) Temperature bath.
- (3) Instruments for sample preparation.

The basic design of the apparatus used in this research is similar to that used by Schmidt and Santucci.<sup>(4)</sup>

#### Dilatometer

The dilatometer is illustrated in Figure 2. It consists of an expansion measuring capillary tube, an aluminum cell, a stainless steel washer, and synthetic rubber "O" rings. A molded asphalt sample is put into the cell and methanol is filled into the remaining space between the sample and the cell. The flange of the capillary works as the sealing cap together with "O" rings so that the volumetric changes in the contents of the cell are measured by the change in height of methanol column in the capillary.

Two sets of identical dilatometers were used in this investigation.

#### Temperature Bath

A temperature bath which could produce wide variations of temperatures was designed with a temperature range of -60 F to +60 F. In order to have flexibility, a cooling system which utilized liquid nitrogen was used. The



temperature bath, the cooling system, and the temperature control heater are shown in Figure 3. Methanol was used as the bath liquid with a freezing point of -144 F. The bath temperature was controlled by adjusting the valve of the liquid nitrogen tank and the powerstat of the immersion heater. For cooling mode, liquid nitrogen was introduced in the cooling coil which was immersed in the bath liquid. Liquid nitrogen was stored in an insulated container with the maximum pressure controlled by a safety valve. In this work, 160-liter containers with 100 psi safety valve were used. The liquid nitrogen stored in such containers evaporates and blows off in five to ten days depending on the insulation of the container. It was calculated that approximately 14 liters of liquid nitrogen are consumed in one cycle of testing.

The bath temperatures were measured using a special wide-range thermometer made by attaching (fusing) a 3-ml bulb to a capillary tube. The special thermometer was filled with blue-colored methanol and calibrated by using standard ASTM 33C thermometer and a methanol bath, the temperature of which was raised or lowered at a rate of 3.6 F (2.0 C) per minute. The calibration chart is shown in Figure 4. Because of the comparatively large heat capacity of the methanol in the bulb, two lines are obtained: one for the cooling mode and one for the heating mode. A magnified chart was used for actual reading of the temperatures.

#### Instruments for Sample Preparation

For sample preparation the following instruments were used:

- (1) Molds and a brass plate.
- (2) A glass evacuation cap.

- (3) A 30-in. long No. 20 hypodermic needle and a syringe.
- (4) A stand to support the capillary of the dilatometer while it is assembled.
- (5) A 4-in. diameter, 2-1/2-in. deep can.
- (6) An oven, a hot plate, a vacuum pump, and a refrigerator.

The mold and the glass evacuation cap are shown in Figure 5. The mold was made by cutting and polishing a piece of brass tubing. The glass evacuation cap was used to evacuate the entrapped air in the dilatometer cell which contained a sample and methanol. The vacuum was applied through the top of the evacuation cap and the lower flange was attached to the dilatometer. A 30-in. hypodermic needle was used to adjust the initial height of methanol in the capillary.

## TESTING PROCEDURE

### Sample Preparation

- (1) The container holding the material to be tested was heated in oven set at 325 F until it was fluid enough to be poured into the molds. The molds and the support plate were oiled with silicone and heated in the same oven. The molds and base plate were put on a hot plate to be kept hot while pouring. After filling, they were returned to the oven and allowed to stand for about 5 min to allow any bubbles to rise to the top. The base and molds were then removed and air cooled for 15 min.

- (2) Next, excess asphalt from the top of the mold was trimmed using a hot knife edge and the mold and sample were separated from the base plate. If the sample was too soft to separate from the base plate at room temperature, it was first cooled in the refrigerator.
- (3) The mold and sample were chilled in a cold methanol bath to shrink the sample away from the mold. The bath temperature was kept from -31 F to -40 F and the sample was immersed in the cold methanol for 45 to 60 sec. An over-cooled sample was extremely easy to break.
- (4) The extrusion assembly, which was 1-3/4 in. high and had a slightly larger inner diameter than the mold, was put into a 2-1/2-in. deep can containing methanol between 32 F to 40 F (see Figure 6). The chilled mold and sample were then placed on the extrusion assembly and the sample was pushed gently down into the cold methanol by a rod. The extruded samples could be stored in the same cool methanol until they were ready for testing.

#### Assembly of Dilatometer

- (1) The aluminum cell fitted with "O" ring was immersed in the methanol which was also used to store specimens and the specimen was dropped gently into the cell. The glass evacuation cap was held in place on the cell and the vacuum was applied for about 1 min. During this period, the cell was tapped and tilted until all air bubbles were removed.

- (2) The bottom part of the measuring capillary was put into methanol and a slight vacuum was applied through the top of the capillary so that the entire capillary was filled with methanol. This was accomplished by connecting a rubber hand pump to the top of the capillary and applying an appropriate negative pressure (Figure 7). Keeping the capillary filled with methanol, the bottom flange of the capillary was placed on the cell. Subsequently the cap and washer were placed and fastened. During this operation care should be taken to hold the bottom of the capillary immersed in methanol.
- (3) After removing the rubber hand pump from the capillary, the height of methanol was adjusted to about 40 cm. A drop of methanol colored with methylene blue was added to the top of the methanol filling the capillary tube to aid in reading of the fluid level. The adjustment of the initial capillary height was done by using the 30-in. hypodermic needle.
- (4) Since the top of the wide-range thermometer is open to the air, the fluid level changed as methanol evaporated slowly. Therefore, every day methanol was filled to the level of 50 cm, while the bulb was immersed in ice water. This adjustment was done using the calibration chart shown in Figure 4.
- (5) The dilatometer unit and the wide-range thermometer prepared as described were placed in the temperature bath as shown in Figure 3. A jack supporting the insulated bath was adjusted until the level of the bath fluid was about 1/2 in. over the cell top. The bath temperature was held at about 50 F for 10 min.

- (6) For the cooling mode, after standing for 10 min at 50 F, liquid nitrogen was introduced into the cooling coil at a rate greater than necessary to maintain the cooling rate of 3.6 F (2.0 C) per minute. The rate of cooling was controlled by a valve on the vent. It took several minutes to obtain the desired rate of cooling because of the heat capacity of the tubing which carried the liquid nitrogen. Shortly before the desired cooling rate was obtained, the immersion heater was also turned on so that the desired rate of cooling was maintained. It was difficult to control the rate of cooling only by the adjustment of the valve for liquid nitrogen. This is because the total cooling system has larger heat capacity than the immersion heater. In such a case precise control of temperature is best accomplished by adjusting the power applied to the immersion heater.
- (7) After the desired rate of cooling was achieved, the levels of methanol in the dilatometer capillary and the thermometer were recorded every 2 min. Reading of the wide-range thermometer was taken once every minute and checked to maintain 3.6 F (2.0 C) per minute. The cooling or heating rate of 3.6 F (2.0 C) per minute corresponded to the change in the capillary height of 1.65 cm per minute for this particular case. Practically, the bath temperature was controlled in the range of 1.6 cm to 1.7 cm (3.5 F to 3.7 F per minute). The measurement was continued until the level of methanol in the thermometer showed 0 cm which implied -80 F.

(8) The heating mode was next. At the end of the cooling mode, liquid nitrogen and the immersion heater were turned off. After standing for 10 min at the low temperature, the immersion heater was turned on and the variable transformer was adjusted so the 3.6 F (2.0 C) per minute of heating was obtained. The same readings as for the cooling mode were made until the thermometer showed 60 cm which equaled about 50 F. During the measurement for both the cooling and heating modes, the level of bath fluid was adjusted to maintain a uniform submergence of the dilatometer and the thermometer. This was achieved by adjusting the jack supporting the bath.

#### MATERIALS SELECTED

All together 38 asphalts were tested. The materials used in this investigation were supplied by the Bituminous Testing Laboratory of the Michigan Department of State Highways. Twenty-three of the asphalts were selected from the research samples which the Bituminous Testing Laboratory had collected and coded as 73B-1 through 73B-23. The penetration of these asphalts ranged from 60-70 to 250-300 and they were obtained from 15 different sources as shown in Table III.

Among the 38 asphalts, 12 samples came from the Michigan Test Road.<sup>(7)</sup> Six of them were original samples which had been stored in the Bituminous Testing Laboratory and 6 were extracted asphalts from the bituminous concrete which had been subjected to traffic for 19 years. Available values of penetration at 77 F, viscosity at 140 F, and viscosity at 275 F for the asphalts are tabulated in Table III.

## RESULTS AND ANALYSIS

The results of glass transition measurements on 38 asphalts are tabulated in Table III. A typical example of laboratory readings and curves for the dilatometer and thermometer are given in Figure 8. The temperature at which an extension of the two tangent lines of a curve intercept was interpreted as the  $T_g$ .\* Slightly different values for  $T_g$  were obtained in the cooling mode and heating mode and an average of two readings was used. It should be pointed out that once the equipment was set up, the running of the test and graphical determination of the glass transition temperature was a relatively simple matter.

### PENETRATION, VISCOSITY, AND $T_g$

From what is known in the literature no correlation between penetration value at 77 F and  $T_g$  was anticipated. Figure 9 is presented here to show that soft asphalts with penetration above 200 can have  $T_g$  similar to that of harder 50 penetration asphalts. Also, two asphalts with an identical penetration of 50 can have glass transition temperatures at -12.5 F or -25 F.

Figures 10 and 11 show similar relationships when viscosities at 140 F and 275 F are compared with  $T_g$  values.

As mentioned previously and shown in Table III, the 38 asphalts tested included several sources of supply. Figure 12 shows separate curves for  $T_g$

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\*The heating and cooling affect the volumes of the sample holder, the capillary tube, and the methanol. Such volume changes would produce straight-line relationships similar to Figure 4. The break in the lines in Figure 8 are due to the asphalt sample.

versus penetration at 77 F for asphalts from the same source. In this case certain asphalts, such as A, B, and C, show some "logical" trends: the harder the asphalt at 77 F, the higher the glass transition temperature (the sooner it becomes brittle). Also, it can be seen that the  $T_g$  values for similar penetration grades are always higher for asphalts from source A as compared to source B. Therefore, in cold climates source B asphalts may be preferable to source A asphalts.

#### CALCULATION OF LOW-TEMPERATURE VISCOSITIES

The measurement of asphalt viscosities at temperatures around the  $T_g$  point and in the cold regions above this temperature is not an easy task. In order to characterize an asphalt over the whole service range in pavement (say between -20 F and 140 F or higher) the knowledge of viscosity-temperature curve as shown in Figure 13 could be very helpful. As discussed in the literature review, so-called WLF equation has been used for polymers to obtain curves as shown in Figure 13. The calculation requires a value for  $T_g$  and one actual measured viscosity at a point above the  $T_g$ .

Using the WLF equation, the viscosities at low temperatures were calculated for several of the asphalts tested. Two of the asphalts were 73B-13 and 73B-10, both 85-100 penetration grade and had high and low values for  $T_g$ , respectively.

Two additional asphalts were selected from the original samples used in the Michigan Test Road corresponding to Sections 4 and 6. The Michigan Test Road data will be discussed later.

The measured values of viscosity at one given temperature and  $T_g$  were substituted in the WLF equation and the viscosities at low temperatures were



calculated. Two independent calculations were performed on the same asphalt using the viscosity measured at 140 F and 275 F. The results are plotted on ASTM viscosity temperature chart as shown in Figures 13, 14, and 15. These figures show that the plots are nearly straight lines. The calculated curves using 140 F viscosity as the base do not agree completely with those using 275 F viscosity, as shown by Figures 13 and 14. The viscosities at  $T_g$  for the asphalts look almost similar (about  $10^{14}$ ) regardless of the values of  $T_g$ .

#### ASPHALTS USED IN THE MICHIGAN TEST ROAD

The Michigan Test Road was constructed in July, 1954 on US-10 in the Flint-Pontiac area. This was a bituminous concrete overlay placed on the top of a 40-ft, four-lane reinforced concrete pavement built in 1931. The test road was three miles long with six equal length test sections. Each section was overlaid using one source of asphalt. The main purpose of this experiment was to compare the six different asphalts.

The glass transition temperatures were determined on the asphalts used in each section of the test road. The original asphalts stored in the Bituminous Testing Laboratory and the recently extracted asphalts from the bituminous concrete were tested. The change in glass transition temperatures between the original asphalts and extracted asphalts is shown in Figure 16.

The asphalts used in Sections 1, 2, 3, and 6 show only a slight change in glass transition temperature after nineteen years and for all practical purposes, these transition temperatures could be called unchanged with years. Asphalts from Sections 4 and 5 appear to have a decrease in the glass transition temperature which may be opposite to what is expected. As discussed in

the literature review, small amounts of solvent remaining in the asphalts after extraction may have affected the results, lowering (improving) the  $T_g$  in these two cases. A similar phenomenon may have been present also with asphalts from Sections 1, 2, 3, and 6. Therefore, the glass transition temperatures as obtained in this testing may be valid for a relative comparison between the extracted asphalts and not necessarily with the original samples.

The main reason for measuring the  $T_g$  values for the six Michigan Test Road asphalt samples was to see whether cracking and deterioration of the road sections would show any correlation with the glass transition temperatures measured. It could be expected, that other conditions being equal, the asphalt with a high glass transition temperature will become brittle sooner as the temperature drops, and, therefore pavements containing such asphalt would be more susceptible to cracking in climates like Michigan.

In order to estimate the present condition of the test road sections, a visual survey was performed by walking the six sections and comparing the severity of:

- (1) Raveling.
- (2) Cracking.
- (3) Patching.
- (4) Edge deterioration.
- (5) Rutting
- (6) Roughness of riding surface.

The survey was performed by three highway engineers who evaluated the test road independently by grading on a scale between 0 to 5. Statistical

analysis was performed by taking the average of readings of the three individuals and using the Duncan's Multiple Range Test.<sup>(8)</sup> As a result the order for performance of the test sections was established as shown in Figure 17. Sections 4 and 5 had the highest grade (the best relative performance) and Section 6 the lowest.

A comparison between the condition of the test road sections and the glass transition temperatures of the asphalt for each section is shown in Figure 18. The values for the glass transition were obtained by taking the average  $T_g$  of the original and the extracted samples for each asphalt. Although there are only six points and a considerable scatter is present, there is a general trend showing that sections with higher cracking and other deterioration had asphalt with a higher glass transition temperature. This is what would normally be expected to happen, since asphalts which get brittle at higher service temperatures should be associated with more cracking if used in pavement mixes. The scatter which is present may be explained by difference in other factors in this test road, such as the condition of the old concrete pavement underneath. More field surveys of other roads in Michigan and comparisons of cracking and  $T_g$  of the asphalts should be of value.

## DISCUSSION

### METHOD OF $T_g$ MEASUREMENT

The idea of measuring glass transition temperatures for polymers by the dilatometer method is not new and the present research shows that it is a practical procedure which can be applied to asphalts (or tars). Following is the discussion of the accuracy of this method.

Table III gives three values for the  $T_g$ : (1) from the cooling mode, (2) from the heating mode, and (3) the average  $T_g$  of the two. In order to get an estimate of the variability in the measurements, six identical tests were run using sample 73B-23 and the results are listed in Table III. The range of the average  $T_g$  values was between -21.5 F and -25.5 F and the standard deviation was 1.6 F. This indicates that under similar conditions the variation of  $\pm 3.2$  F is expected to cover about 95% of the data. This kind of accuracy appears to be adequate for practical purposes.

In similar comparisons the  $T_g$  values for the heating mode vary between -17.5 F and - 22.2 F with standard deviation of 1.8 F and for the cooling mode between 24.7 F and 28.8 F with standard deviation of 1.5 F.

In order to shorten the test procedure by omitting the cooling mode measurements, an attempt to estimate the average  $T_g$  value from the heating mode test was made. Using all the test data listed in Table III, the variation of differences between  $T_{gc}$  and  $T_{gh}$  ( $T_g$  values obtained from cooling and heating modes) was analyzed. The mean value of D (difference between  $T_{gc}$  and  $T_{gh}$ ) was

8.4 F and standard deviation 2.0 F. Then, it can be said that\*:

$$D = \bar{D} \pm 2\sigma = 8.4 \pm 4.0 \text{ F}$$

where  $\bar{D}$  = mean of D

$\sigma$  = standard deviation of D

The standard deviation estimated using the six replicates for sample 73B-23 was 1.85 and therefore\*:

$$T_{gh} = \bar{T}_{ga} \pm 2\sigma = \bar{T}_{gh} \pm 3.7 \text{ F} .$$

Then the average  $T_g$  value of cooling and heating mode,  $T_g$  can be estimated as follows:

$$T_g = T_{gh} - \frac{D}{2}$$

Substituting for  $T_{gh}$  and D:

$$T_g = (\bar{T}_{gh} - 4.2) \pm 5.7 \text{ F}$$

This means that  $\bar{T}_g$  can be calculated by subtracting 4.2 from measured  $\bar{T}_{gh}$  and the variation of  $\pm 5.7 \text{ F}$  is anticipated. This is rather high as compared to the single mode values.

Another approach to shorten the test would be by simply using the heating mode alone for reading  $T_{gh}$  values (and knowing that the average  $T_g$  value is about 5 F lower). The test time would thus drop from approximately 2 1/2 hr

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\*Using the 95% confidence limit.

to about 2 hr which is not a very great saving.

Finally, efficiency could be increased by testing say five samples simultaneously in which case about 30 min per sample is an acceptable length of time.

Various other possibilities of further simplification of the  $T_g$  test were discussed, but due to low test temperatures, required strict rates of cooling-heating, and also due to limited funds no progress was made in this area at this time.

Occasionally there was a leakage of methanol in the dilatometer. This leakage occurs at very low temperatures. When it has taken place, the test should be stopped and repeated again after examining the "O" ring, the flange of measuring capillary, and tightness of the cap. The leakage can be easily detected by examining the curves of capillary heights of the dilatometer and the thermometer. An example of the curve is shown in Figure 19. Comparing this with Figure 8, it can be seen that when leakage has taken place, the curve of cooling mode changes the slope downward at the low temperature. The other sign of leakage is also the distance of two lines. This distance is explained by the leakage during the 10 min of standing at the low temperature. The frequency of leakage cases probably could be reduced by using a different type of "O" ring.

#### RANGE OF $T_g$ VALUES OBTAINED

The 38 asphalts tested for  $T_g$  were taken from the shelves of the MDSH Testing Laboratory. Among these, 6 were original samples (1954)\* and 6

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\*These were the only original samples available in the MDSH Testing Laboratory which were older than 1973 samples.

extracted samples (1972) from the Michigan Test Road. The remaining 26 were 1972 refinery samples which had been tested in the MDSH Laboratory. These samples were chosen essentially in a random fashion without any prior knowledge for expected  $T_g$  values. They included 15 sources and penetrations between 28 and 262. The highest  $T_g$  value obtained was -11.4 F and the lowest -32.4 F. Thus the range of about 30 F is found between the asphalts of the lowest and the highest  $T_g$ . Also, none of the asphalts had  $T_g$  above 0 F.

#### CRACKING ON THE ROAD AND $T_g$

Literature review indicates that if two bituminous roads were built under identical conditions, the one containing asphalt with lowest  $T_g$  would have a tendency to have less cracks. In this work 6 asphalts from six test sections on the Michigan Test road indicate, that the general expected trend is there (see Figure 18). As pointed out before, it is rather difficult to build six test sections with completely similar supports and in identical manner. Also, the highest  $T_g$  for the Michigan Test Road samples was found to be -11.4 F (the lowest -32.4 F). This temperature may be low enough as not to cause serious cracking potential for Michigan conditions in the Pontiac area. In other words, it is possible that great differences in cracking frequency in Southeast Michigan cannot be expected with asphalts having a range of -11.6 F to -32.4 F for  $T_g$ .

#### PRACTICAL APPLICATION OF RESULTS

The present measurements for asphalt consistency are occasionally taken at 32 F (penetration, ductility) but the usual stopping point is 77 F. These temperatures are almost always well above the glass transition temperature which is to represent a point where asphalt turns from a viscoelastic to an

elastic (brittle) material. Therefore the inclusion of glass transition temperature as one of the basic and routine measurements in asphalt specifications appears to be desirable. However, before the test can be introduced in specifications, the desirable maximum (highest) glass transition temperature for Michigan conditions should be firmly established. From literature study and observations in this work, it is probable that the highest desirable  $T_g$  temperature is around 0 F.

In order to set a maximum  $T_g$  limit more field cracking comparisons with  $T_g$  values for asphalts used should be obtained.

One way to achieve this would be by measuring  $T_g$  values for all incoming Plant Samples and then gathering pavement performance data for selected road sections with asphalts which have as wide a range of  $T_g$  values as possible. It is recognized that about 2600 Plant Samples were received by the MDSH Testing Laboratory in 1972. To measure the  $T_g$  for all of them about 1300 man-hours would be needed. This can be shortened, if necessary, by choosing at random only part of the 2600 samples.

The measurement of  $T_g$  may also have another very important practical by-product. Using the WLF equation and knowing the  $T_g$  temperature and the usual viscosity measurement at 140 F, an estimate of other viscosities between 140 F and  $T_g$  can be tried. Low temperature viscosity measurements will be pursued during our 1973-1974 research studies at which time a practical application of this relationship will be checked. This may open the way for plotting viscosities for asphalts for the entire range of temperatures on the road (see Figures 13, 14, and 15).



## CONCLUSIONS

This research was concerned with the development of equipment and measurement of glass transition temperatures ( $T_g$ ) for asphalts used on roads in Michigan. The following conclusions are pertinent:

- (1) Equipment was built and a procedure was established for measuring glass transition temperatures for asphalts using specific volume change as a basis.
- (2) The glass transition points were measured for 38 asphalts from 15 different sources, covering penetrations between 28 and 262.
- (3) Asphalts from the same source have a tendency for lower  $T_g$  values with increasing penetration (softness). This partly supports the claim by some asphalt technologists, that "softer asphalts should be used in cold climates to reduce low temperature cracking."
- (4) Field performance comparisons of 6 asphalts in the Michigan Test Road show a possible trend of increased cracking and deterioration for mixes containing asphalts with higher  $T_g$  values. However, all  $T_g$  values in the Michigan Test Road were rather low (between -11.4 F and -30.2 F).
- (5) Some extracted asphalts from the Michigan Test Road had lower  $T_g$  after 18 years of service as compared to the original asphalts which were kept in cans and tested together with the extracted asphalts. It is thought that small amounts of solvent left after the extraction has affected the  $T_g$  of the extracted asphalts.

## RECOMMENDATIONS

There are a number of recommendations which can be made. However, in order not to obscure the main purpose of this investigation only the most pertinent practical suggestions will be made:

- (1) At least one person from the MDSH Testing Laboratory should thoroughly familiarize himself with the glass transition measurement technique and equipment.
- (2) There were only six samples of original old asphalts available in the MDSH Testing Laboratory for  $T_g$  measurement and field cracking comparisons. In order to get more conclusive data on relation between cracking and  $T_g$  a systematic field correlation program should be established. The authors are willing to help to set up such a program.

## REFERENCES

1. A. X. Schmidt and C. A. Marlies, "Principles of High-Polymer Theory and Practice," 1st ed. New York, McGraw-Hill Book Co., 1948.
2. M. L. Williams, R. F. Landel, and J. D. Ferry, "The Temperature Dependence of Relaxation Mechanism in Amorphous Polymers and Other Glass-Forming Liquids," *Journal of American Chemistry Society*, Vol. 77, 1955.
3. G. H. Jones, M. I. Darter, and G. Littlefield, "Thermal Expansion-Contraction of Asphaltic Concrete," *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 37, 1968.
4. R. J. Schmidt and L. E. Santucci, "A Practical Method for Determining the Glass Transition Temperature of Asphalts and Calculation of Their Low Temperature Viscosities," *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 35, 1966.
5. K. O. Anderson, B. P. Shields, and J. M. Dacyszyn, "Cracking of Asphalt Pavements Due to Thermal Effects," *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 35, 1966.
6. B. P. Shields and K. O. Anderson, "Some Aspects of Transverse Cracking in Asphalt Pavements," *Canadian Technical Asphalt Association*, 1964.
7. W. K. Parr, P. J. Serafin, and Tom Humphries, "Michigan State Highway Experimental Bituminous Concrete," *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 24, 1955.
8. C. R. Hicks, "Fundamental Concepts in the Design of Experiments," published by Holt, Rinehart, and Winston, 1965, p. 31.
9. P. C. Doyle, "Cracking Characteristic of Asphalt Cement," *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 27, 1958.
10. C. L. Monismith, G. A. Secor, and K. E. Secor, "Temperature Induced Stresses and Deformations in Asphalt Concrete," *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 34, 1965, pp. 248-285.
11. R. J. Schmidt, "The Relationship of the Low Temperature Properties of Asphalt to the Cracking of Pavements," *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 35, 1966, pp. 263-268.

TABLE I  
GLASS TRANSITION TEMPERATURES  
MEASURED FOR POLYSTYRENE

Polymer	Molecular Weight	T <sub>g</sub> , Kelvin
Polystyrene	1675	313
	2085	326
	2600	335
	3041	338
	3590	348
	6650	350
	13300	359
	19300	362

TABLE II  
INFLUENCE OF CHEMICAL COMPOSITION OF ASPHALT ON GLASS TRANSITION TEMPERATURE, AFTER G. M. JONES, M. I. DARTER, AND G. LITTLEFIELD  
(Data were taken from investigation performed by Wada and Hirose)

Sample	Asphaltene Content % by Weight	Density (68 F) gm/cm <sup>3</sup>	T <sub>g</sub> , F
A. Asphaltenes	100	1.079	None
B. Mixture of Samples A and I, 3:1 proportions	75	1.053	None
C. Blown Asphalt	62	1.039	35.6
D. Blown Asphalt	59	1.034	32.0
E. Blown Asphalt	57	1.030	28.4
F. Blown Asphalt	52	1.027	20.3
G. Blown Asphalt	51	1.026	18.5
H. Straight Run Asphalt	29	1.014	- 8.5
I. Maltenes	0	1.004	-35.5

TABLE III

## GLASS TRANSITION AND VISCOSITY DATA FOR 38 MICHIGAN ASPHALTS

No.	Sample Identification		Sample Source	Glass Transition Temperature, T <sub>g</sub> , F				Penetration at 77 F		Viscosity (Pois)	
	MDSH Code No.	Penetration Grade		Cooling Mode	Heating Mode	Average Cooling-Heating	Grand Average	at 140 F	at 275 F	at 140 F	Calculated at T <sub>g</sub> (x 10 <sup>1.2</sup> )
1	73B-1	60-70	Lion -'72	-22.2 -16.6 -22.0	-13.5 - 8.9 -10.3	-17.9 -12.7 -16.2	-15.6	64	2840	5.62	2.36
2	73B-2	85-100	Lion -'72	-18.4 -18.0 -20.4	-13.6 -11.2 -10.3	-16.0 -14.6 -15.4	-15.3	94	1270	3.71	1.03
3	73B-3	120-150	Lion -'72	-14.4	- 8.3	-11.4	-11.4	130	790	2.94	0.507
4	73B-4	200-250	Lion -'72	-30.6	-20.7	-25.7	-25.7	233	387	2.14	0.578
5	73B-5	60-70	AMOCO -'72	-22.2	-13.9	-18.1	-18.1	63	2140	3.89	2.06
6	73B-6	85-100	AMOCO -'72	-24.0	-14.8	-19.4	-19.4	92	1200	3.06	1.25
7	73B-7	120-150	AMOCO -'72	-25.6	-13.5	-19.6	-19.6	143	629	2.27	0.0664
8	73B-8	200-250	AMOCO -'72	-34.2	-23.8	-29.0	-29.0	239	324	1.65	0.581
9	73B-9	60-70	Petrofina -'72	-27.4	-17.7	-22.5	-22.5	69	2680	4.94	3.34
10	73B-10	85-100	Petrofina -'72	-31.2	-22.9	-27.1	-27.1	89	1760	4.20	2.84
11	73B-11	120-150	Petrofina -'72	-31.7	-19.7	-25.7	-25.7	140	870	3.10	1.30
12	73B-12	250-300	Petrofina -'72	-33.5	-20.7	-27.1	-27.1	262	430	2.36	0.695
13	73B-13	85-100	Ashland -'72	-19.8	-10.8	-15.3	-15.3	87	1690	3.66	1.38

TABLE III (Concluded)

No.	Sample Identification		Sample Source	Glass Transition Temperature, T <sub>g</sub> , F				Penetration		Viscosity (Poises)	
	MDSH Code No.	Penetration Grade		Cooling Mode	Heating Mode	Average Cooling-Heating	Grand Average	at 77 F	at 140 F	at 275 F	Calculated at T <sub>g</sub> (x 10 <sup>14</sup> )
27	Test Rd. Sec. 4 (Original)	60-70	Std. Ind. -'54	-28.3	-21.8	-25.1	-25.1	49	4480	5.11	6.47
28	Test Rd. Sec. 5 (Original)	60-70	Lion -'54	-18.0	-11.0	-14.5	-14.5	41	6570	7.35	5.11
29	Test Rd. Sec. 6 (Original)	60-70	Petrofina -'54	-26.7	-18.4	-22.6	-22.6	49	8070	8.94	10.03
30	Test Rd. Sec. 1 (Extracted)	60-70	Trumbull -'54	-23.1	-15.7	-19.4	-19.4	29	--	--	--
31	Test Rd. Sec. 2 (Extracted)	60-70	Bitumuls -'54	-18.0	-9.8	-13.9	-11.6	30	--	--	--
32	Test Rd. Sec. 3 (Extracted)	60-70	Leonard -'54	-20.4	-11.0	-15.7	-15.3	28	--	--	--
33	Test Rd. Sec. 4 (Extracted)	60-70	Std. Ind. -'54	-39.6	-28.7	-34.3	-30.4	37	--	--	--
34	Test Rd. Sec. 5 (Extracted)	60-70	Lion -'54	-32.4	-23.1	-27.7	-24.5	32	--	--	--
35	Test Rd. Sec. 6 (Extracted)	60-70	Petrofina	-29.4	-19.5	-24.4	-23.0	33	--	--	--
36	72B-5262	40-50		-28.3	-17.7	-23.0	-12.3	50	--	--	--
37	72B-5262 (Extracted)	40-50		-14.8	-9.8	-12.3	-17.1	--	--	--	--
38	KOCH	85-100	KOCH	-20.6	-13.5	-17.1	-18.3	--	--	--	--
				-20.9	-15.7	-18.3	-17.3	92	--	--	--
				-21.3	-13.4	-17.3	-20.2				
				-24.7	-15.7						

TABLE III (Continued)

No.	Sample Identification		Sample Source	Glass Transition Temperature, T <sub>g</sub> , F				Viscosity (Poises)				
	MDSH Code No.	Penetration Grade		Cooling Mode	Heating Mode	Average Cooling-Heating	Grand Average	Penetration at 77 F	at 140 F	at 275 F	Calculated at T <sub>g</sub> (x 10 <sup>14</sup> )	
14	73B-14	60-70	ARCO - '72	-29.0	-20.7	-24.9	-24.9	-24.9	65	1960	4.21	2.80
15	73B-15	85-100	ARCO - '72	-23.8	-15.7	-19.8	-19.8	-19.8	90	1140	3.22	1.21
16	73B-16	120-150	ARCO - '72	-28.3	-18.9	-23.6	-23.6	-23.6	134	720	2.87	0.956
17	73B-17	200-250	ARCO - '72	-28.5	-17.9	-23.2	-23.2	-23.2	222	372	2.07	0.483
18	73B-18	85-100	Leonard - '72	-26.1	-21.3	-23.7	-23.7	-23.7	90	1590	3.87	2.12
19	73B-19	120-150	Leonard - '72	-20.2	-15.7	-18.0	-18.0	-18.0	136	885	2.90	0.850
20	73B-20	200-250	Leonard - '72	-32.6	-27.6	-29.6	-29.6	-29.6	208	475	2.11	0.880
21	73B-21	60-70	Trumbull - '72	-30.6	-21.6	-26.1	-26.1	-26.1	66	2340	4.20	3.75
22	73B-22	85-100	Trumbull - '72	-18.0	-13.5	-15.8	-15.8	-15.8	88	1460	3.42	1.23
23	73B-23	120-150	Trumbull - '72	-27.0	-20.6	-23.8	-23.8	-23.8	145	784	2.58	1.01
				-28.8	-22.2	-25.5	-25.5	-25.5				
				-26.9	-18.2	-22.6	-22.6	-22.6				
				-25.6	-17.5	-21.6	-21.6	-21.6				
				-24.7	-18.2	-21.5	-21.5	-21.5				
				-27.8	-20.7	-24.3	-24.3	-24.3				
24	Test Rd. Sec. 1 (Original)	60-70	Trumbull - '54	-21.3	-10.5	-15.9	-15.9	-15.9	46	4010	5.11	3.39
25	Test Rd. Sec. 2 (Original)	60-70	Bitumuls - '54	-19.1	-11.2	-15.2	-15.2	-15.2	52	5570	7.51	4.52
26	Test Rd. Sec. 3 (Original)	60-70	Leonard - '54	-22.3	-13.0	-17.7	-17.7	-17.7	48	3390	4.84	3.19

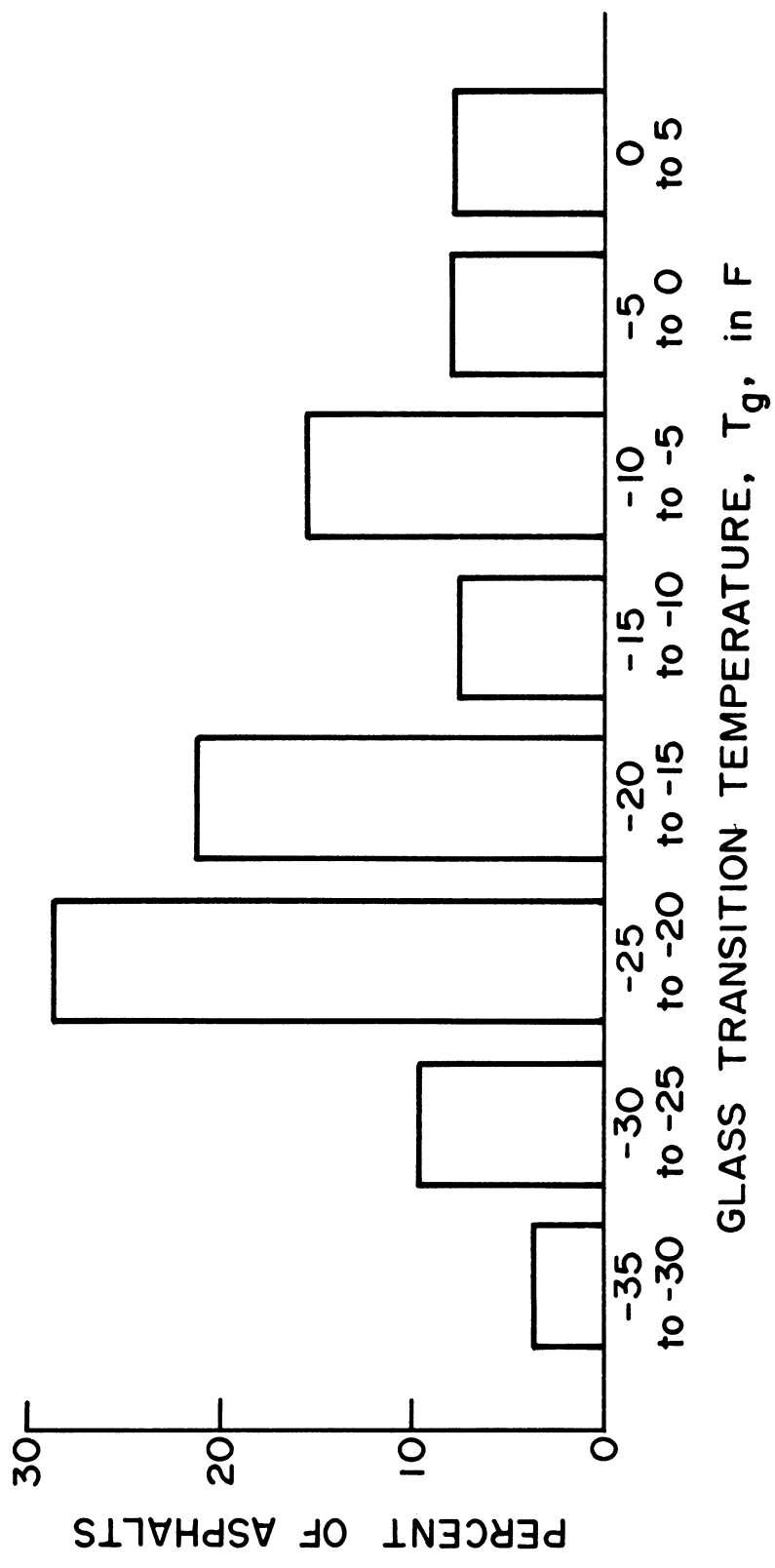


Figure 1. Distribution of glass transition temperature measured by R. J. Schmidt and L. E. Santucci for 52 asphalts.<sup>4</sup>



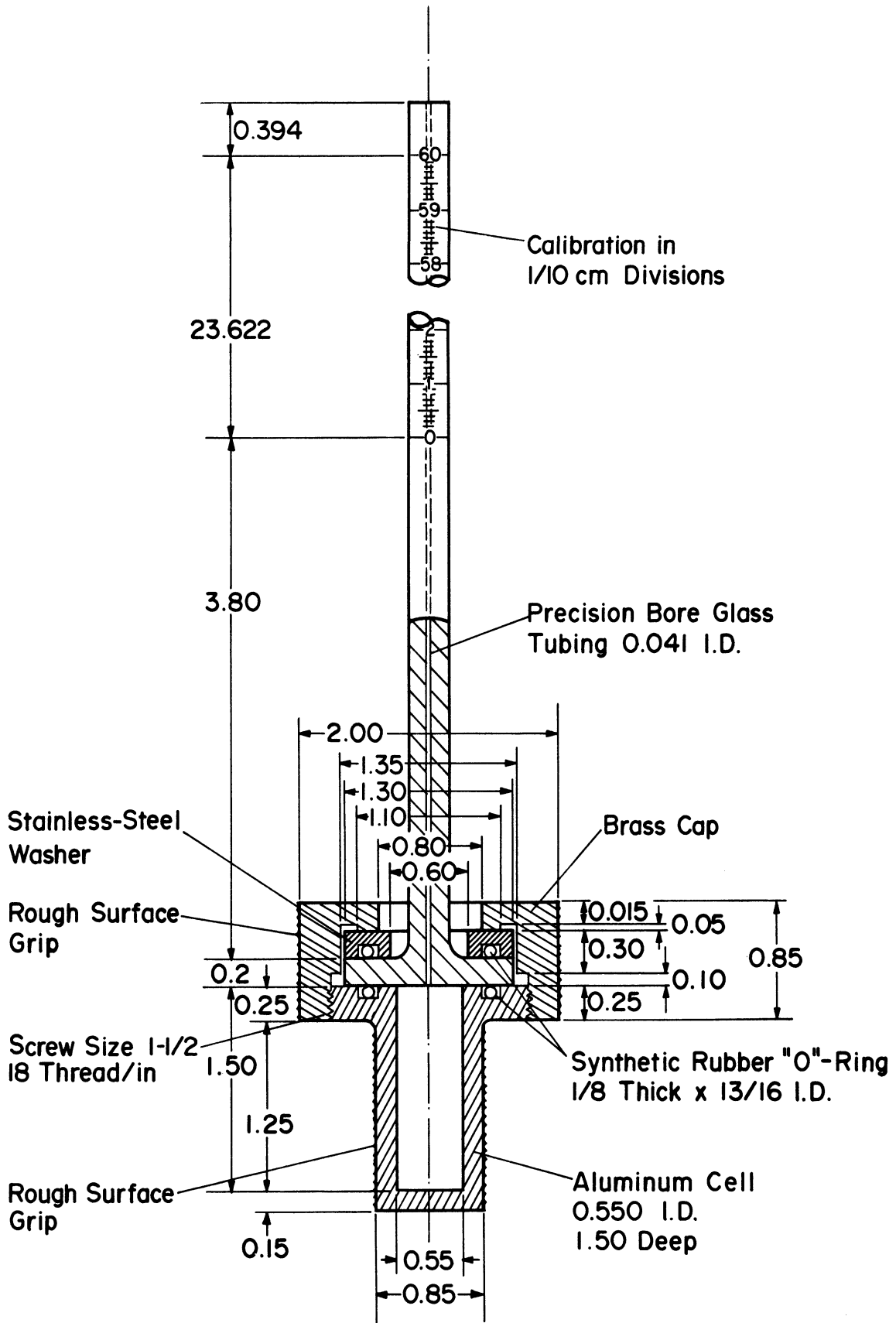


Figure 2. Dilatometer used in this study (dimensions in inches).

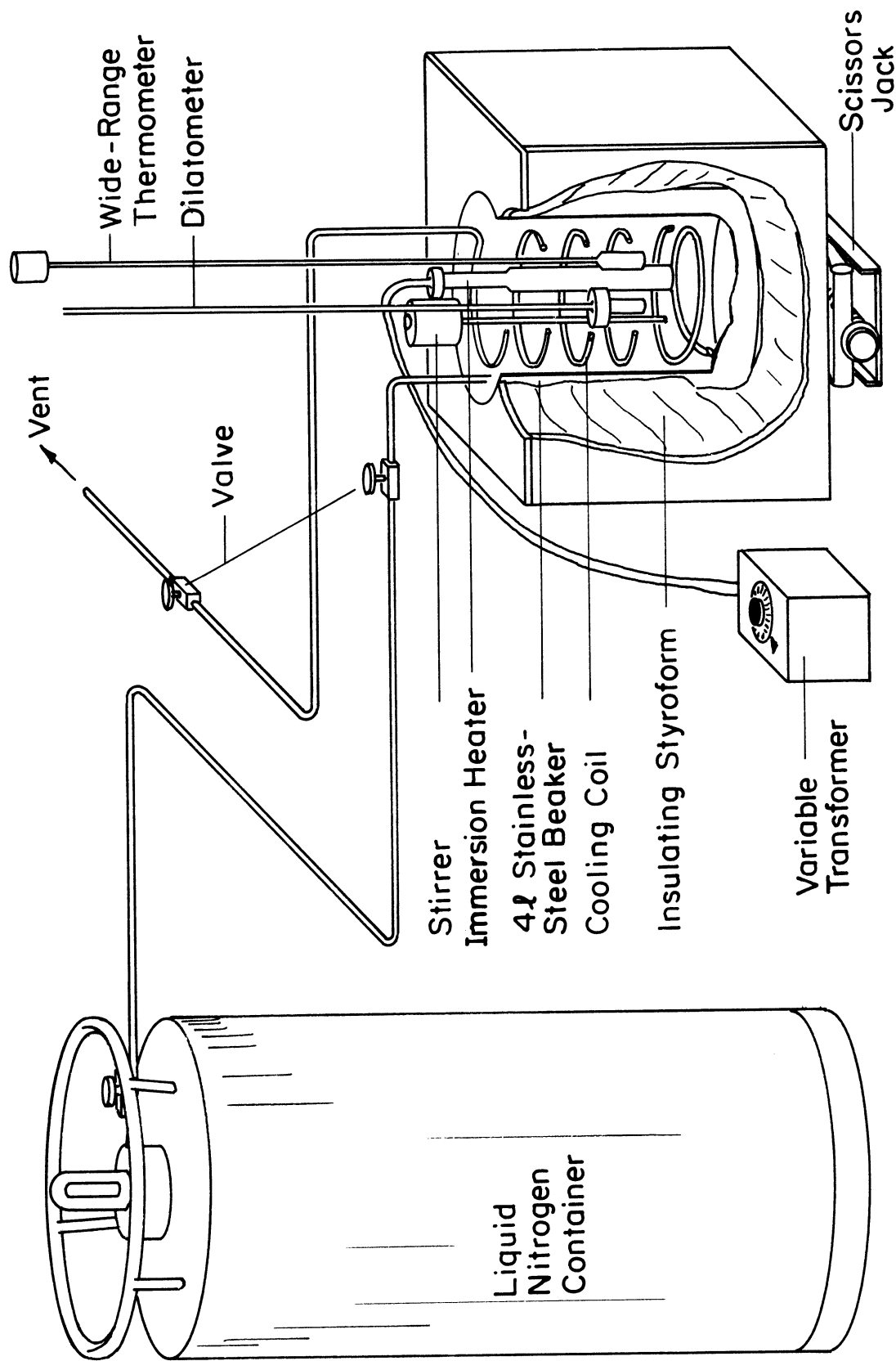


Figure 3. Temperature bath used in this study.

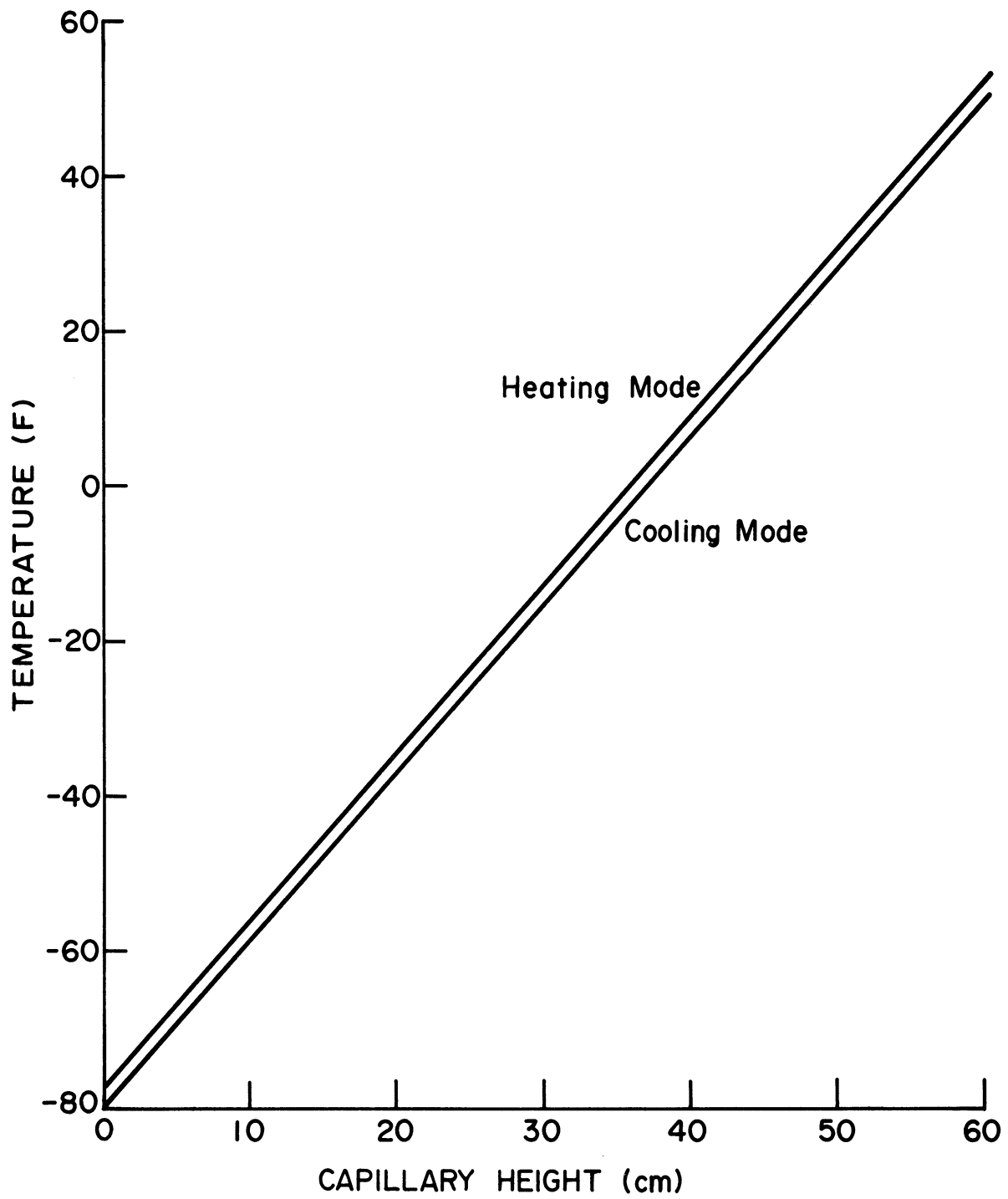


Figure 4. Calibration chart for wide-range thermometer.

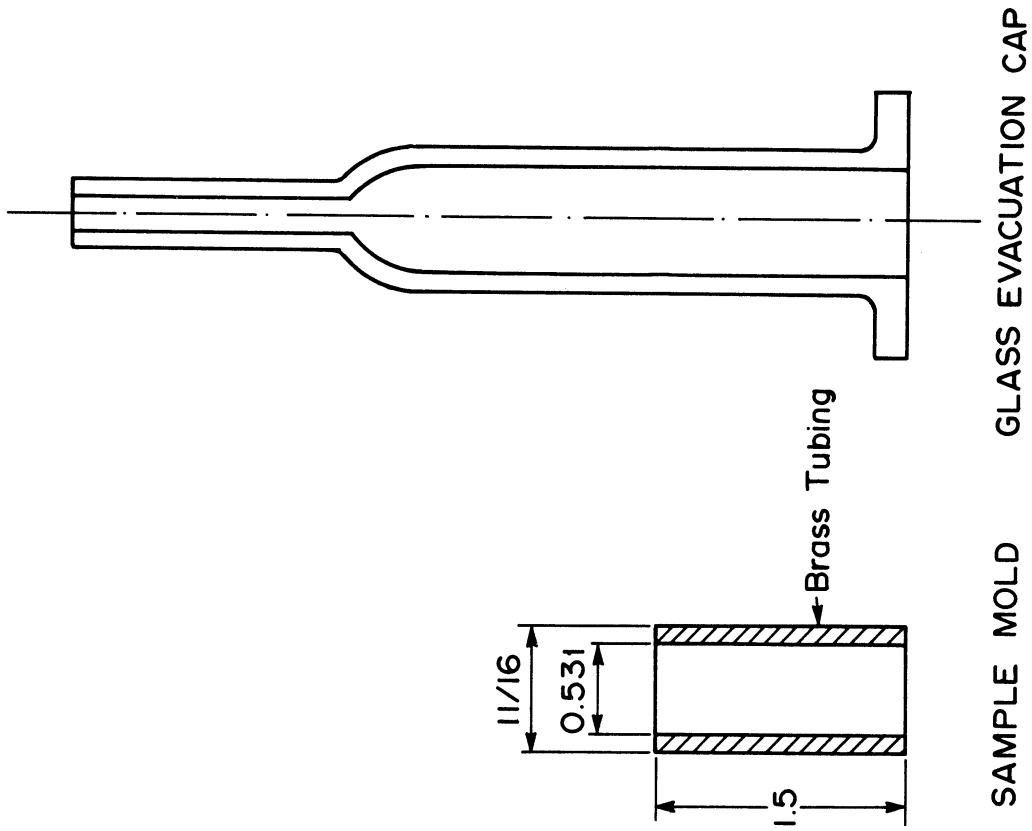


Figure 5. Sample mold and glass evacuation cap (dimensions in inches).

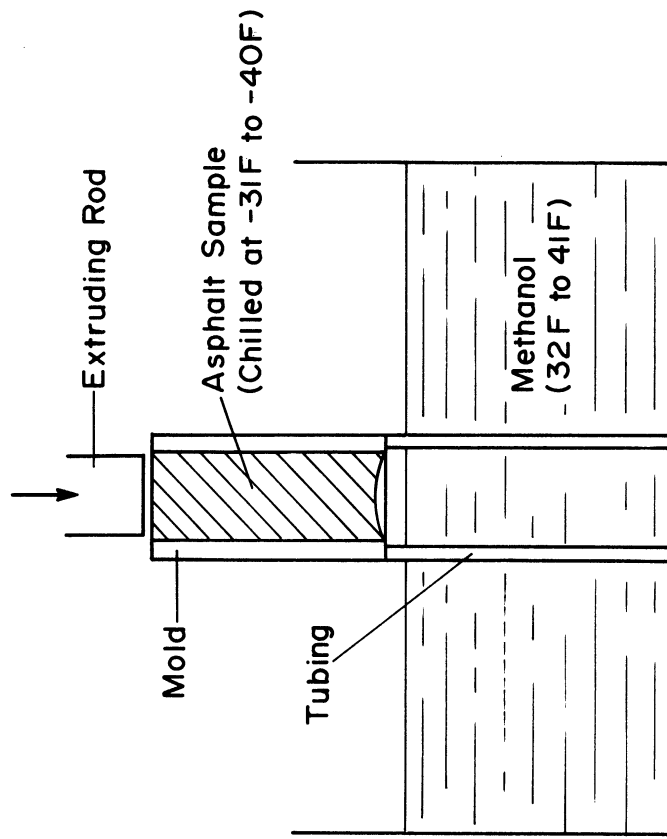


Figure 6. Extrusion of sample.

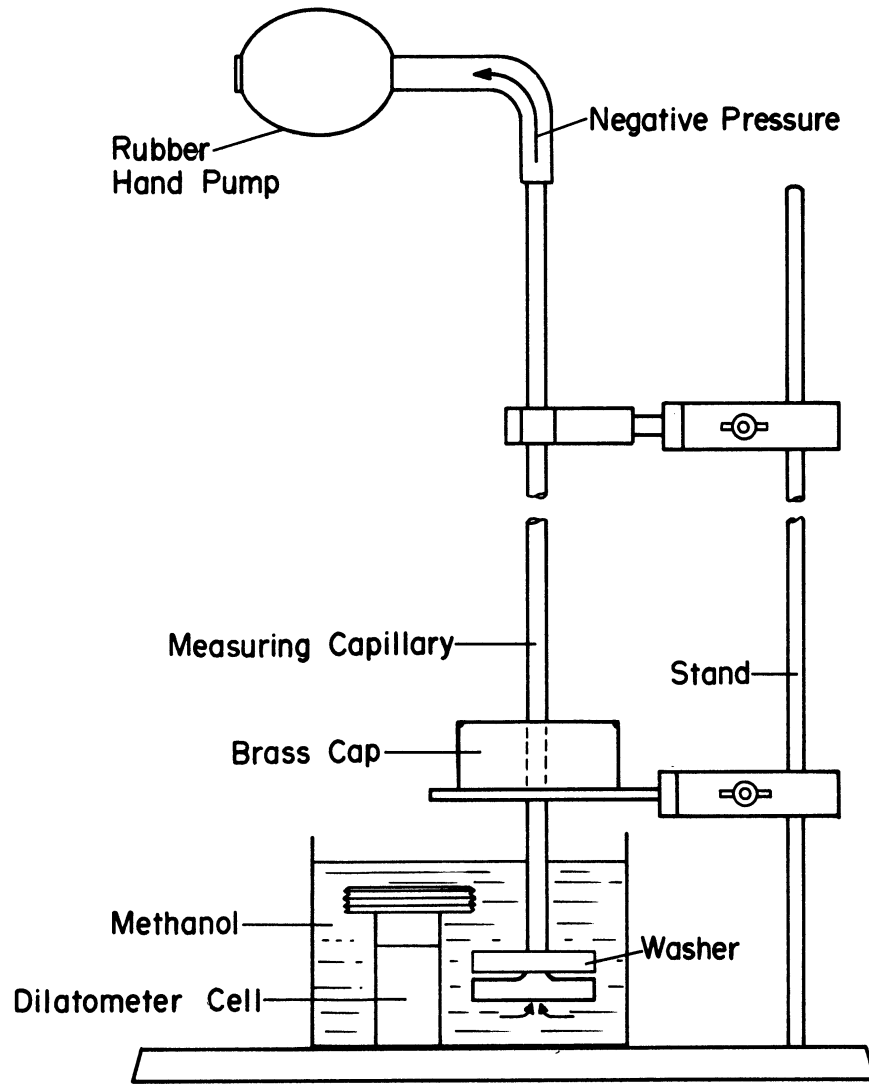


Figure 7. Assembly of dilatometer.

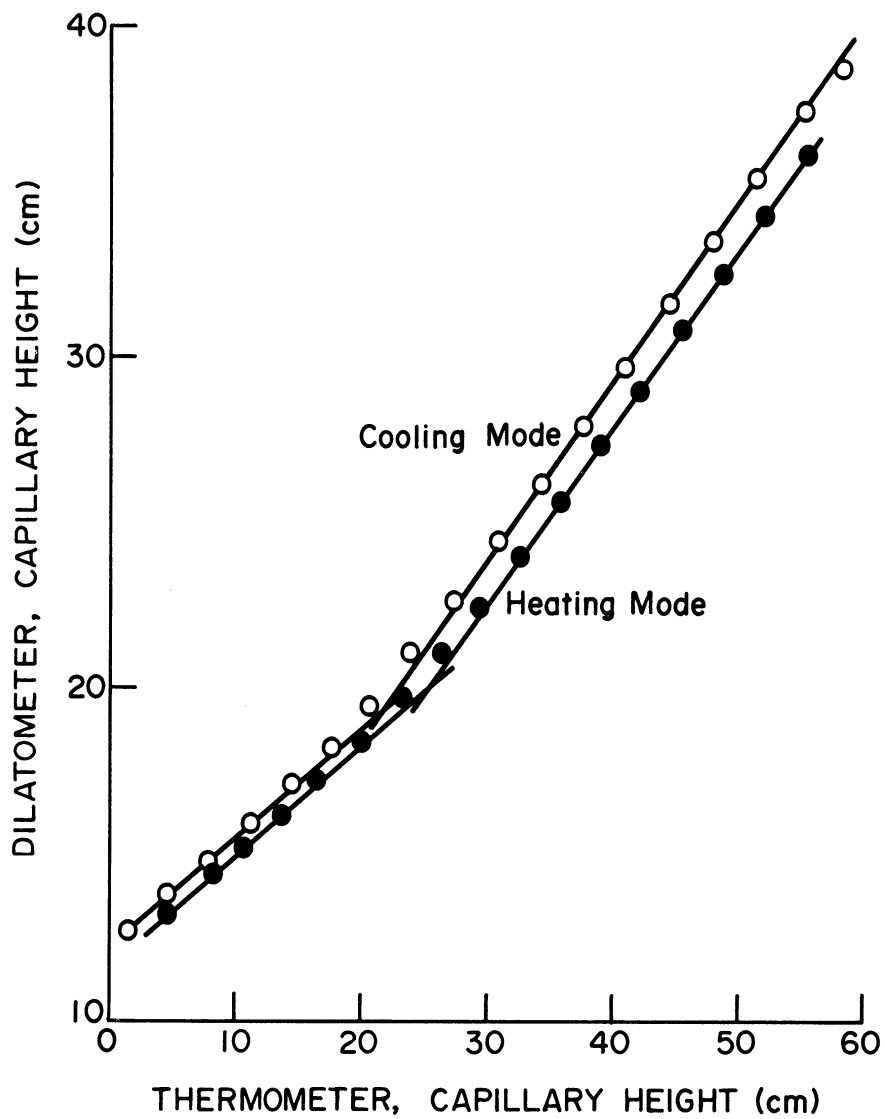


Figure 8. Determination of glass transition temperature.

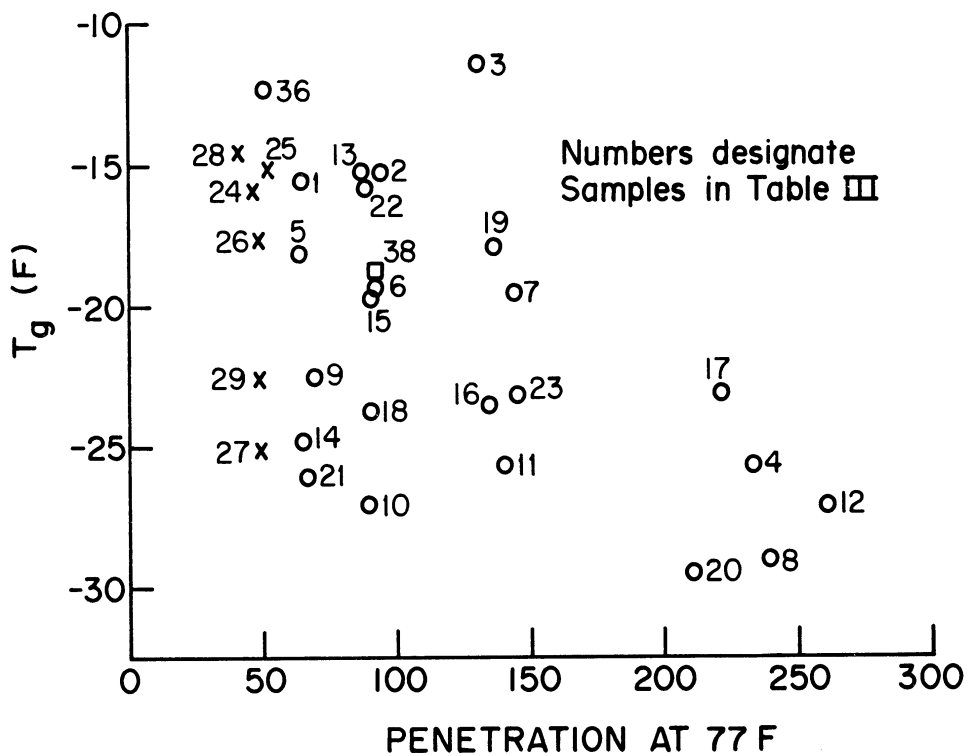


Figure 9. Penetration vs. T<sub>g</sub>.

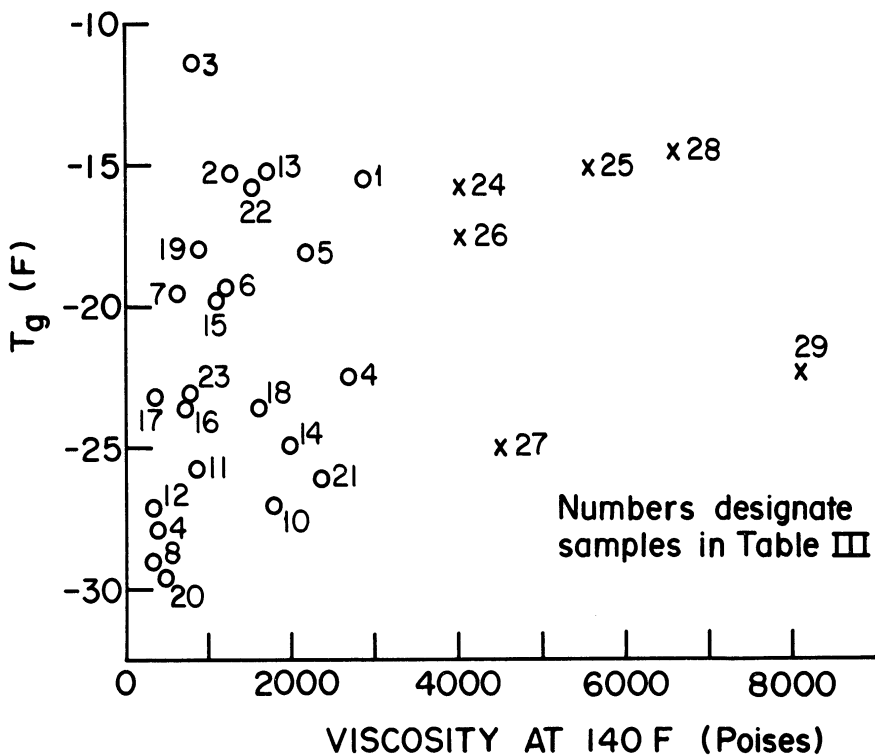


Figure 10. Viscosity at 140 F vs. T<sub>g</sub>.

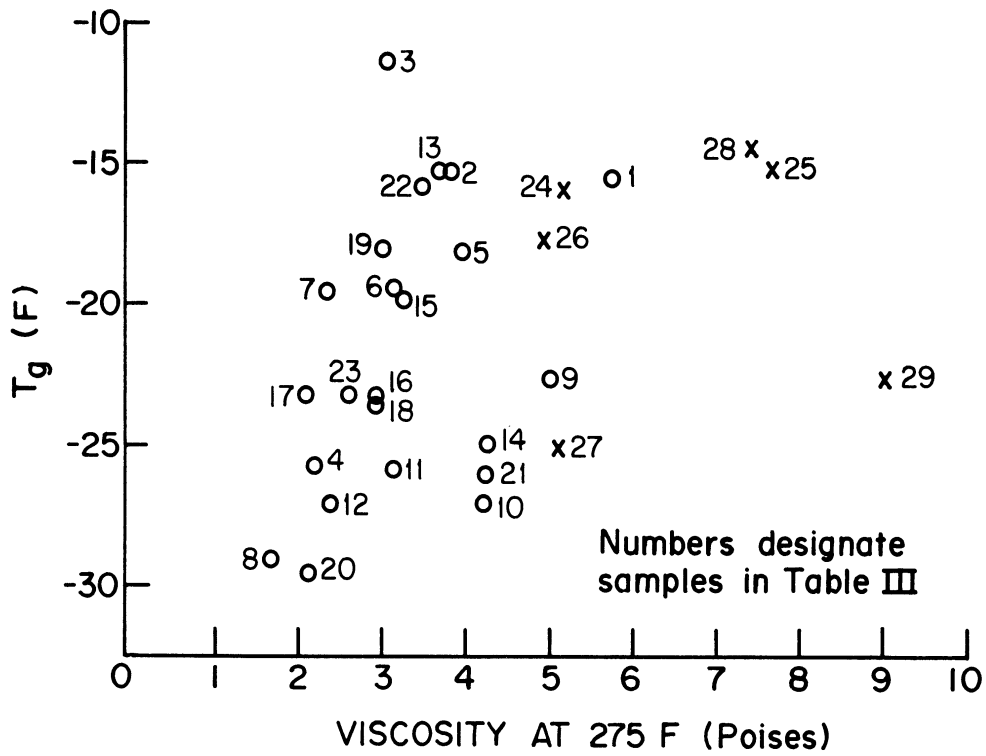


Figure 11. Viscosity at 275 F vs.  $T_g$ .

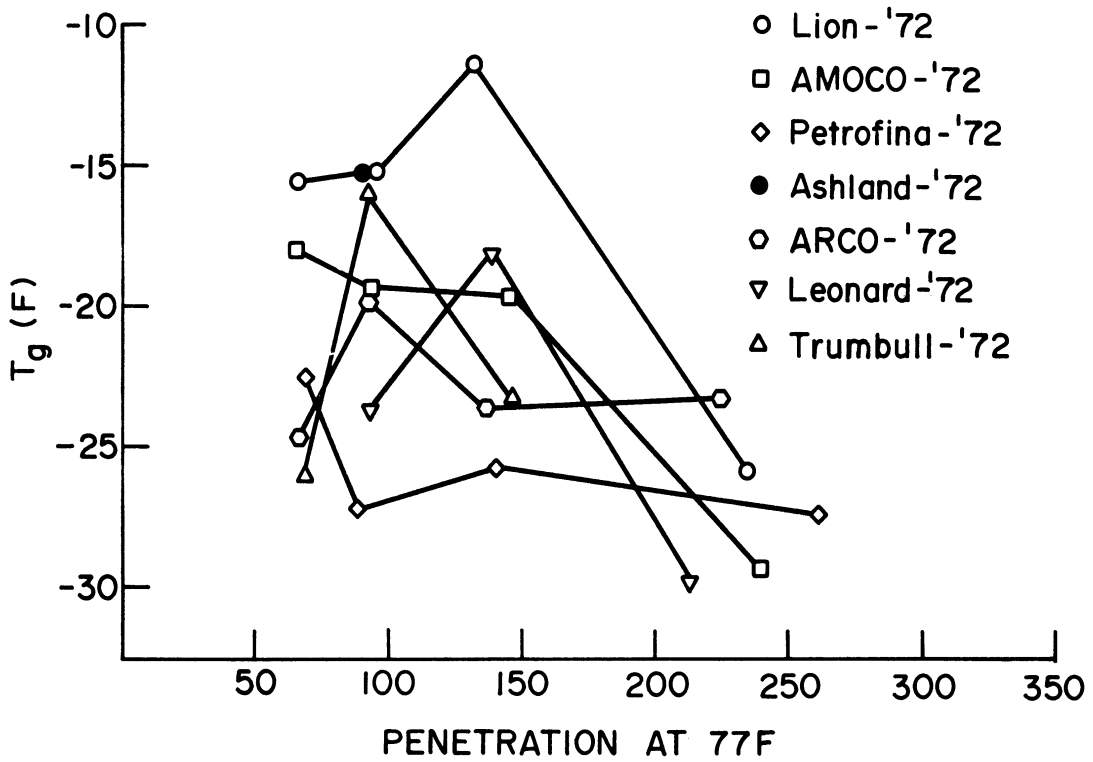


Figure 12. Penetration vs.  $T_g$  for sources A, B, C, D, E, F, and G asphalts.



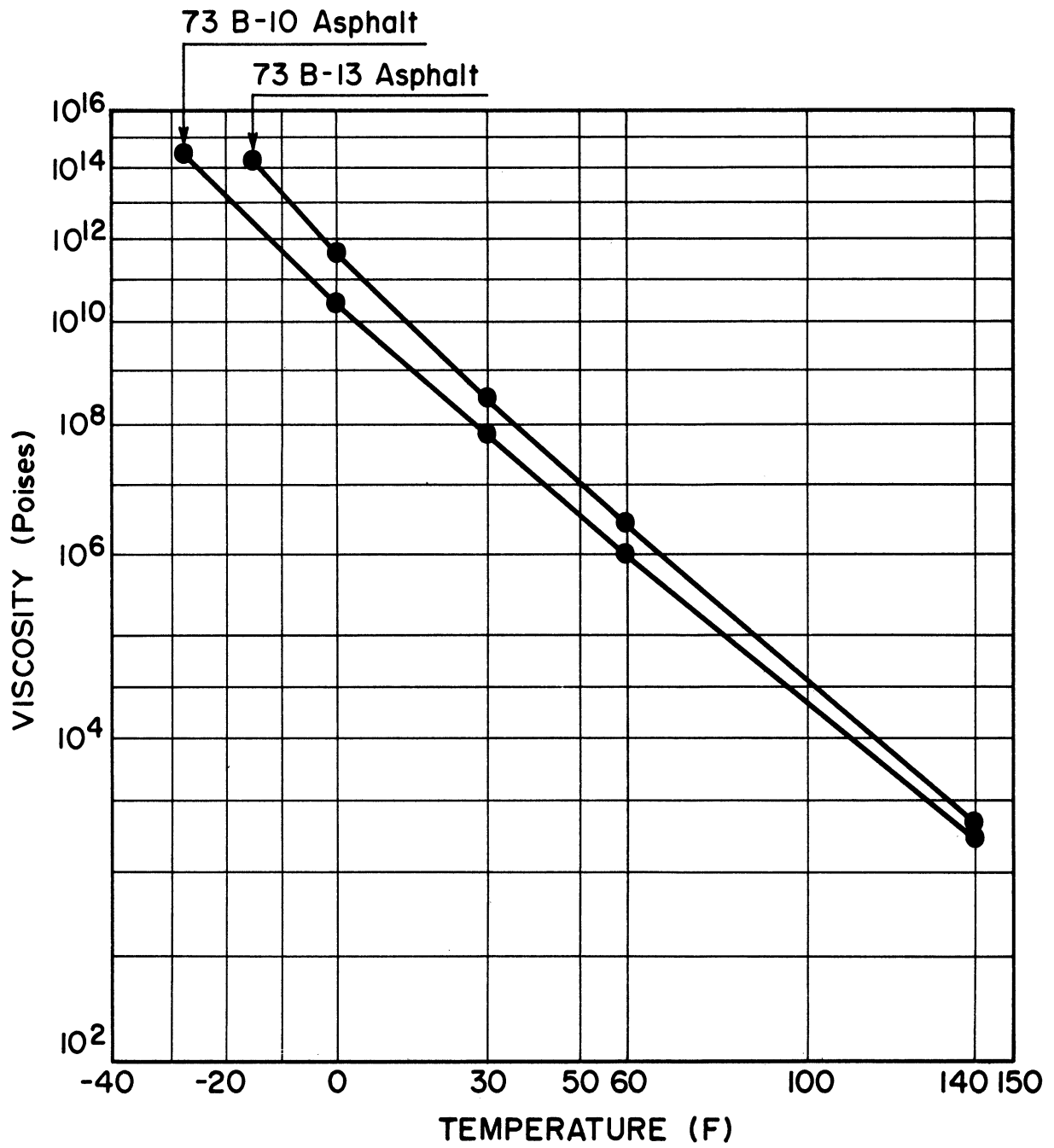


Figure 13. Calculated viscosity using WLF equation,  $T_g$ , and viscosity at 140 F.

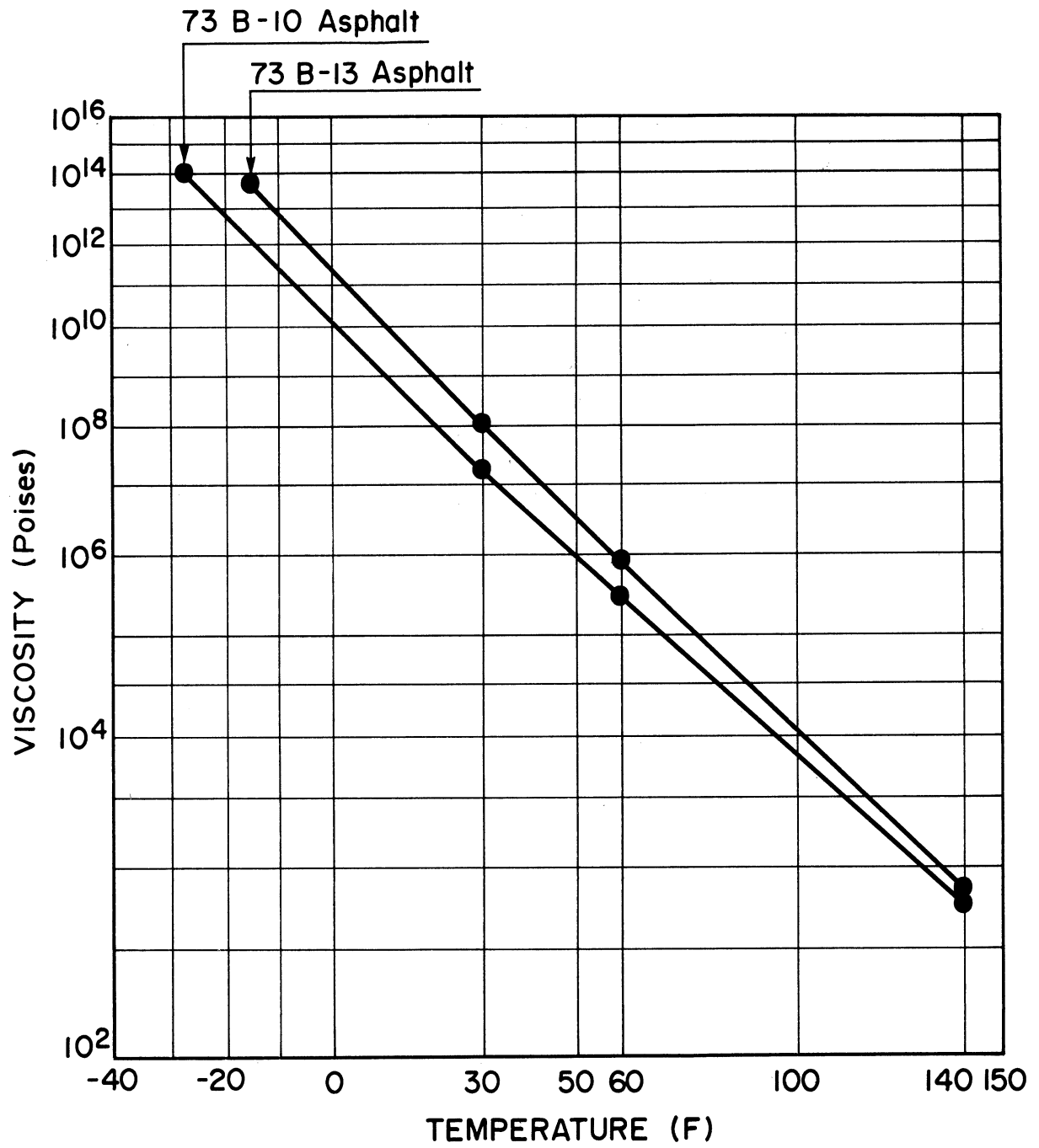


Figure 14. Calculated viscosity using WLF equation,  $T_g$ , and viscosity at 275 F.

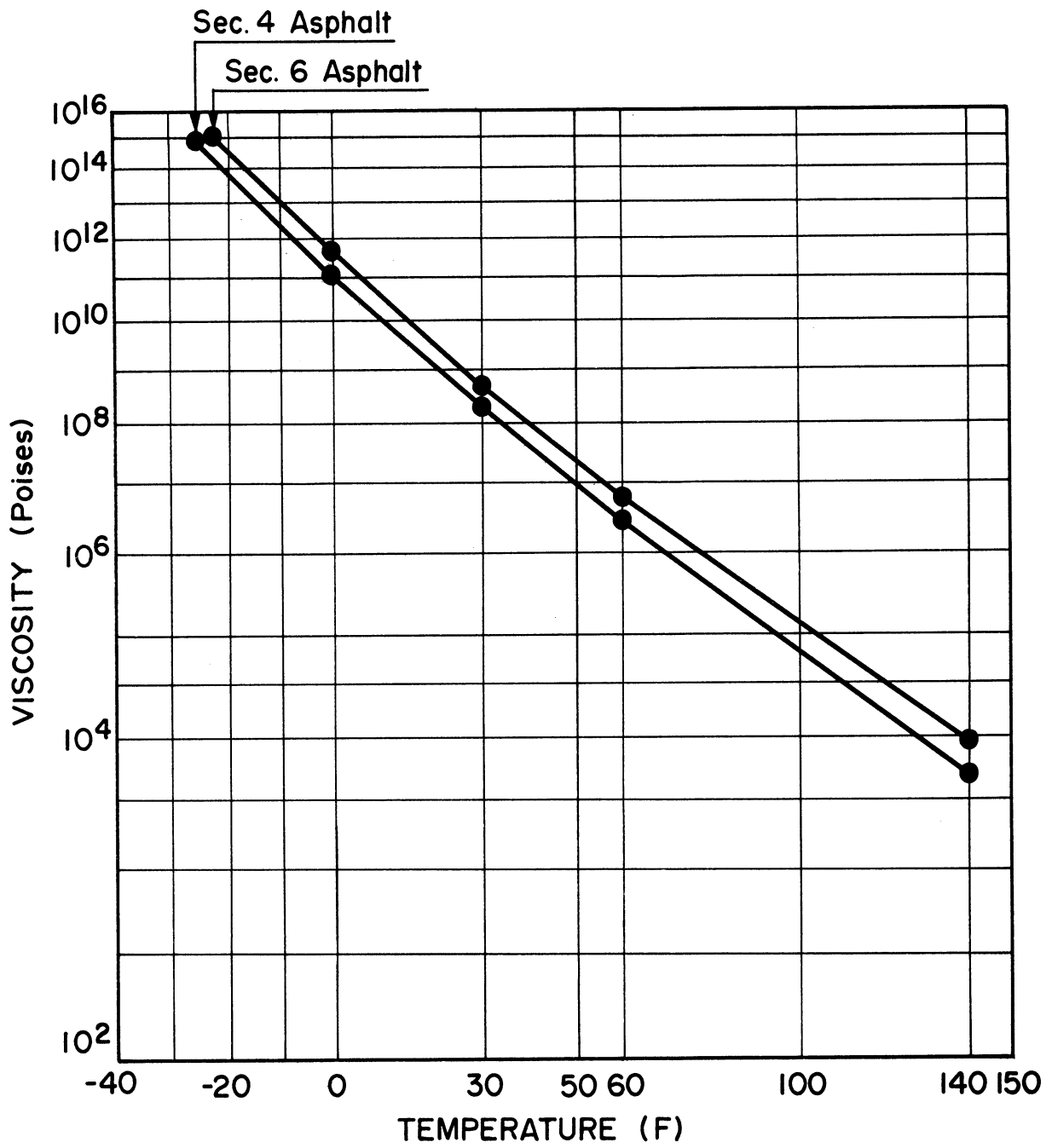


Figure 15. Calculated viscosity using WLF equation,  $T_g$ , and viscosity at 140 F.

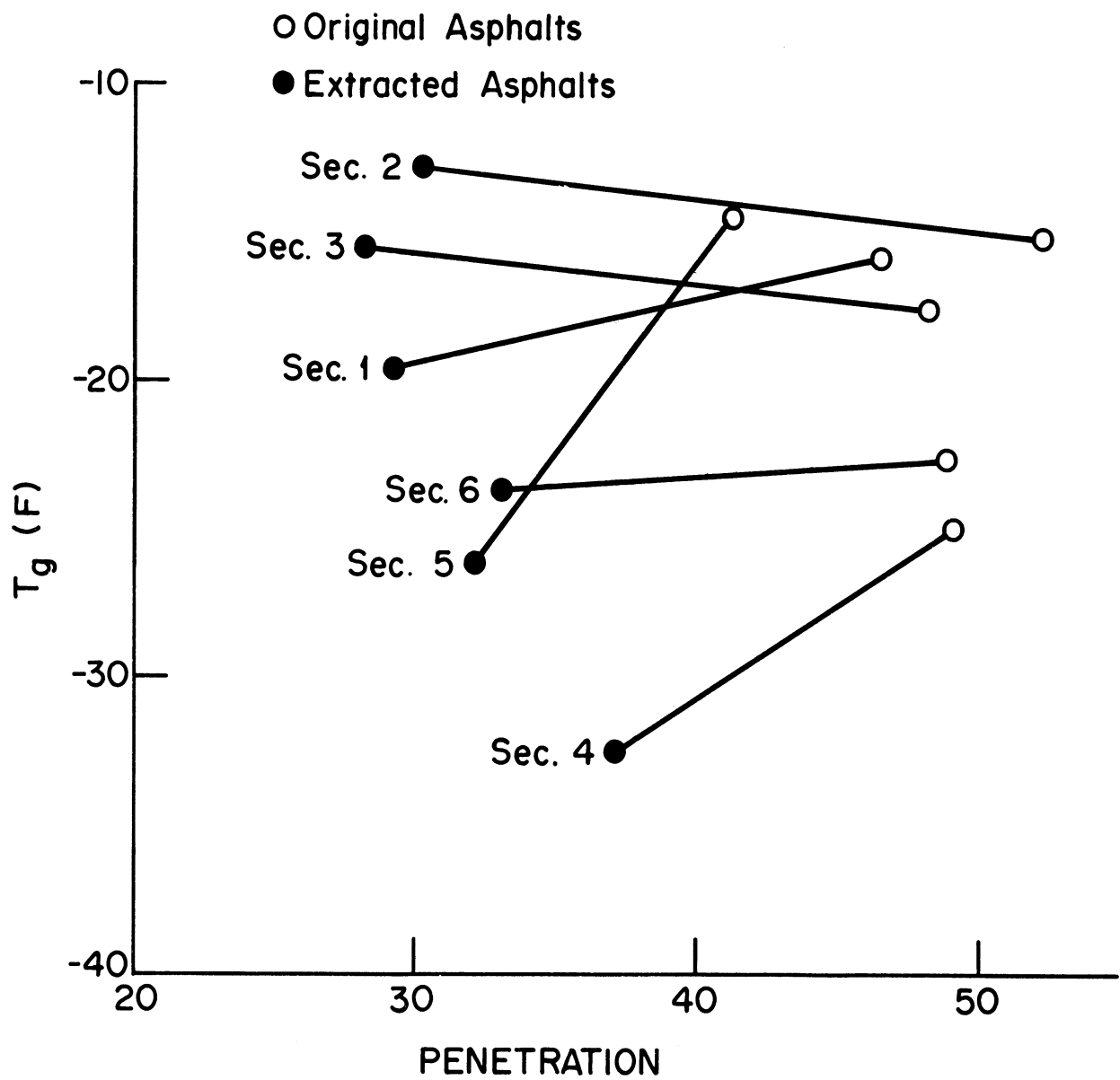


Figure 16. Changes in glass transition temperature and penetration between original asphalts and extracted asphalts used in Michigan Test Road.

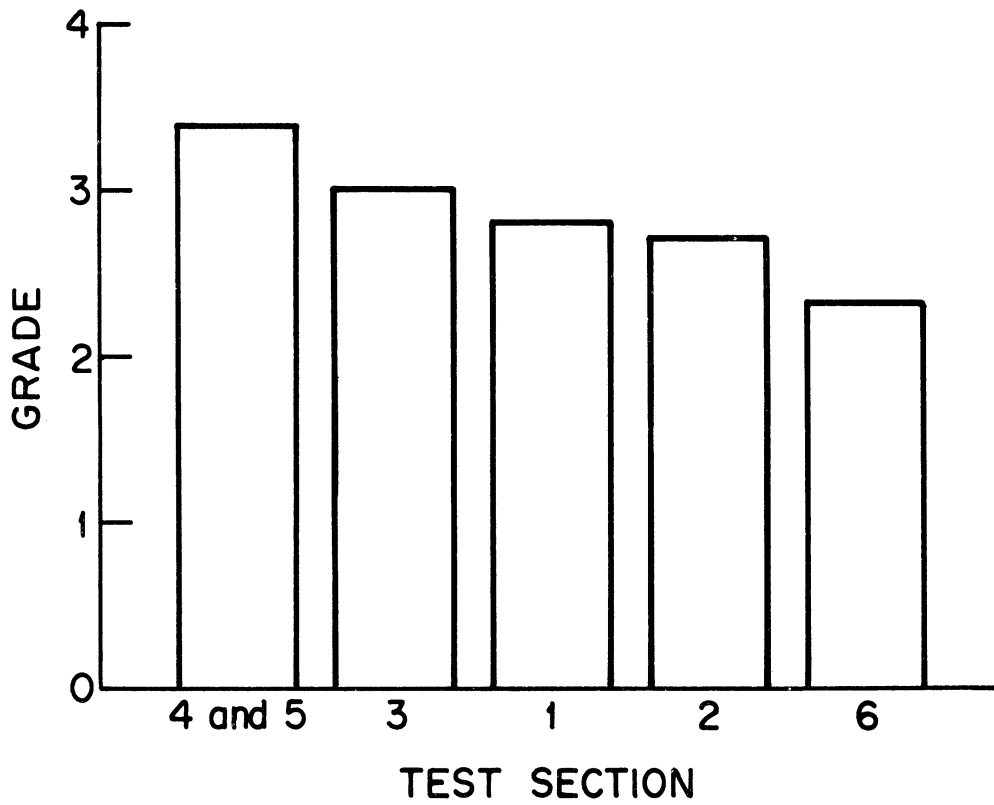


Figure 17. Order of test sections according to estimated performance, Michigan Test Road.

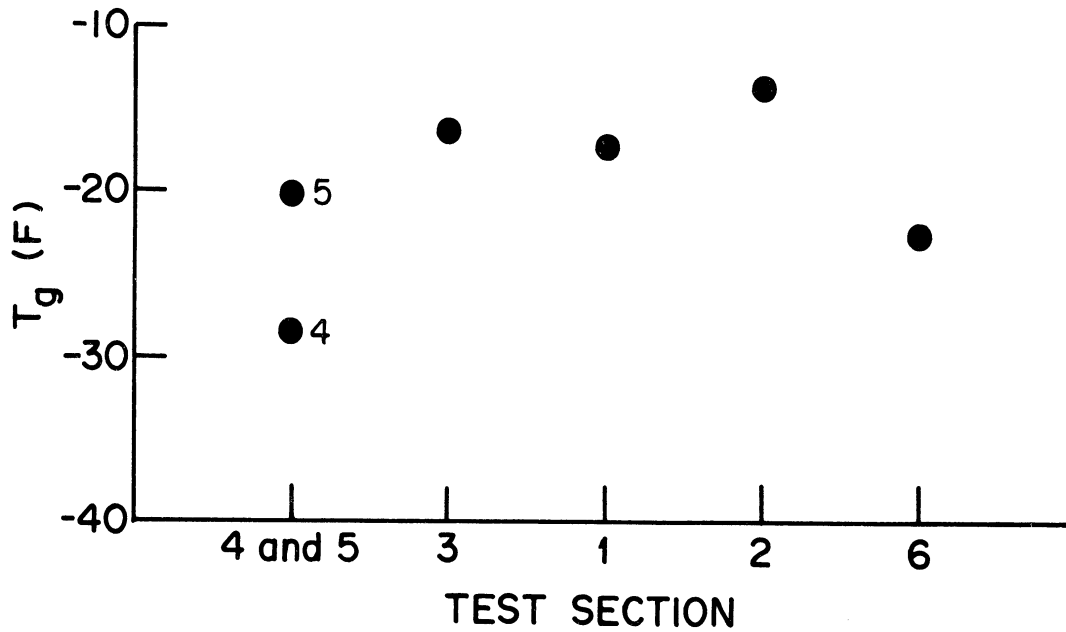


Figure 18. Field performance and T<sub>g</sub>, Michigan Test Road.

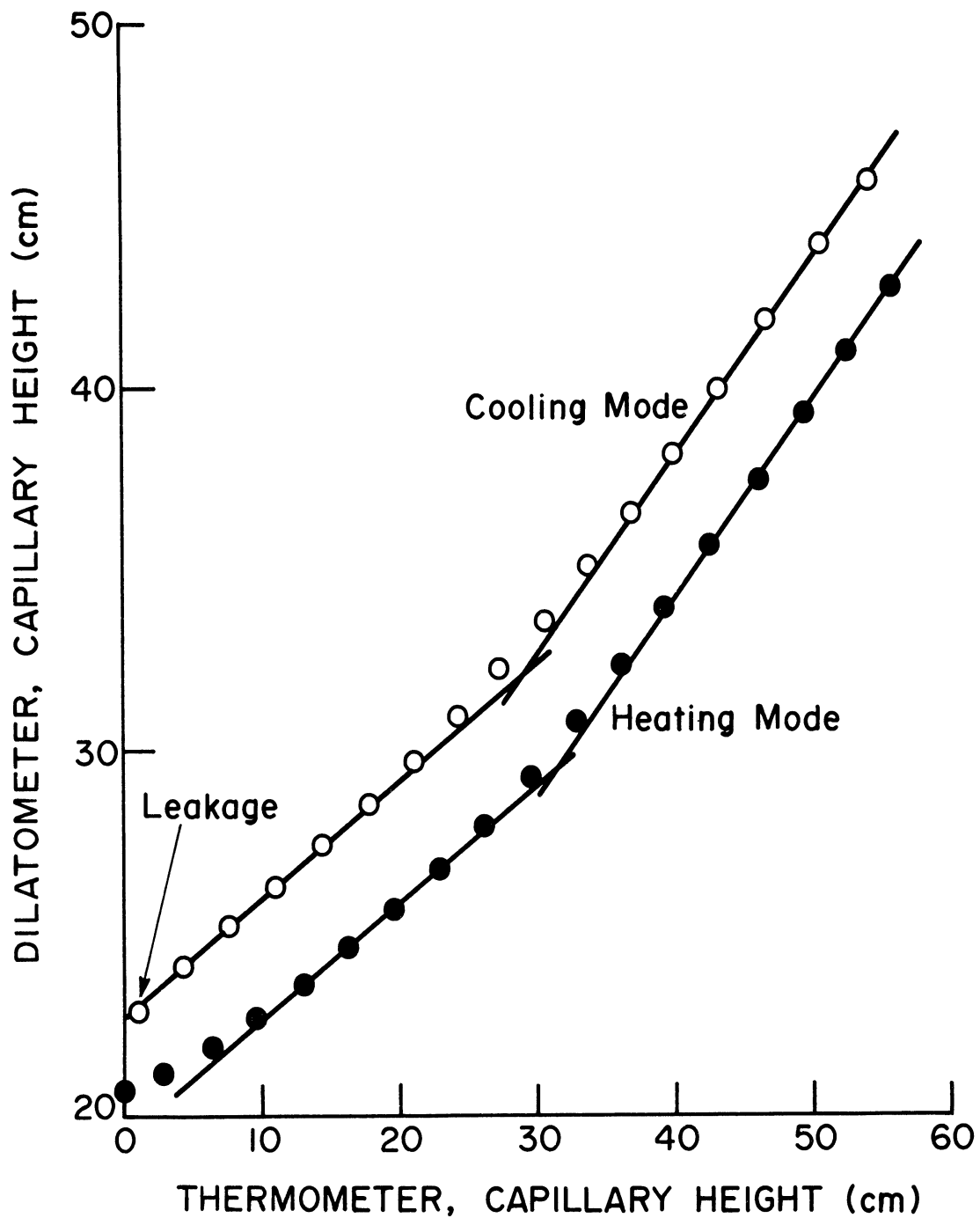


Figure 19. Plots of capillary heights of thermometer and dilatometer which show the leakage of methanol in the dilatometer.

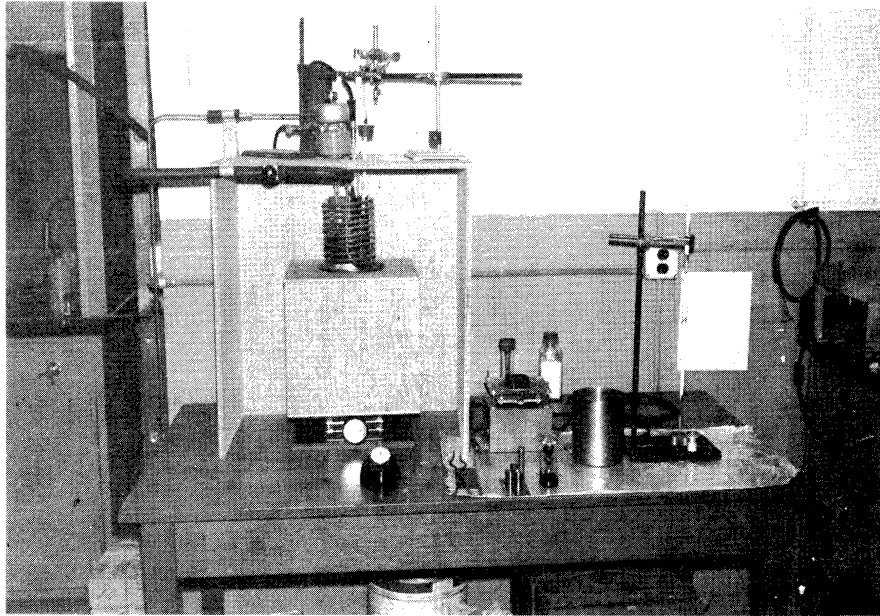


Figure 20. General view of T<sub>g</sub> measurement set-up.

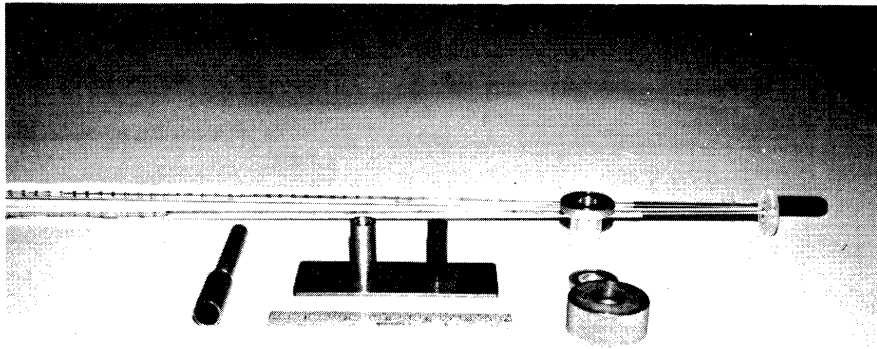


Figure 21. Specimen cell and accessories.

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