

Effect of Aging on Flow Properties of Asphalts

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The effect of aging on flow properties of three asphalts of different origins was studied at different temperatures. The variables considered included: the type of asphalt, the degree of aging, the temperature, and the shear rate. The flow of asphalts was measured by three different viscometers and the aging was done with a modified thin film oven procedure. In order to determine the extent of change in chemical compositions of the three asphalts with the change in degree of aging, a limited study was performed to determine the change in average molecular weights of asphalts, and their asphaltene and maltene components. The results of this study showed that: (a) the degree of aging influences the non-Newtonian response of the asphalts, (b) the aging of the asphalts to any degree does not seem to change their average molecular weights substantially, and (c) a significant change takes place in the flow behavior around the softening point of the asphalts.

•THE aging of asphalt and its subsequent influence on pavement performance have received substantial attention in recent years. Most of the early work used the conventional consistency measures: penetration, ductility, and softening point (1, 2, 3), as a basis for comparison. Some work, however, was done considering various durability tests such as abrasion, weathering, strength, and the Shattuck test (4), as measures of aging. Later with the advent of convenient viscometry techniques, various viscosity measurements were used to study the effect of aging on flow properties of asphalts (5, 6).

The aging technique has also received some attention. The earliest oven test was ASTM's Loss on Heating of Oil and Asphaltic Compounds. A study by Lewis and Welborn (1) was one of many that expressed dissatisfaction with this test. The next development was the Thin Film Oven Test (ASTM, Effect of Heat and Air on Asphaltic Materials). Several investigators suggested that this test be used as a standard method of test for studying the effect of aging on physical properties of asphalts (1, 2, 4).

Following this work came the suggestion that asphalt should be aged under conditions similar to those that exist in the road pavements. Following this line of thinking, Griffin et al (7) and Van Oort (8) investigated microfilm aging. Films of asphalt ranging to 5- μ thick were subjected to the effects of heat, light, and oxygen. Thus, it was realized that other factors besides heat may be operative in the aging process. Griffin et al (7) showed that a large part of hardening was due to loss of volatiles, but that oxidation and light when the samples were in extremely thin films contributed significantly to hardening. Van Oort (8) developed differential equations for the oxygen aging process. Halstead and Zenewitz (6) made a comparison study of hardening as measured using the sliding plate microviscometer between the microfilm test and the thin film test. Their results showed greater hardening for the former test for asphalts with aging indices greater than two.

Another approach to thin film aging was the tilted, rotating-shelf oven. This procedure first developed by Vallerga et al (3) was used in a study of the aging effect of heat,

infrared light, and ultraviolet light. The results showed that generally weathering severity increased with tests using ultraviolet radiation, infrared radiation, and heat, respectively. Several other methods of aging and of detecting aging have been proposed. One such study (9) involved weathering thin films of roofing asphalts in an Atlas Weather-Ometer. An infrared spectrophotometer was used to scan the samples before and after aging. The change in the absorption of the carbonyl band was used as a measure of oxygen-containing functional groups within the asphalt.

A third general type of study which must be used in conjunction with the development of measuring and aging techniques is represented by full scale, unaccelerated aging investigations. Gallaway (10) reported the results of standard and special tests on several surface treatment type pavements in various parts of Texas. The annual changes in rheological and compositional characteristics of in service pavements were compared with artificially aged samples. Two articles by Welborn and Halstead (11) and Welborn et al (12) reported the results of a general nationwide study of several hundred asphalts. The study revealed the wide variation on paving grade asphalts from different producers and different sources, and the need for more adequate test methods and specifications. A report by Simpson et al (5) on the Zaca-Wigmore Experimental Project used a micro-film durability test to predict failure occurrences of different asphalts used in a test road. Actual failure occurrence was reported as in agreement with the predictions of the durability tests.

The information available on the behavior of aged asphalts thus shows that a thorough investigation of the effects of aging on flow properties of the asphaltic materials should provide some information necessary for prediction of the pavement performance during its service life.

MATERIALS

The three asphalt-cements used in this study were a 60-70 penetration grade asphalt-cement from a Venezuelan crude, an AC-20 grade asphalt-cement coded B-3056, and an AC-20 grade asphalt-cement coded B-2960, the latter two were from The Asphalt Institute-Bureau of Public Roads Cooperative Study of Viscosity-Graded Asphalts. The results of conventional tests on the asphalts are given in Table 1.

PROCEDURE

The flow measurements were made with three different types of viscometers. A sliding plate microviscometer, made by Hallikainen Instruments, and a Varian Model G-14 graphic recorder were used to obtain data in a shear rate range of 10^{-6} to 1 reciprocal seconds and temperature range of 5 to 60 C. Capillary tests were run with Cannon-Manning vacuum viscometers using the Cannon vacuum regulator and a model H-1 high temperature oil bath.

At least three tests were run at each test temperature to describe the range of shear rates available. Test temperatures varying from 45 to 160 C were used. The principal limitation of these viscometers was the range of shear rate. Using any workable combination of tube size and vacuum gave little over one decade of shear rate in reciprocal seconds for any one temperature. In order to provide data for low shear rates at higher temperatures, a Haake Rotovisco with coaxial cylinders was used. This instrument and its test procedure is well described by Van Wazer et al (13).

This viscometer provided a minimum shear rate of 3×10^{-3} reciprocal seconds. The minimum test temperature used with this instrument was 45 C. Below this temperature, stress levels exceeded the instrument limits.

Aging

Aging of the asphalt was done with a modified thin film oven procedure developed by Vallerger et al (3). The oven was vented to the atmosphere at the bottom. The

TABLE 1
RESULTS OF CONVENTIONAL TESTS

Test	Asphalt		
	60-70	B-3056	B-2960
Specific gravity 77/77 F	1.010	1.020	1.034
Softening point, ring and ball	123 F	—	125 F
Ductility 77 F	150 + cm	250 + cm	—
Penetration			
100 gm, 5 sec, 77 F	63	—	—
200 gm, 60 sec, 39.4 F	23.5	30	—
Flash point, Cleveland open cup	465 F	545 F	515 F

rotation shelves were canted at 10 deg to the horizontal and rotated at 5 to 6 rpm throughout the test.

Separation of Asphalt into Asphaltenes and Maltenes

The procedure followed for separation was identical to that used by Dabin (14) and described in detail by authors elsewhere (21).

Intrinsic Viscosity Determination

Five different solutions of asphalt in benzene were made in concentrations ranging from 0.2 to 6.0 gm/100 cc of solution. The viscosity of these solutions was determined at 77 F using a capillary viscometer. The viscosity tests were conducted at different shear rates to check the effects of gelation. Gelation effects (reduction in viscosity with a higher shear rate) were noticed for 10 percent solutions of asphalts in benzene (15).

The viscosity of benzene (the solvent) was similarly determined, and the following procedure was then used to determine the intrinsic viscosity. Relative viscosity is defined as

$$\eta_{rel} = \frac{\eta_{solution}}{\eta_{solvent}}$$

and the specific viscosity as

$$\eta_{sp} = \eta_{rel} - 1$$

If c denotes the concentration of the solution in grams of asphalt per 100 cc of solution, the intrinsic viscosity of the solution, by definition is

$$\eta_{intr} = \lim_{c \rightarrow 0} \left(\frac{\eta_{sp}}{c} \right)$$

hence the plot of η_{sp} vs c , and extrapolation of this to $c = 0$, yields intrinsic viscosity, which when used in Standing relation gives the molecular weight of the material.

Molecular Weight Determination

Two procedures for the direct molecular weight determination were used in this study, the ebullioscopic method and a vapor pressure Osmometer (Mechrolab Osmometer). The test procedures are described in the Appendix.

RESULTS AND DISCUSSION OF RESULTS

Analysis of Flow

To display the relative consistency differences among the three asphalts used in this study and to establish a flow model for the asphalts, shear rate vs shear stress diagrams on a logarithmic scale were constructed. Figures 1, 2, and 3 show diagrams for the three asphalts at test temperatures varying from 5 to 160 C. In general, the data produced straight lines and a power function of the type

$$\tau = A(\dot{\gamma})^n \quad (1)$$

could be used to represent the flow behavior of these asphalts, with the slope of the line, n , being an indication of the non-Newtonian behavior. As n deviates from unity (the Newtonian case) the flow behavior becomes more non-Newtonian. The three asphalts show non-Newtonian flow at temperatures equal to or below 45 C. The data

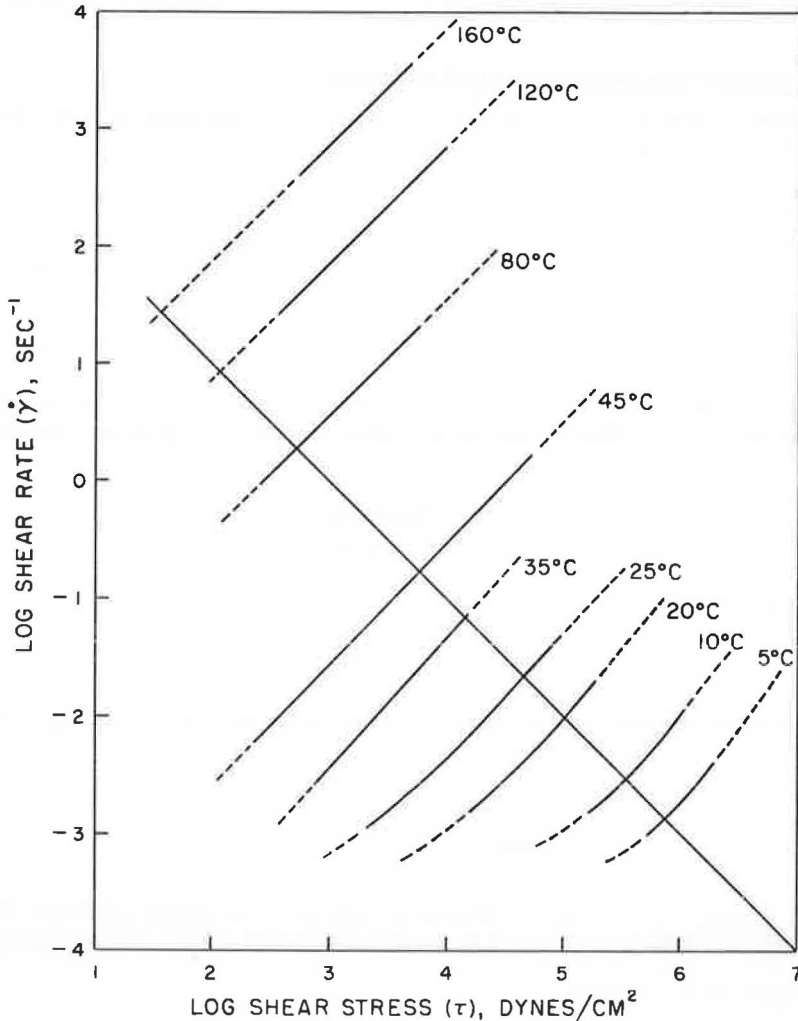


Figure 1. Shear rate vs shear stress on log-log scales for 60-70 penetration grade asphalt at all test temperatures.

curves at 45 C and lower temperatures also indicate that the B-3056 asphalt is the most non-Newtonian in flow behavior. This is evident from the slope of the flow diagrams. The B-3056 asphalt has the lowest values of the slope, n , while the value of the slope for the 60-70 penetration is the closest to unity.

The Temperature Effect—For Newtonian materials it has been shown that viscosity is independent of shear stress and/or shear rate, and is a constant at any one temperature. For such a material, the relationship describing the temperature dependency of viscosity is independent of shear rate or shear stress, and can be expressed satisfactorily by the Arrhenius equation.

$$\eta = A \exp (\Delta E/RT) \quad (2)$$

where R is the universal gas constant, and A and ΔE can be considered as constants over limited temperature ranges.

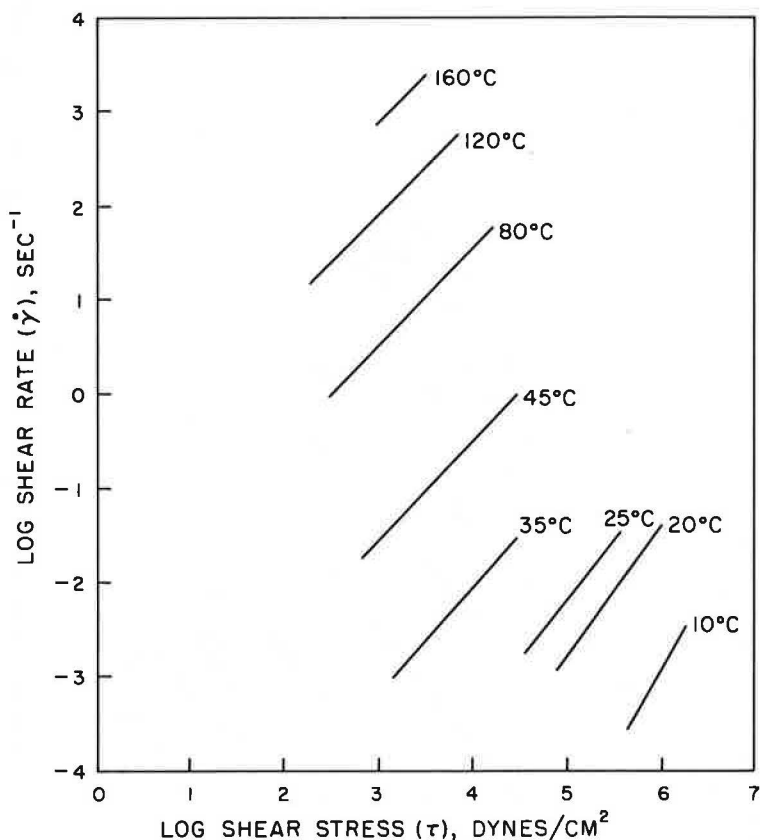


Figure 2. Shear rate vs shear stress on log-log scales for B-3056 asphalt at all test temperatures.

For non-Newtonian materials, however, the viscosity at a fixed temperature is dependent on shear stress or shear rate. Therefore, in order to develop an expression such as Eq. 2 to represent the temperature dependency of the viscosity of a non-Newtonian material, either A or ΔE or both must be considered as functions of shear stress or shear rate. To avoid this dependency on shear stress or shear rate, and still be able to compare viscosities at different test temperatures, viscosity is measured at a constant shear stress, shear rate, or power input.

In the case of the data obtained for the three asphalts of this study, the comparison of viscosities at different test temperatures for fixed shear stresses or shear rates would necessitate excessive extrapolation of the data at either of the extremes of temperature. The method of constant power input although rather arbitrary in nature, does offer the advantage that very little extrapolation of data is necessary. Consequently this method of comparison was used, and a constant power input of $1000 (\tau \times \dot{\gamma})$ per unit volume was chosen as convenient.

The most suitable method of representing the viscosity change with a change in temperature was to plot the logarithm of apparent viscosity, as determined by a constant power input, versus the reciprocal of the absolute test temperature as shown by the lowest curve in Figures 4, 5, and 6. In the case of all three unaged curves, the viscosity-temperature relationship is two straight lines intersecting at a point near the ring and ball softening point of the asphalt. Then, except for the small range of temperature around the softening point, the temperature dependency of viscosity may be represented by an Arrhenius type equation of the form of Eq. 2 with different slopes above and below the softening point, but constant in each range.

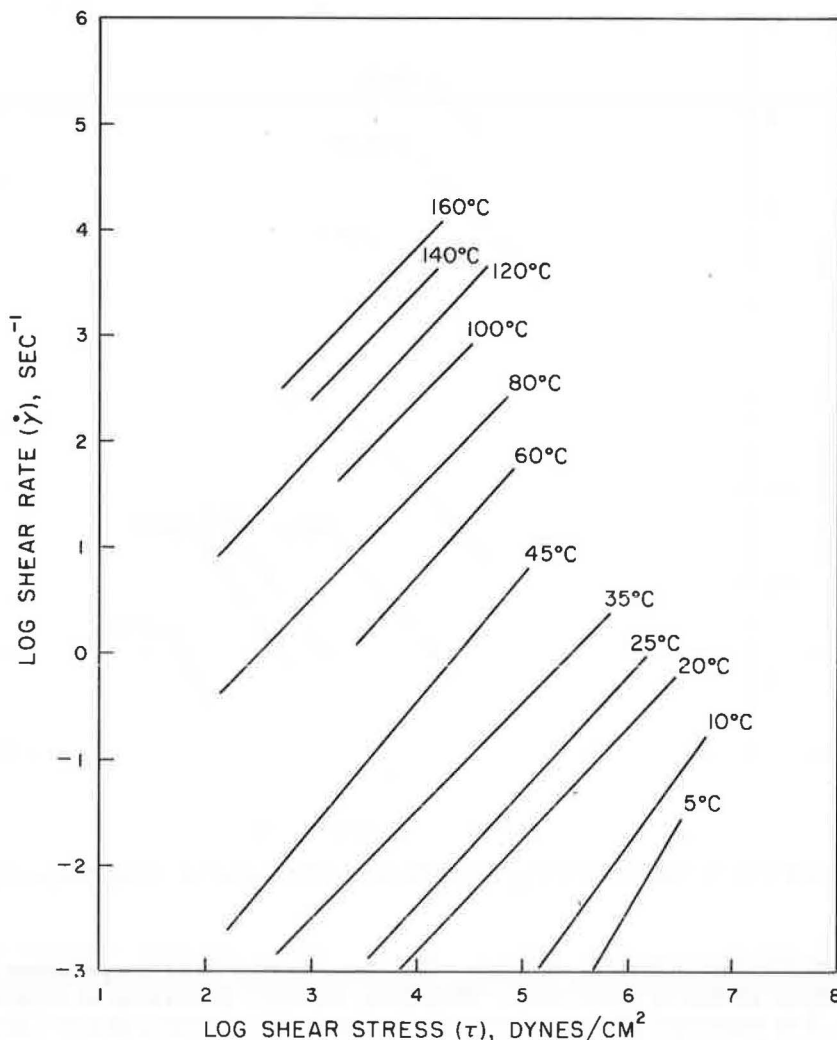


Figure 3. Shear rate vs shear stress on log-log scales for B-2960 asphalt at all test temperatures.

The curved portion of the viscosity-temperature curve denotes some relatively rapid physical changes in the flow behavior of the three asphalts at about the temperature measured as the softening point of the material. This transition zone is discussed in detail in subsequent sections.

Although this study encompassed a relatively wide range of test temperature and shear rate, instrument limitations confined the useful shear rate range at any one test temperature to a maximum of three logarithmic decades of shear rate in reciprocal seconds. Since, under ordinary pavement conditions, an asphaltic binder could be subject to very low shear rates such as thermal expansion and contraction, and to very high shear rates such as during the compaction process, it would be very useful to establish the flow diagram of an asphalt over a much wider range of shear rate than is possible with all but the most sophisticated equipment. To obtain an indication of the behavior of materials over a wide range of shear stress or shear rate, Ferry's principle of reduced variables (16) was used and Figures 7, 8, and 9 were constructed using appropriate values of the shift factor, a_T . These figures show that a master curve can be constructed for the three asphalts covering approximately seven logarithmic decades

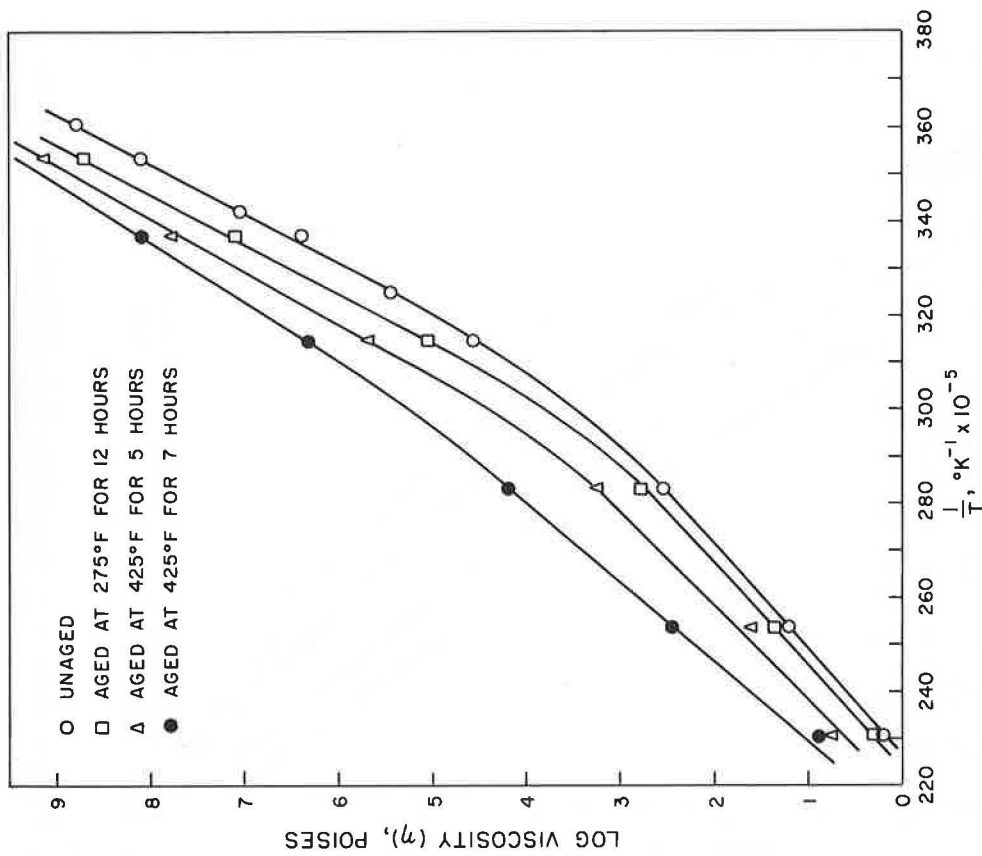


Figure 4. Viscosity vs reciprocal absolute test temperature for unaged and various agings of 60-70 penetration grade asphalt.

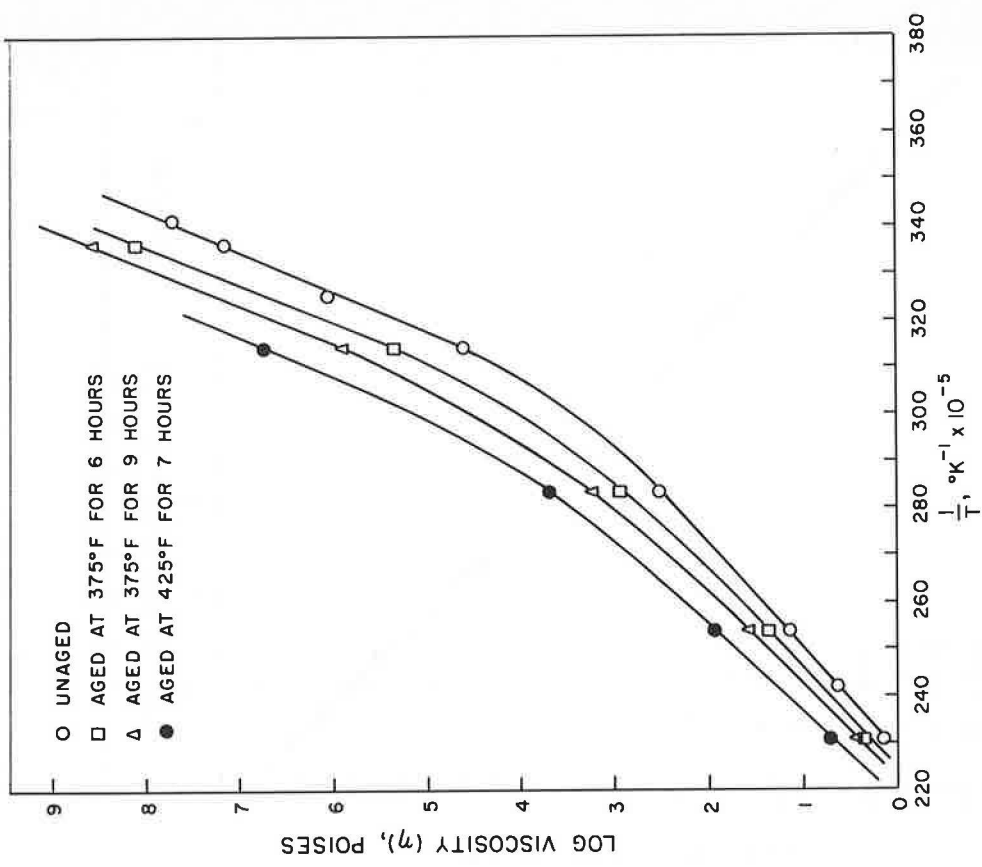


Figure 5. Viscosity vs reciprocal absolute test temperature for unaged and various agings of B-3056 asphalt.

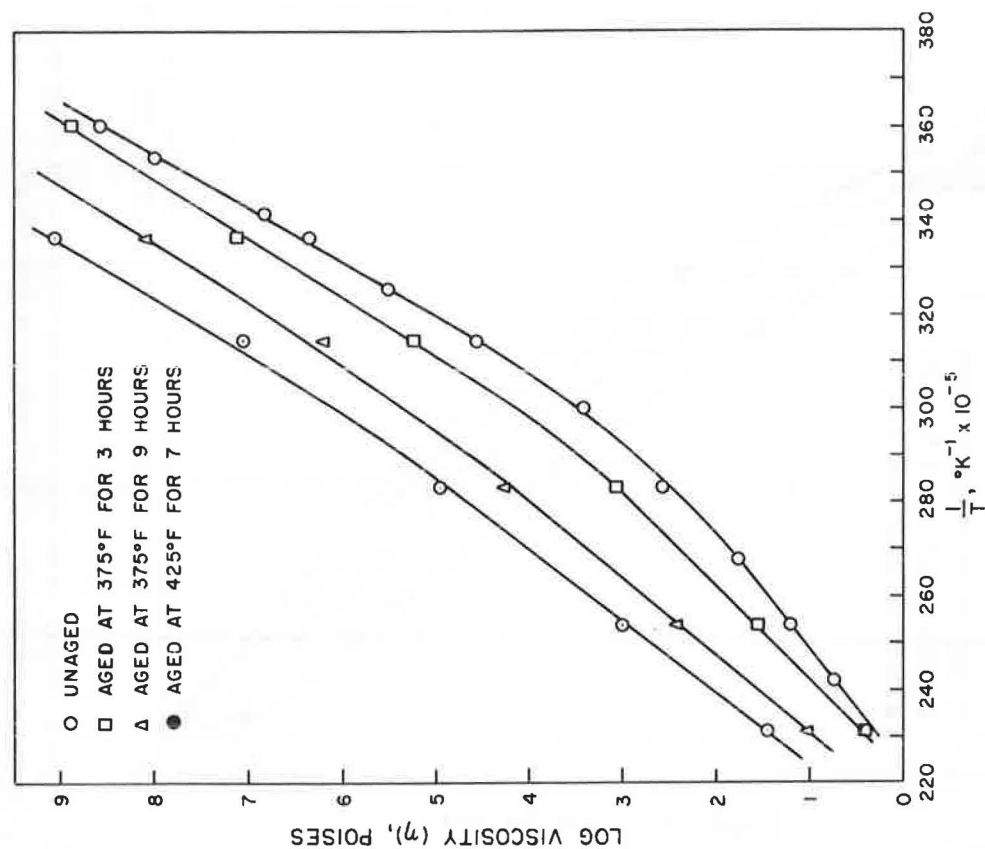


Figure 6. Viscosity vs reciprocal absolute test temperature for unaged and various agings of B-2960 asphalt.

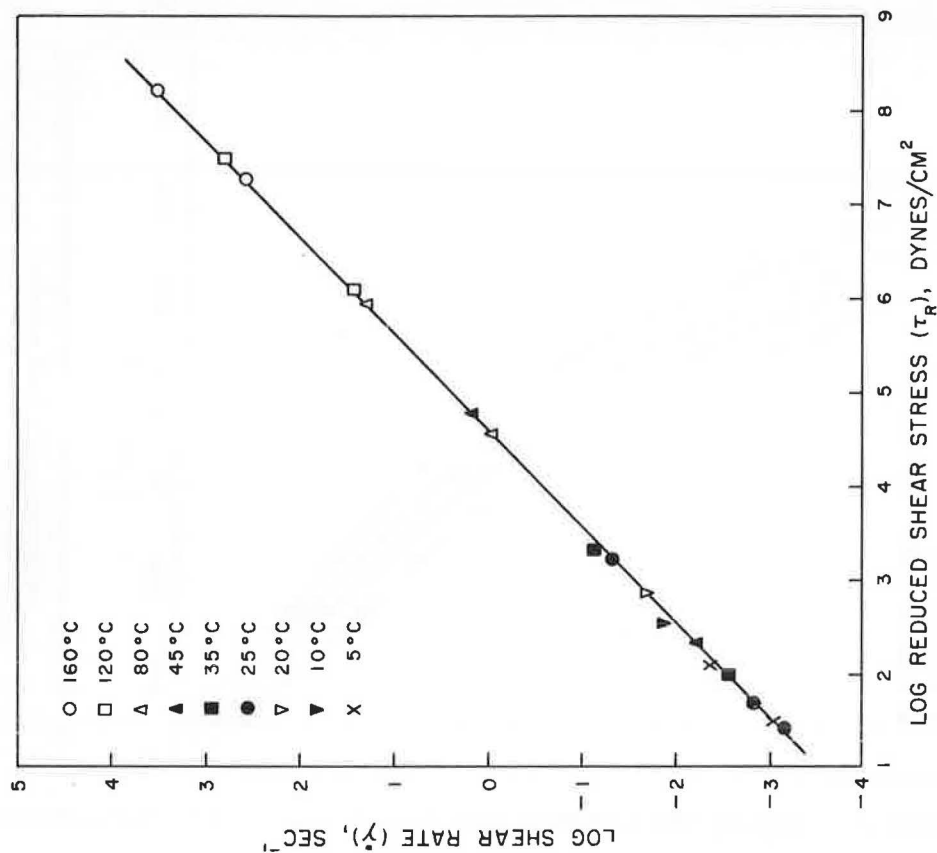


Figure 7. Master flow diagram for 60-70 penetration grade asphalt.

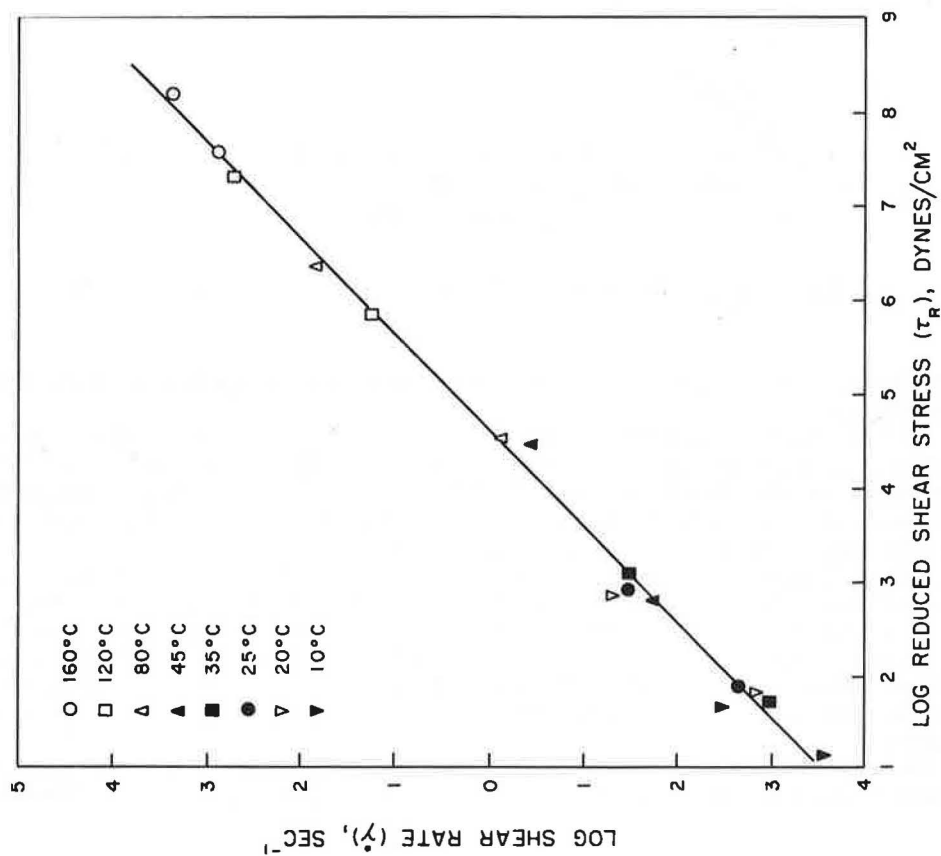


Figure 8. Master flow diagram for B-3056 asphalt.

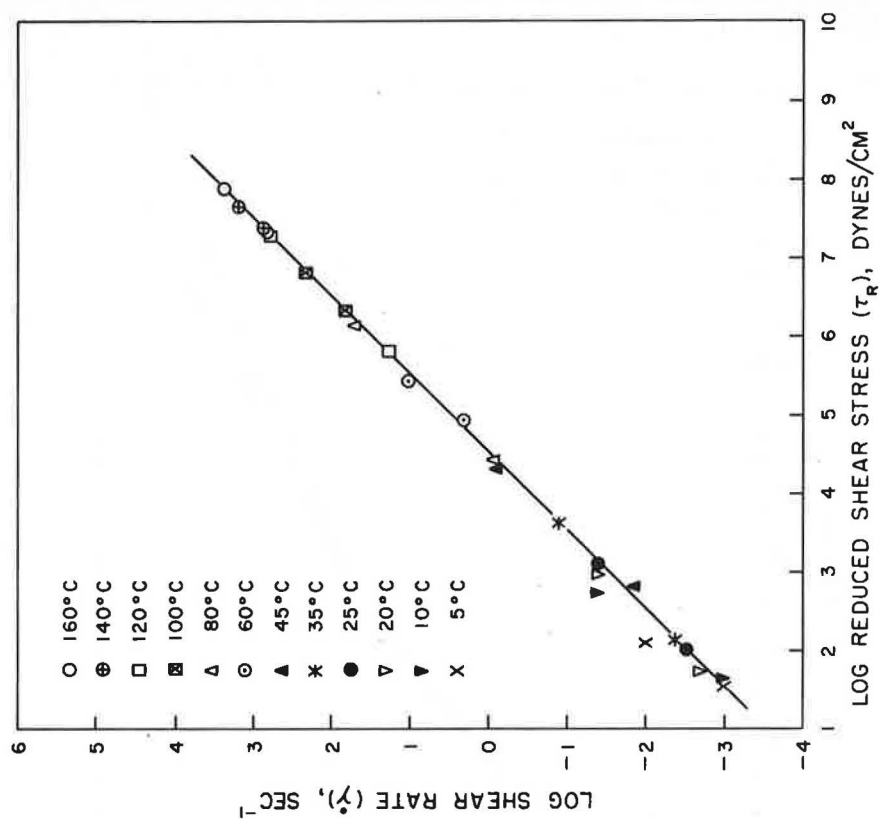


Figure 9. Master flow diagram for B-2960 asphalt.

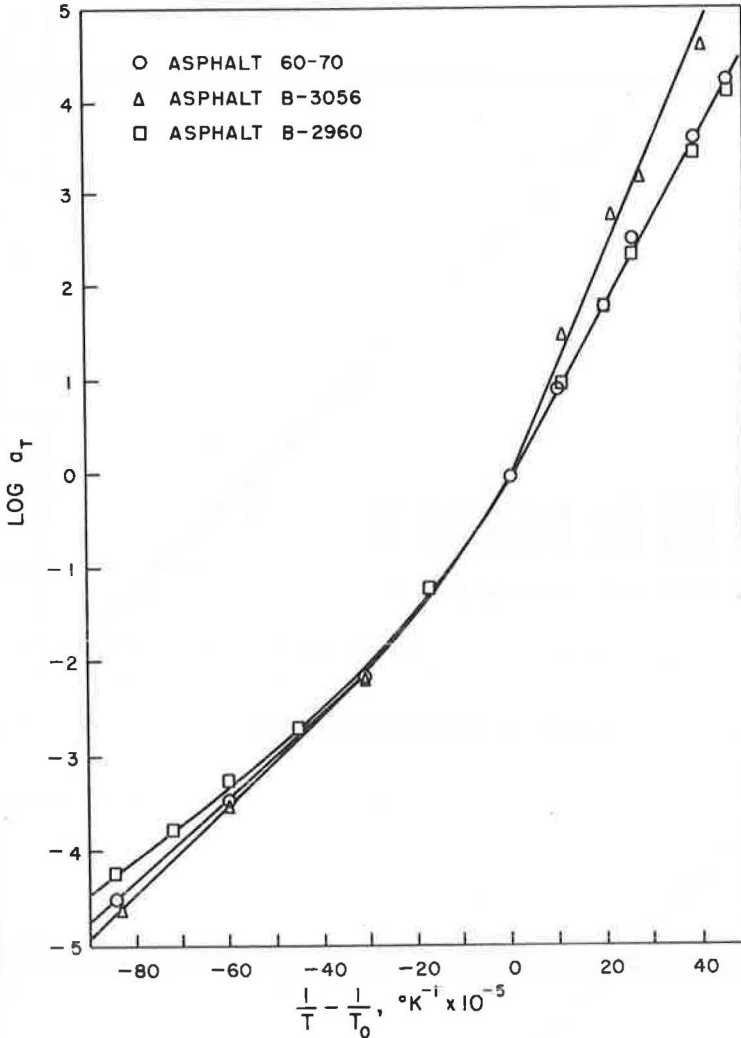


Figure 10. Shift factor vs $1/T - 1/T_0$ for all unaged asphalts at $T_0 = 318^\circ\text{K}$.

of shear rate and the curves of the different temperatures superimpose in a continuous straight line.

Previous work in the investigation of the principle of reduced variables has shown that in general the viscous response of materials is influenced by a singular mechanism, and therefore, the shift factor calculated for any one variable reduction should be transferable to another variable reduction. For this reason it would be desirable to express the variation of the shift factor with temperature.

Figure 10 plots the logarithm of a_T versus $(1/T - 1/T_0)$. For all three asphalts, a_T is a continuous function of temperature for the range of temperatures studied. The form of the curve is also the same as that for the viscosity-temperature curves (Figs. 4, 5 and 6). The curves are made of two straight line segments joined by a relatively narrow transition range. As in Figures 4, 5, and 6, the transition range on the curves is around the point conventionally described as the ring and ball softening point of the asphalt.

The apparent activation energy of the asphalts can be calculated from the Arrhenius equation (Eq. 2) as developed for the unaged curves (Figs. 4, 5, and 6). Dividing each

curve at the point of curvature into two segments gives two models for the flow behavior:

$$\eta_a = A' \exp (\Delta E'/RT) \quad T > \text{softening point} \quad (3)$$

$$\eta_a = A \exp (\Delta E/RT) \quad T < \text{softening point} \quad (4)$$

It is clear that within their ranges, A , A' , ΔE , and $\Delta E'$ are constants. ΔE and $\Delta E'$ have units of energy and are the apparent activation energies of the asphalt. Based on the theory of rate processes, Glasstone et al (17) have shown that the constant A can be related to the molar volume of the material, entropy of activation, and Planck's constant so that

$$A = \frac{hN}{V} \exp (-\Delta S/R) \quad (5)$$

where h is Planck's constant, N is Avogadro's number, V is the molar volume of the material in the liquid state, and ΔS is the change in the entropy of activation. From Figures 4, 5, and 6 it can be seen that $A > A'$ and that $\Delta E' > \Delta E$. In other words, around the point of curvature, either the entropy of activation or the molar volume, or both must decrease with an increase in test temperature.

The activation energy may also be calculated either from the shift factor a_T (16), or the hyperbolic sine model for flow (18). Table 2 gives the apparent activation energies as calculated by the three methods of analysis for each of the three asphalts in both the high and the low temperature ranges. The deviation of the values calculated from the hyperbolic sine relationship is due to the existence of a limiting shear stress for any material beyond which hyperbolic sine relationship fails to represent the flow behavior of the material. This point is discussed in detail elsewhere (18).

Table 2 indicates that the values of apparent activation energy for all three asphalts at high temperatures are less than one-half the values at low temperatures. Both the 60-70 penetration grade and the B-2960 asphalts have a ratio of high temperature ΔE 's to low temperature ΔE 's of 0.46 ± 0.01 . These two asphalts have previously shown similar behavior. The B-3056 has a ratio of 0.40 ± 0.01 , and has previously shown consistently different behavior from the other two asphalts. It is possible then that this ratio could be used as an index of flow behavior over a wide range of temperature.

Structural Concept—The consistency-temperature relationship for asphalt is in general characterized by three distinct regions of behavior: the flow region, the softening transition region, and the glassy transition region. The flow region can be defined as that region of temperature above the point of curvature, or the softening point of the material. The connotation of "softening point" as used here is slightly different from that which is commonly used. Rather than a certain temperature at which a distinct event occurs, the softening point is used to denote a range of temperatures over which

a transition takes place in the material. Within the flow region, asphalts behave as Newtonian materials and are very temperature susceptible. Adhering to the idea that asphalt is a three phase colloidal system of asphaltenes, resins, and oils in this temperature range, the asphaltenes are completely unassociated and the high temperature susceptibility is due to the released oily fraction which is normally held by the asphaltenes at lower temperatures.

TABLE 2
APPARENT ACTIVATION ENERGY AS CALCULATED BY
DIFFERENT METHODS

Asphalt	Temp. Range	ΔE Kcal/°K mole Calculated from		
		Figures 4-6	Figure 10	Ref. 18
60-70 pen.	high	20.8	19.1	13.5
	low	45.0	41.0	24.1
B-3056	high	20.8	21.8	19.5
	low	53.9	53.9	29.9
B-2960	high	18.35	16.95	17.6
	low	39.3	39.3	24.5

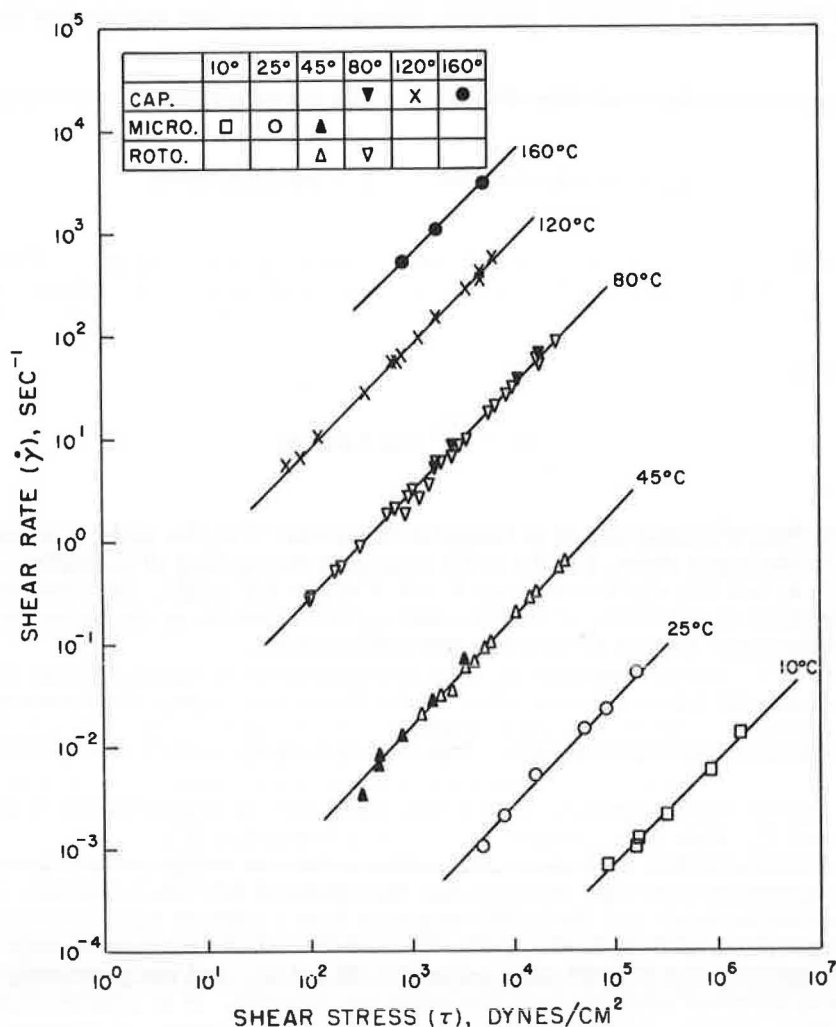


Figure 11. Shear rate vs shear stress on log-log scale for 60-70 penetration grade asphalt at all test temperatures, aged at 275 F for 3 hours.

In a much simplified manner the viscosity of the system, in this flow region, is almost entirely dependent on the amount of oil that is freed to "lubricate" the system.

Descending on the temperature scale, the next region is that described as the softening transition region. This region is bounded by the softening point on the upper end and the glass transition temperature on the lower end. Here again, the glass transition temperature refers to a range of temperature rather than one specific temperature. In the softening transition region, the material is less temperature susceptible than in the flow region, and the principal mechanism of changing viscosity with changing temperature is the disassociation of the asphaltene molecules. As the temperature increases over this range, the higher thermal agitation and smaller flow units result in a lower viscosity. The process is possible because the association bonds holding the flow units together can operate only over very short distances.

Dropping still further in the glassy state, it is found that the molecules of asphaltene are practically immobile. A definite structure has been formed and in this region flow is very much like the creep of solids. The asphaltenes have formed strong association bonds throughout the structure and have trapped most of the oils which could have made

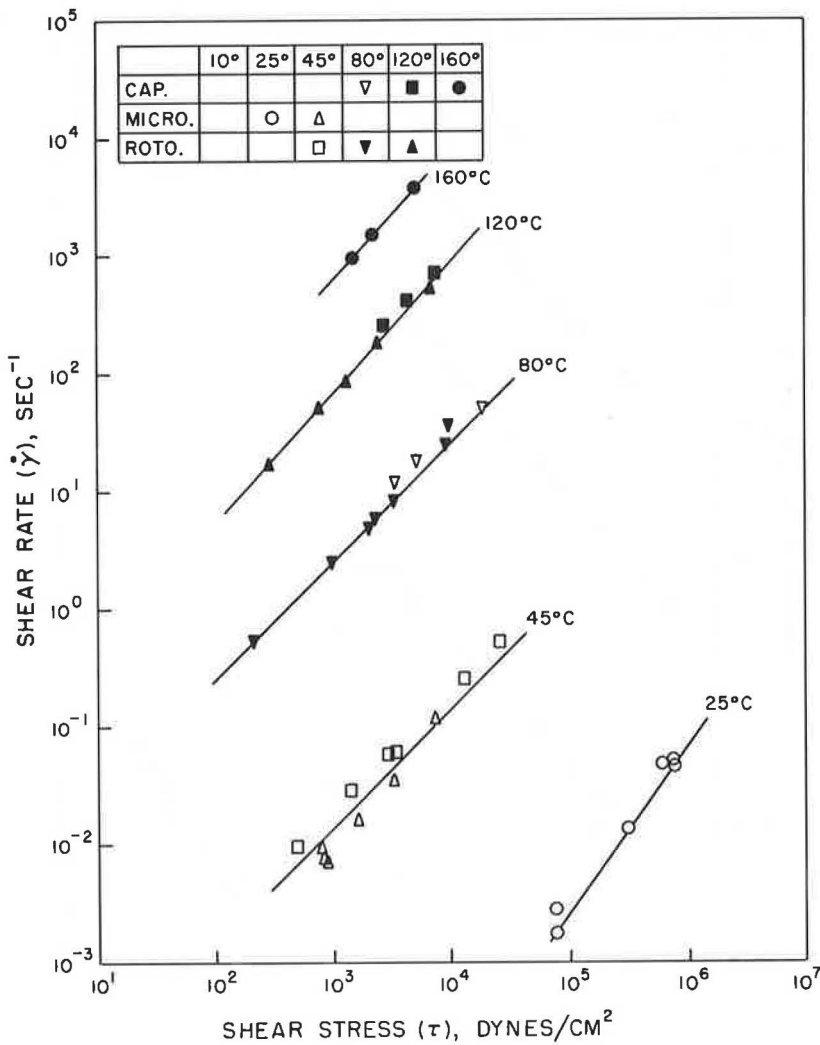


Figure 12. Shear rate vs shear stress on log-log scales for B-3056 asphalt at all test temperatures, aged at 275 F for 3 hours.

flow possible. In each of the three flow regions there is a process of continuous change. At the division points, some relatively radical changes occur. At the softening point, the change may be attributed to an increased rate of colloidal degradation. The change at the glass transition temperature could be attributed to the increased rate of formation of strong association bonds among the asphaltene units. In any case, the temperature zones divided by these points are well behaved in terms of flow, and may be subjected to prediction from basic analysis and limited testing.

Effect of Aging

The testing and analysis of flow data for the aged asphalts followed essentially the same course as the unaged analysis, except that flow behavior measurements were limited to fewer points than those taken for the unaged asphalts. Figures 11, 12, and 13 are the flow diagrams at a representative aging of 275 F and for 3 hours.

As was observed for the unaged data, the flow curves for the aged asphalts form generally straight lines suggesting that the power function model also holds for the aged

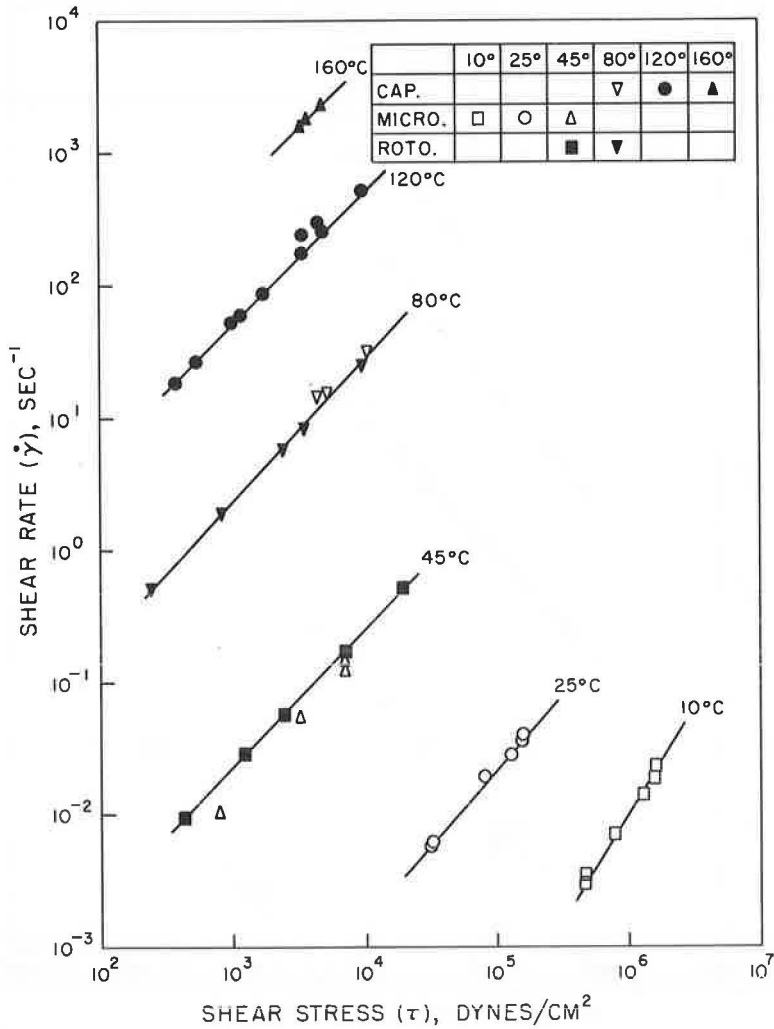


Figure 13. Shear rate vs shear stress on log-log scales for B-2960 asphalt at all test temperatures, aged at 275 F for 3 hours.

asphalts. The effects of aging as shown by this type of flow diagram are twofold; first, the flow curve at a particular test temperature moves downward on the shear rate axis with an increased degree of aging indicating an increased viscosity with increased aging. Second, the curves rotate in a clockwise direction, or the slopes of the curves decrease with an increasing degree of aging. As previously defined, the slope of the curve, n , is a measure of the deviation from Newtonian flow. Observation of the flow diagrams of successively greater degrees of aging shows that n becomes smaller. Therefore, for these three asphalts, and for the method of aging used, aging increases the degree of non-Newtonian flow behavior. It also can be observed that aging increases the maximum temperature at which non-Newtonian flow behavior is exhibited. As was the case with the unaged materials, the aged asphalt can be ordered with respect to decreasing non-Newtonian behavior as the B-3056, the B-2960, and the 60-70 penetration grade for any particular degree of aging.

Figures 14, 15, and 16 are representative apparent viscosity vs shear rate flow diagrams for the 275 F, 3-hr degree of aging. Due to the generally straight lines produced by the data, these figures affirm the applicability of the power function to describe

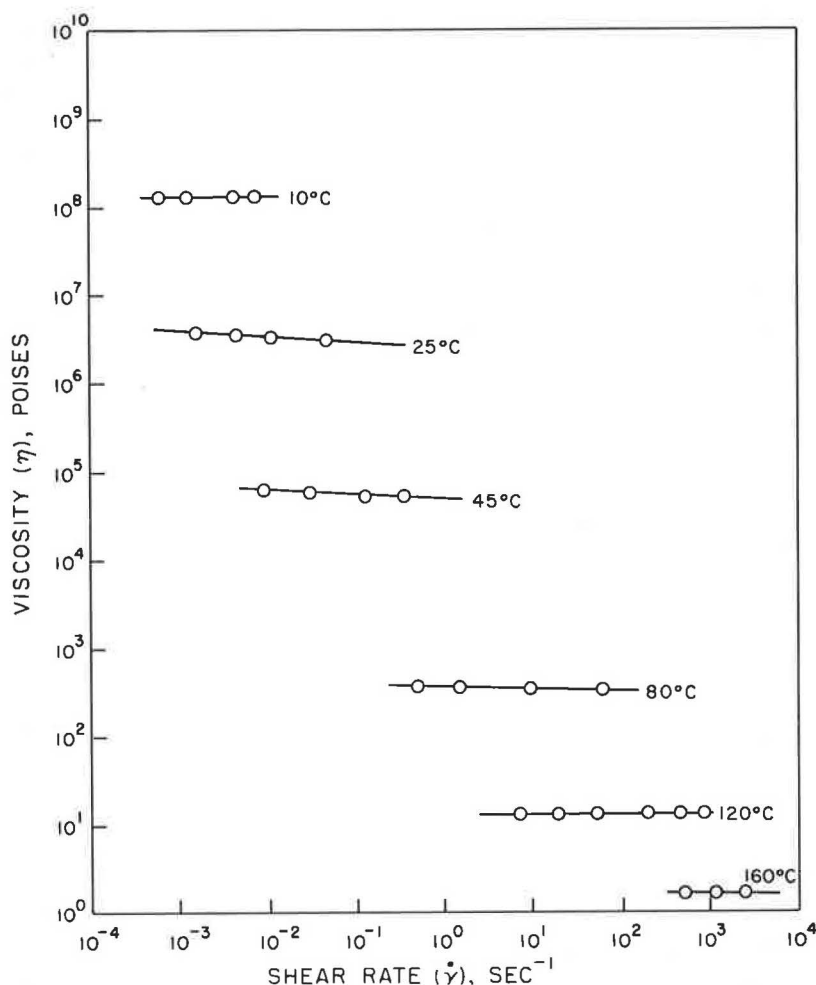


Figure 14. Viscosity vs shear rate on log-log scales for 60-70 penetration grade asphalt at all test temperatures, aged at 275 F for 3 hours.

the flow behavior of the aged asphalt. Recalling that Newtonian flow behavior on this type of a plot is a horizontal line, it can be observed (in agreement with the previous discussion) that aging increases both the deviation from the Newtonian flow, and the temperature at which non-Newtonian flow ceases. These figures also affirm the previous observations that the B-3056 asphalt is the most non-Newtonian and that the 60-70 penetration grade asphalt is the most Newtonian of the three asphalts studied.

Temperature Effect—The effect of aging of asphalt can also be shown by the study of the temperature effect on the flow behavior of the aged materials. Figures 4, 5, and 6 plainly show that the aging of the asphalts increases their viscosities at any particular test temperature. Two observations, however, can be made that would seem contrary to the reasonable expectations of flow behavior.

First, the curves tend to flatten with an increasing degree of aging. In other words, the slope of the curve decreases in the upper portion and increases in the lower portion so that for the highest degree of aging, for each asphalt, the curve is almost a straight line along its entire length. The normal expectation would be that both segments of the curve should increase or decrease in slope, but both should display the same direction of change. From a physical-chemical point of view, aging of the asphalt is understood

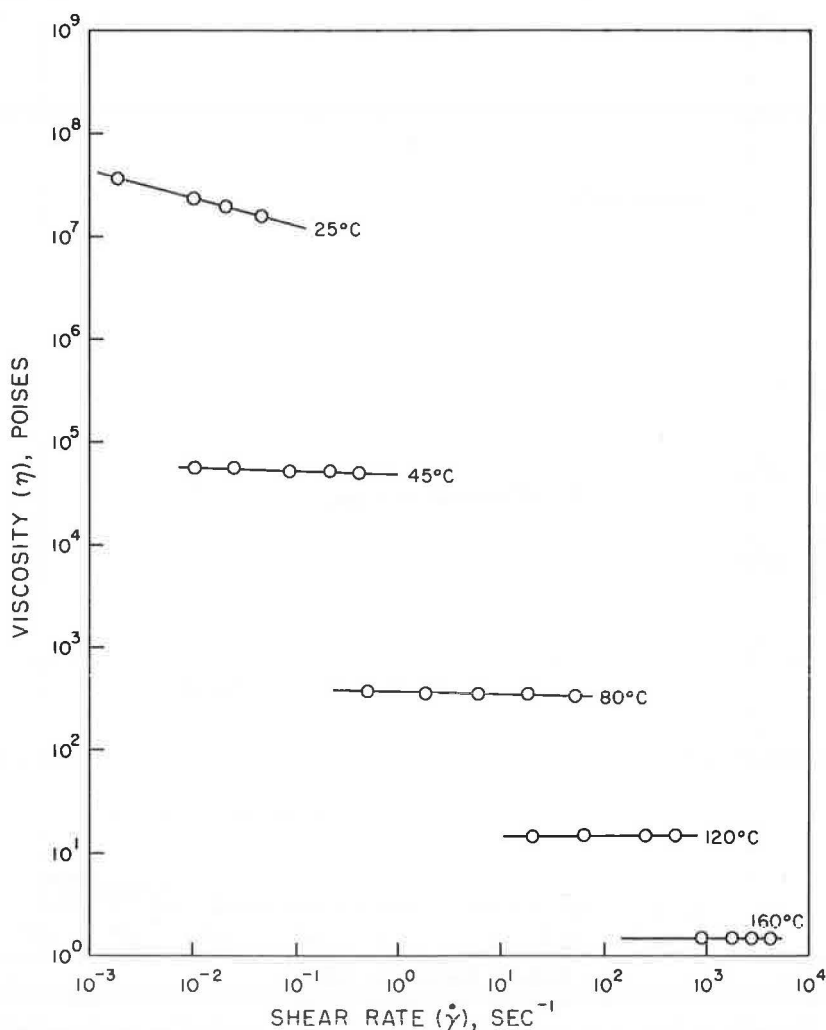


Figure 15. Viscosity vs shear rate on log-log scales for B-3056 asphalt at all test temperatures, aged at 275 F for 3 hours.

to be a mechanism for the formation of larger size molecular units. In other words, the aging process causes the asphalt to form larger and more complex molecular units or associations of molecular units which have a greater resistance to flow. Figures 4, 5, and 6 illustrate this, but they also suggest that the argument must be carried a step further. The concepts of physical chemistry imply that as the condition of aging occurs in the asphalt, there is some point at which molecular buildup slows down or stops and the material begins to breakdown or degrade. If the argument is formulated so that the transition from the buildup to the breakdown process is gradual and that in most cases both processes are occurring at the same time but to different degrees, then the shape of the curves in Figures 4, 5, and 6 may be explained.

During the aging process, both molecular buildup and breakdown take place, but with two different molecular groups. The breakdown takes place in those flow units of low molecular weight. Then the aging process is such that the average molecular weight remains relatively constant, but the deviation of molecular weight from the average becomes less. In the lower temperature regions, as the temperature is increased, much of the decrease in viscosity may be attributed to the dissociation of the large

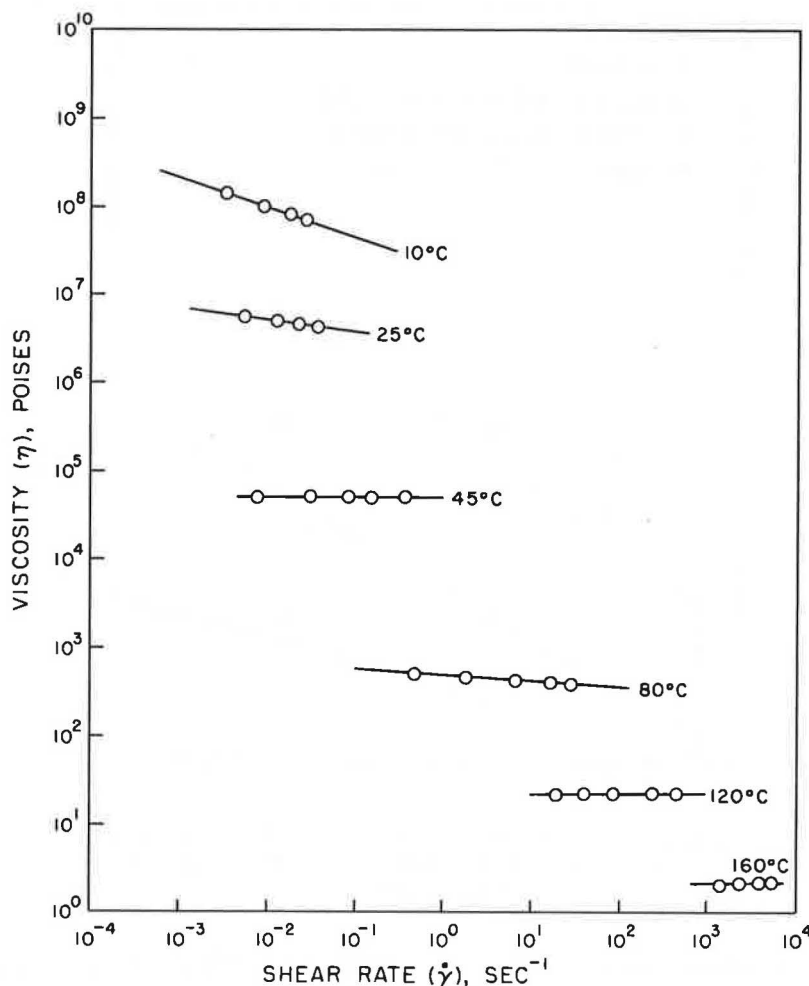


Figure 16. Viscosity vs shear rate on log-log scales for B-2960 asphalt at all test temperatures, aged at 275 F for 3 hours.

molecules, and very little of the smaller molecules (the oils) are released into the system.

Considering the electron microscope evidence of Katz and Betu (19) that polar forces do in fact act in the association process within the asphalt and that their influence is dependent on the degree to which suitable neighbors may be attracted, then as the aging process reduces the size of the larger units, they will become more mobile and more likely to assume positions favorable to the polar associative forces. Thus, as the aging progresses, the asphalt becomes more strongly bonded and less temperature susceptible.

In the higher temperature ranges, however, the situation is quite different. Above the softening point, because of the high degree of thermal activity, essentially no association bonds exist in the material. The decreasing viscosity with increasing temperature is probably entirely due to the release of trapped oils from the larger asphaltene molecules. As the aging process reduces the size of the large molecules, their ability to trap the small oily molecules is restricted so that they are more loosely held. Increasing the test temperature can more easily release these molecules, and therefore the asphalt is more susceptible in the higher temperature range after it is aged.

The second apparent conflict with conventional behavior as shown in Figures 4, 5, and 6 is that the temperature at the point of curvature changes very little with increased

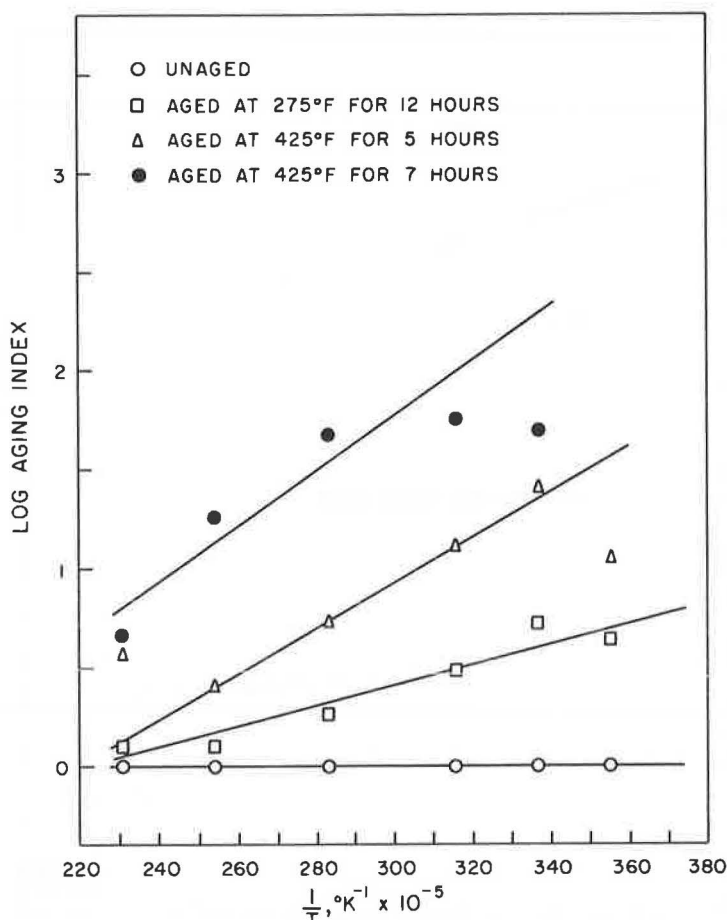


Figure 17. Aging index vs reciprocal absolute test temperature for 60-70 penetration grade asphalt at various degrees of aging.

aging. Formerly this curvature was referred to as the softening point range, but the softening point has been shown to increase with aging. It is also noticed that the conventional softening point increases as the viscosity of the material increases. However, based on the assumption that the average molecular weight of the asphalt changes very little with aging and the experimental evidence that the point of curvature changes very little with aging, then the point of curvature can remain relatively constant while the softening point increases because of its viscosity dependence. The agreement of this argument with experimental observation tends to strengthen the assumption that the aging process is one of breakdown and buildup simultaneously. Recalling that the slope of the curves in Figures 4, 5, and 6 are the apparent activation energies of the material, as the degree of aging was increased, the slope of the viscosity vs reciprocal absolute temperature curves decreased in the low temperature region and increased in the high temperature region. In terms of the apparent activation energy, ΔE , this means that for the low test temperatures, the energy barriers that must be overcome to produce flow are decreased. At any one temperature the force necessary to maintain flow is greater, as evidenced by a higher viscosity, because of the greater number of asphaltene units that can form associative bonds. But, from the rate process theory, is dependent on the size of the flow unit. In the low temperature region, the principal unit of flow is the asphaltene unit, and as the aging progresses, this unit decreases in

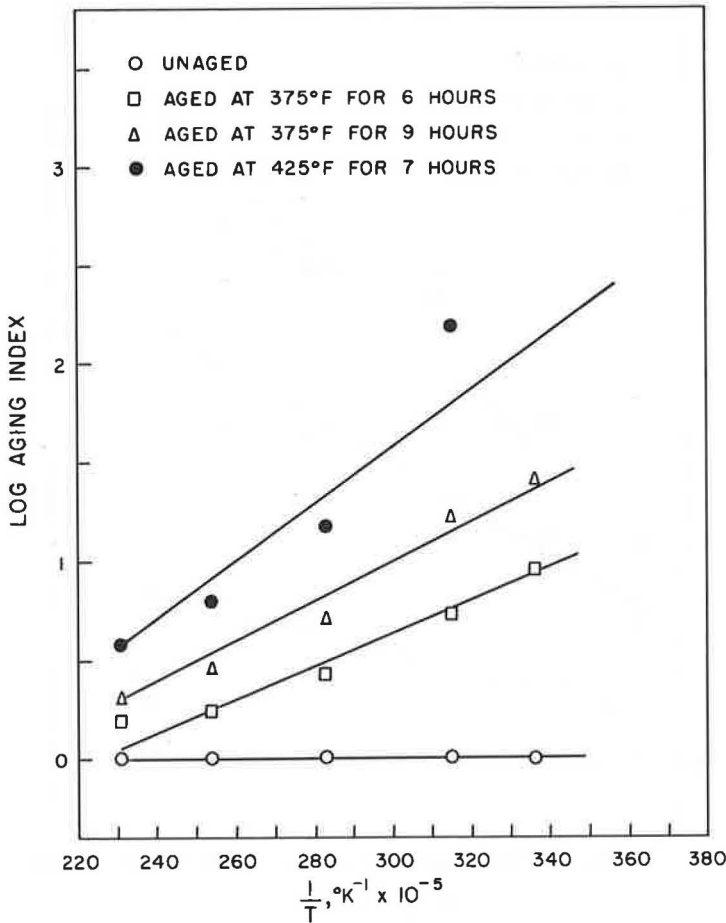


Figure 18. Aging index vs reciprocal absolute test temperature for B-3056 asphalt at various degrees of aging.

size thereby decreasing the activation energy. In the high temperature region, the asphaltene units are suspended in the oily medium, and the principal unit or mechanism of flow is the oily molecular unit. This unit increases in size with the aging process, and therefore, the activation energy increases with aging in this temperature range. Based on these observed changes in the apparent activation energy, it would seem that a correlation between this change and the degree of aging could be established. To describe the effect of aging, we have developed the following expression for the aging index (20), using the theory of rate processes.

$$A.I. = \frac{\eta_a}{\eta_u} = \frac{\alpha_a}{\alpha_u} \exp [(\Delta E_a - \Delta E_u)/RT] \quad (6)$$

or

$$A.I. = \exp [(\Delta F_a - \Delta F_u)/RT] \quad (7)$$

where ΔF is the free energy of activation and subscripts a and u refer to aged and unaged conditions. Eqs. 6 and 7 show that the aging index can be directly related to the

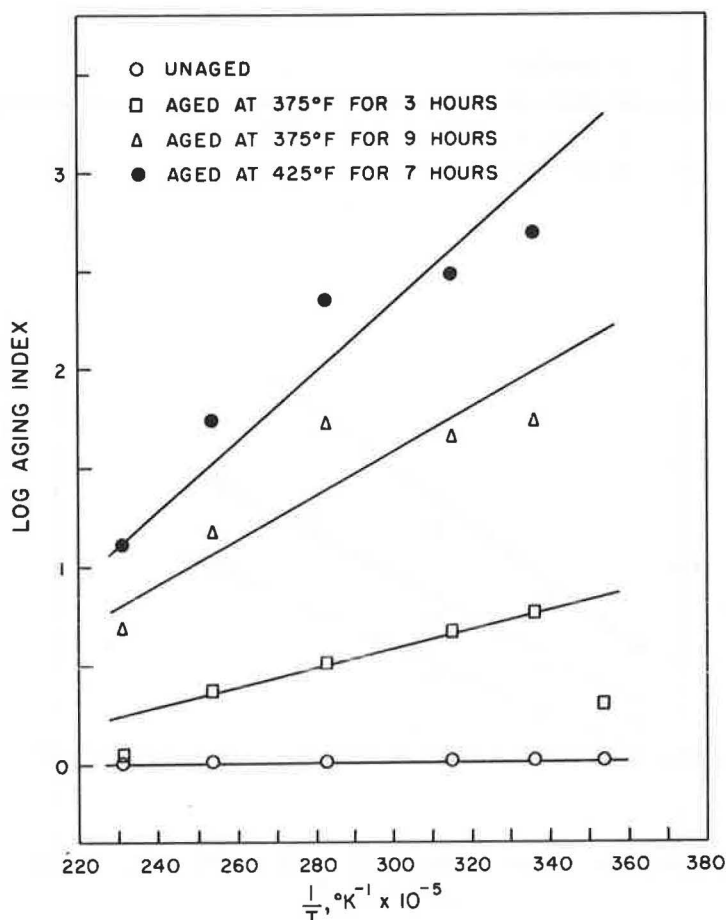


Figure 19. Aging index vs reciprocal absolute test temperature for B-2960 asphalt at various degrees of aging.

change in free energy of activation, and that this change can be calculated from the slope of the plot, $\log A.I.$ vs $1/T$. Figures 17, 18, and 19 show these results for the three asphalts at three different degrees of aging.

Chemical Composition and Molecular Weight

In order to gain more insight into the flow models and the flow hypotheses, and to approach the concept of aging from a different point of view, a limited separation of the asphalts into their main components was made. These components were then examined by different methods to determine their molecular weights.

Asphaltene Content—The results of the separation of each asphalt at each degree of aging into asphaltenes and maltenes are given in Table 3 as the percent asphaltenes based on the total sample weight. Previous work by others on the physical structure of asphalt has indicated that its flow behavior depends on the asphaltene content, and on the ability of the oils and resins to integrate the asphaltenes into the mixture. The general assumption is that non-Newtonian flow behavior increases as a function of increasing asphaltenes, but this is tempered by the degree to which asphaltenes can be taken into solution. The three asphalts used in this study illustrate this as follows. Flow analysis showed that non-Newtonian behavior was descendingly apparent from the

TABLE 3
ASPHALTENE CONTENT FOR INCREASING AGING OF ASPHALT
(Percent Asphaltene Based on Weight of Sample)

Age	60-70 Penetration			B-3056			B-2960		
	1st Run	2nd Run	Average	1st Run	2nd Run	Average	1st Run	2nd Run	Average
Unaged	18.66	18.85	18.75	15.80	15.96	15.88	26.42	26.03	26.23
225-24	21.73		21.73						
275-3	18.68	18.75	18.71	13.98	13.88	13.93	27.42	26.75	27.09
275-7	22.07	21.66	21.86						
275-12	22.52	21.84	22.18						
375-3	24.47	24.29	24.38	18.40	19.30	18.85	29.58	28.94	29.26
375-5	24.50	25.40	24.95						
375-6				20.14	19.93	20.03	34.5	33.8	34.15
375-7	25.47	25.68	25.57						
375-9	24.30	27.00	27.00	27.90	28.60	28.25	35.86	36.86	36.36
425-5	29.04	29.50	29.27						
425-6				29.70	30.10	29.90	39.90	39.10	39.50
425-7	32.02	31.00	31.50	30.74	30.15	30.44	46.77	43.66	44.20

B-3056 asphalt to the 60-70 penetration grade asphalt, however, the percent asphaltene (Table 3) for the unaged asphalts are descending values from the B-2960 asphalt to the B-3056 asphalt. Then by inference, the asphaltene in the B-3056 material were poorly integrated, the asphaltene in the B-2960 asphalt were well integrated, and the asphaltene in the 60-70 penetration grade asphalt were somewhere in between, tending to well integrated.

Table 3 indicates that aging increases the proportion of asphaltene in each asphalt. This increase in asphaltene content is reflected by the increasing non-Newtonian behavior and by the increasing viscosity, as shown by the flow diagrams of the aged asphalts. The relative change in asphaltene content for each asphalt supports the previous hypothesis that aging involves both the formation of more asphaltene units and the breakdown of the more complex asphaltene units into less complex ones. If buildup of the asphaltene content and the asphaltene units were the only mechanism present, then each asphalt would increase in non-Newtonian behavior by some measure of its increase in

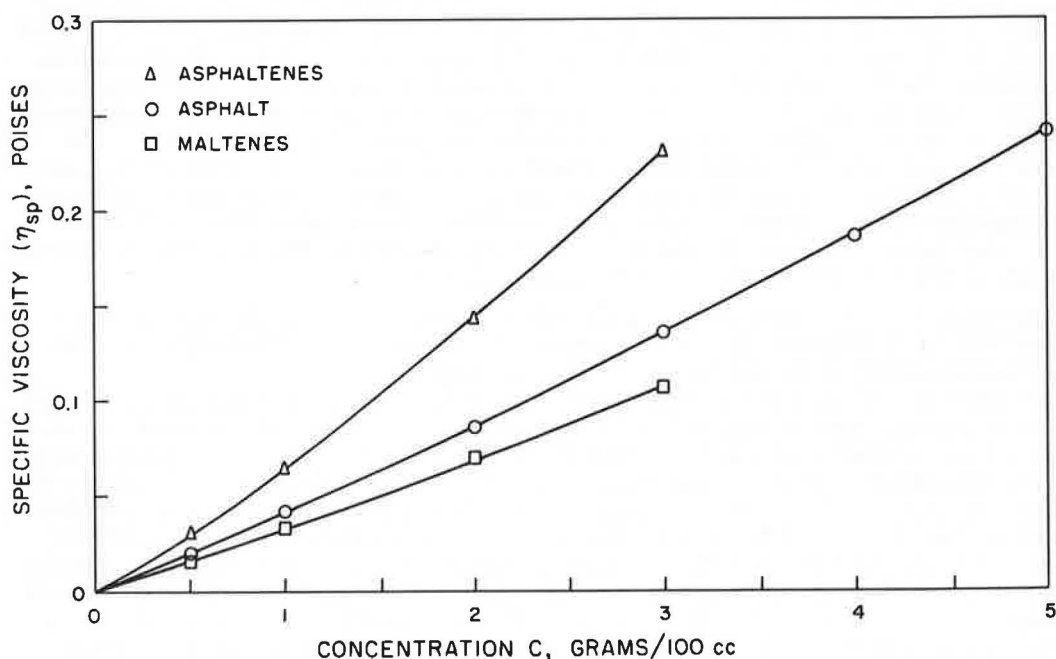


Figure 20. Specific viscosity vs concentration for 60-70 penetration grade asphalt including all components, aged at 275 F for 3 hours.

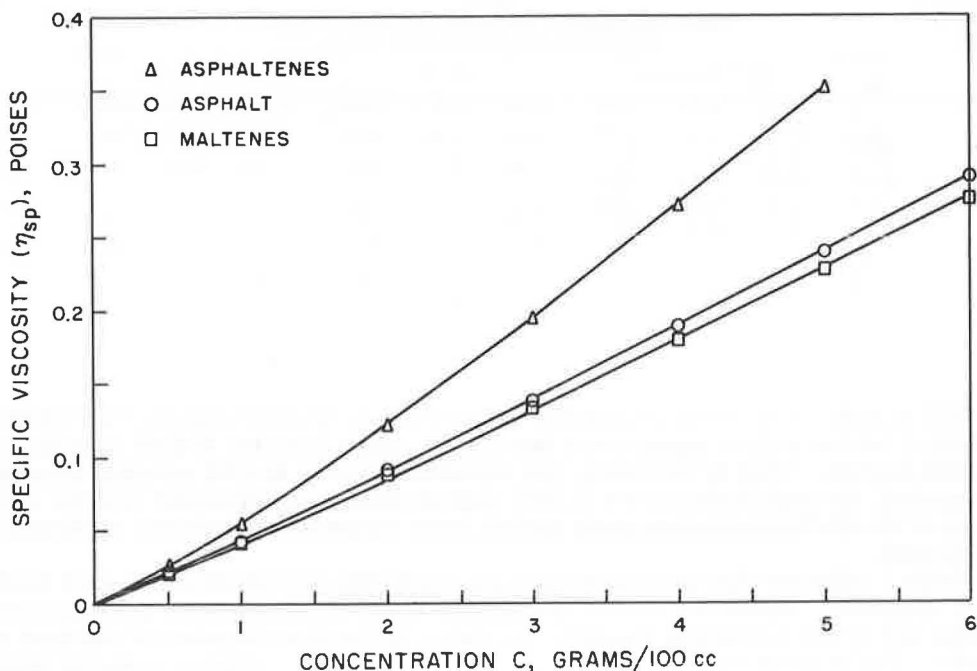


Figure 21. Specific viscosity vs concentration for B-3056 asphalt including all components, aged at 275 F for 3 hours.

asphaltenes. Flow behavior was generally the same for all three asphalts, but for the same degree of aging (425 F for 7 hours), the B-2960 asphalt increased its asphaltene content by about 18 percent, the 60-70 penetration grade by 12 percent, and the B-3056 asphalt by 14 percent. For the B-2960 asphalt to maintain its relative position in the non-Newtonian flow behavior scale, the high increase in asphaltene content would have to be accompanied by either a greater "integrability" of the maltenes, or a breakdown of a more complex asphaltene unit into more easily integrated asphaltene units. The former is unlikely as the increase in asphaltenes is necessarily accompanied by a decrease in maltenes, and presumably the remaining maltenes are less able to integrate the asphaltenes. Therefore, some breakdown of the complex asphaltene units must have taken place. For the highest degree of aging, B-2960 asphalt displays the greatest change in slope of the curves from the unaged condition.

Intrinsic Viscosity—The foregoing discussion seems to indicate that direct knowledge of the molecular weights of the components of asphalt would be helpful in a further understanding of the mechanisms of asphalt flow behavior.

Figures 20, 21, and 22 are plots of the specific viscosity vs concentration for solutions of asphalt, asphaltenes, and maltenes in benzene. The specific viscosity is defined as the solution viscosity divided by the solvent (benzene) viscosity. All measurements were made at 77 F. Initial testing showed that over a range of shear rate there was little variation in the value of specific viscosity for the 6 percent and less solutions. For all three asphalts, the specific viscosities were about the same at any particular concentration. Both the B-2960 and 60-70 penetration asphalts had asphaltene specific viscosities of about the same value, while for the B-3056 asphalt it is about 20 percent lower at a concentration of 3.00 gm/100 cc. The same observation is true for the maltenes except that the value for the B-3056 asphalt is in this case higher than for the other two. Therefore, it would seem that non-Newtonian flow behavior could be scaled by the specific viscosity of the asphaltenes or the maltenes. The results of these limited data for the asphaltenes and the maltenes seem to indicate that a necessary

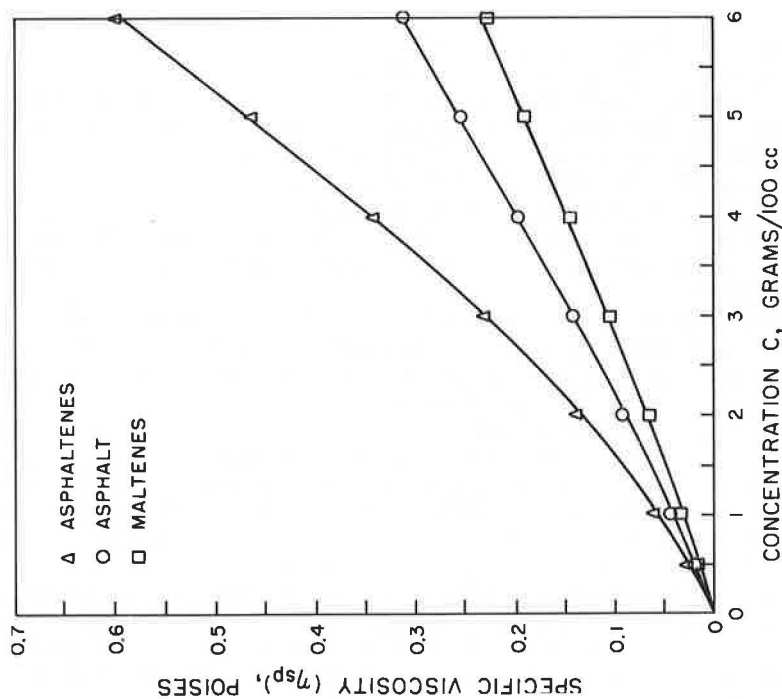


Figure 22. Specific viscosity vs concentration for B-2960 asphalt including all components, aged at 275F for 3 hours.

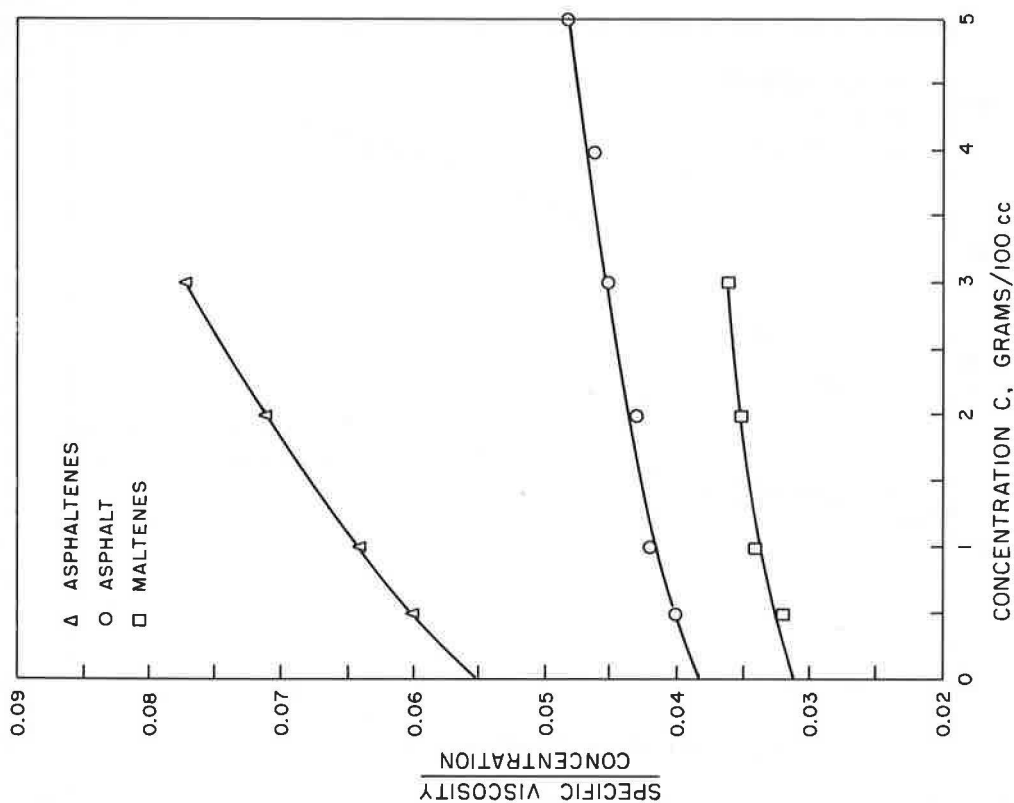


Figure 23. Product of specific viscosity and reciprocal concentration vs concentration for 60-70 penetration grade asphalt including all components, aged at 275 F for 3 hours.

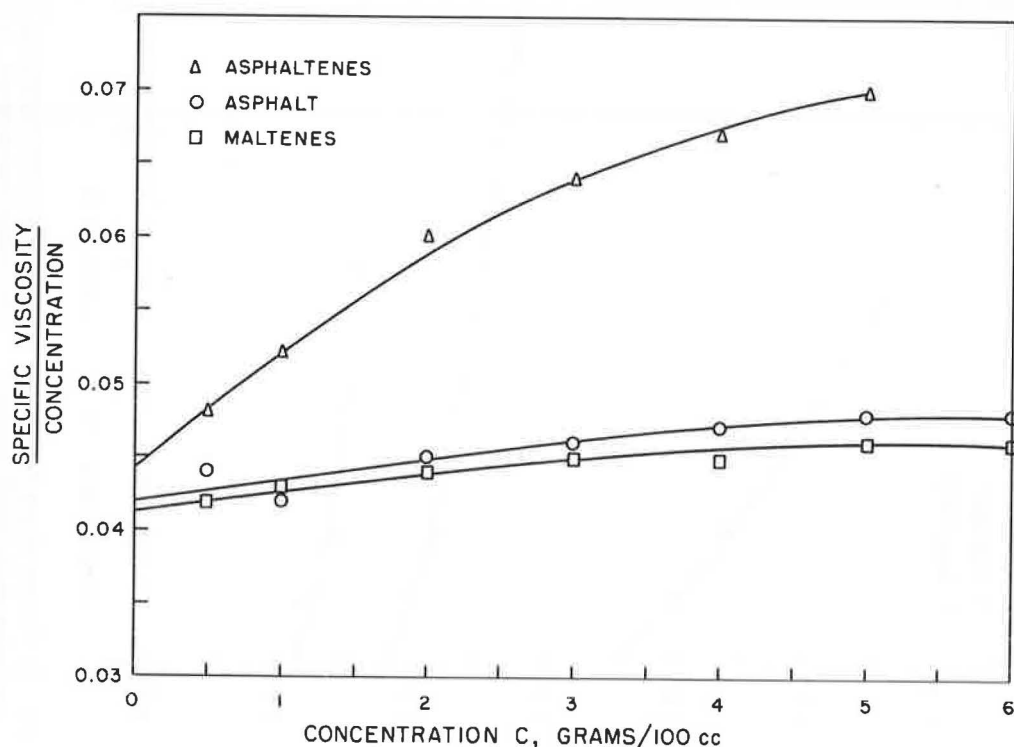


Figure 24. Product of specific viscosity and reciprocal concentration vs concentration for B-3056 asphalt including all components, aged at 275 F for 3 hours.

condition for the non-Newtonian behavior is a relatively small difference between the specific viscosities of the two components.

The specific viscosity data obtained at different degrees of aging showed little change by aging, but the change was increasing with a higher degree of aging. The change in specific viscosity was very little for the B-3056 asphalt which was, from flow behavior analysis, the most non-Newtonian of the three.

The change in specific viscosity of the asphaltenes due to aging was even less noticeable than that for the asphalt. Again, as for the asphalt, the change for the asphaltenes with increased aging time was positive and was the least pronounced for the B-3056 asphalt.

The change in specific viscosity of the maltenes was somewhat larger than that of the asphalts, and was, in general, in the opposite direction of the change for the asphalt and the asphaltenes. Generally speaking, the asphaltenes, despite lower concentrations in the asphalt, have a much greater influence on the specific viscosity of the asphalt than the maltenes.

To obtain the intrinsic viscosity of the asphalt, asphaltenes, and maltenes, the specific viscosity divided by concentration was plotted against concentration. A smooth curve is then fitted to the points (Figs. 23, 24, and 25). The intrinsic viscosity is then the intercept of the curve at a zero concentration. Table 4 gives the values at all the degrees of aging used in this study. A relationship between intrinsic viscosity and aging temperature was sought, but the results seem to show no correlation. The reason for this apparently random nature of the results can be accounted for by the fact that very little change takes place in the specific viscosity as a result of aging, and the experimental techniques are not sufficiently sophisticated to define accurately these small changes.

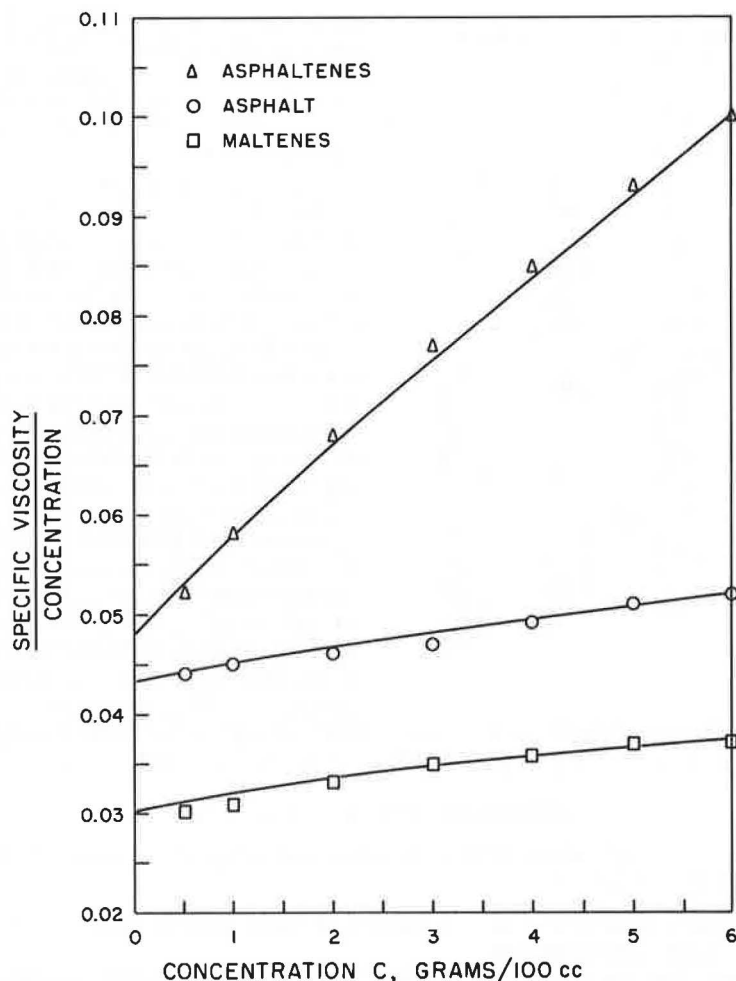


Figure 25. Product of specific viscosity and reciprocal concentration vs concentration for B-2960 asphalt including all components, aged at 275 F for 3 hours.

As shown by Mack (22) and others (23, 24), the intrinsic viscosity is proportional to the molecular weight. The variation of the value of intrinsic viscosity for each component, and the asphalt itself, is about 10 percent from a mean value, with exception of a small number of extreme values. This indicates that the average molecular weights of the asphalt and of the components change very little in the aging process. This further supports the hypothesis that aging is a two-way process of buildup and breakdown of the molecular units in the asphalt.

Molecular Weight—To obtain the constant of proportionality to be used in the intrinsic viscosity-molecular weight relationship and as a check on the intrinsic viscosity method of molecular weight determination, an attempt was made to determine directly the molecular weights of the asphalts and their components. The final goal of this phase of the study was not realized because of experimental difficulties, lack of equipment, and time limitations. The B-2960 asphalt was used as a pilot material. A cryoscopic method of molecular weight determination was first considered, but was discarded after it was discovered that the asphaltenes would precipitate out of the benzene solutions at the low temperatures used in the test. An ebullioscopic method was tried next, but

TABLE 4
INTRINSIC VISCOSITY DATA FOR ALL COMPONENTS
OF ASPHALTS

Aging Temp., (F)	Aging Time	Intercept of η_{sp}/c at $c = 0$		
		Asphalt	Asphaltene	Maltene
(a) 60-70 Penetration Asphalt				
Unaged		0.0344	0.0664	0.0328
275	3	0.0380	0.0555	0.0315
	7	0.0384	0.0560	0.0310
	12	0.0410	0.0562	0.0308
375	3	0.0412	0.0446	0.0306
	5	0.0418	0.0608	0.0335
	7	0.0415	0.0594	0.0353
	9	0.0420	0.0624	0.0335
425	5	0.0443	0.0611	0.0380
	7	0.0445	0.0600	0.0353
(b) B-3056 Asphalt				
Unaged		0.0400	0.0412	0.0379
275	3	0.0418	0.0443	0.0412
375	3	0.0415	0.0500	0.0352
	6	0.0403	0.0496	0.0298
	9	0.0406	0.0506	0.0282
425	6	0.0412	0.0551	0.0252
	7	0.0412	0.0576	0.0341
(c) B-2960 Asphalt				
Unaged		0.0428	0.0474	0.0275
275	3	0.0434	0.0483	0.0302
375	3	0.0438	0.0497	0.0315
	6	0.0426	0.0519	0.0351
	9	0.0428	0.0569	0.0309
425	6	0.0441	0.0610	0.0304
	7	0.0455	0.0716	0.0314

gave very random results. A rough estimate of the molecular weight of the B-2960 asphalt was 535. A vapor pressure osmometer was then tried, and the results for the unaged B-2960 asphalt gave a molecular weight of 528.

The last test completed was for the B-2960 asphalt aged at 375 F for 6 hours. The molecular weight was determined as 549. It was first suspected that these results were too low to be correct as the average molecular weight of asphalt is variously reported to be around 1000, but the establishment of quite comparable values by two different methods led to the conclusion that this asphalt may have an unusually low molecular weight. The very small increase in molecular weight with aging agrees with the results from the intrinsic viscosity tests. For the same degree of aging, the asphaltene content increased by 8 percent of the total B-2960 sample weight. Therefore, it may be concluded, subject to confirmation of the test data, that for the B-2960 asphalt, the aging process involved the conversion of lower

molecular weight components, and the breakdown of higher molecular weight components. Furthermore, these two processes are nearly balanced.

SUMMARY AND CONCLUSIONS

In summary, the work performed on the effect of aging on the flow properties of asphalts has been as follows:

1. The rheologic analysis of flow behavior of three asphalts under different shear rates and at various temperatures.
2. The use of three viscosity-measuring instruments to obtain rheologic properties over a wide range of temperature and shear rate.
3. The aging of asphalts to different levels and the determination of their flow behavior.
4. The chemical separation of the asphalts into asphaltene and maltene components and the determination of the aging effects on these components.
5. The measurement of intrinsic viscosity of the aged and unaged asphalts and their components to determine the effects of aging on composition and molecular weight.

From the results of these investigations, the following can be concluded:

1. Flow data obtained by different viscometers are consistent and different viscometers can be used to obtain shear data over a wide range of shear rate or shear stress. The principle of reduced variables can be used to further extend these ranges by reducing the data obtained at different temperatures to an arbitrary base temperature.
2. For the three asphalts used, the degree of aging influences the non-Newtonian response of the material, and the change in the free energy of activation may be used as a measure of this influence.
3. The aging process used for this study is such that small molecular weight components in the asphalt are increased in size and the larger molecular weight components are decreased in size. The aging of the asphalt to any particular degree does not seem to change the average molecular weight of the asphalt substantially.
4. A significant change takes place in the asphalt flow behavior within a narrow range of temperature, and the ring and ball softening point is within this range.

5. In order to use the intrinsic viscosity as a measure of the molecular weight of the asphalts or their components, the specific viscosity must be measured with a high degree of accuracy.

ACKNOWLEDGMENTS

This research was performed as a part of a project entitled "Durability Characteristics of Asphaltic Materials" sponsored by the Ohio Department of Highways in cooperation with the U. S. Bureau of Public Roads, at the Department of Civil Engineering, The Ohio State University. The authors are indebted to the above agencies for their support of this study.

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Appendix

MOLECULAR WEIGHT DETERMINATION

Two procedures for the direct molecular weight determination were used. The ebullioscopic method uses an apparatus made up of three cottrell boilers with internal electric heaters and reflux condensers (Fig. 26). Four copper-constantan thermocouples were used as temperature sensing devices with the reference junction located in the center boiler. Through a switching device the elevation of boiling point in terms of electromotive force could be measured in either of the outside boilers. A high-gain, low-noise dc amplifier was used to measure the electromotive force.

In operation, 50 ml of pure benzene was placed in each boiler and slowly ($\frac{1}{2}$ hour) brought to a boil. The heaters were adjusted to give a constant emf from either boiler of zero. To calibrate the device, small cylinders of benzoic acid, weighed to ± 0.0002 gm were introduced into the outside two boilers. The change in boiling point was noted after it became constant. Small asphalt samples were prepared and introduced in the same manner and readings were taken.

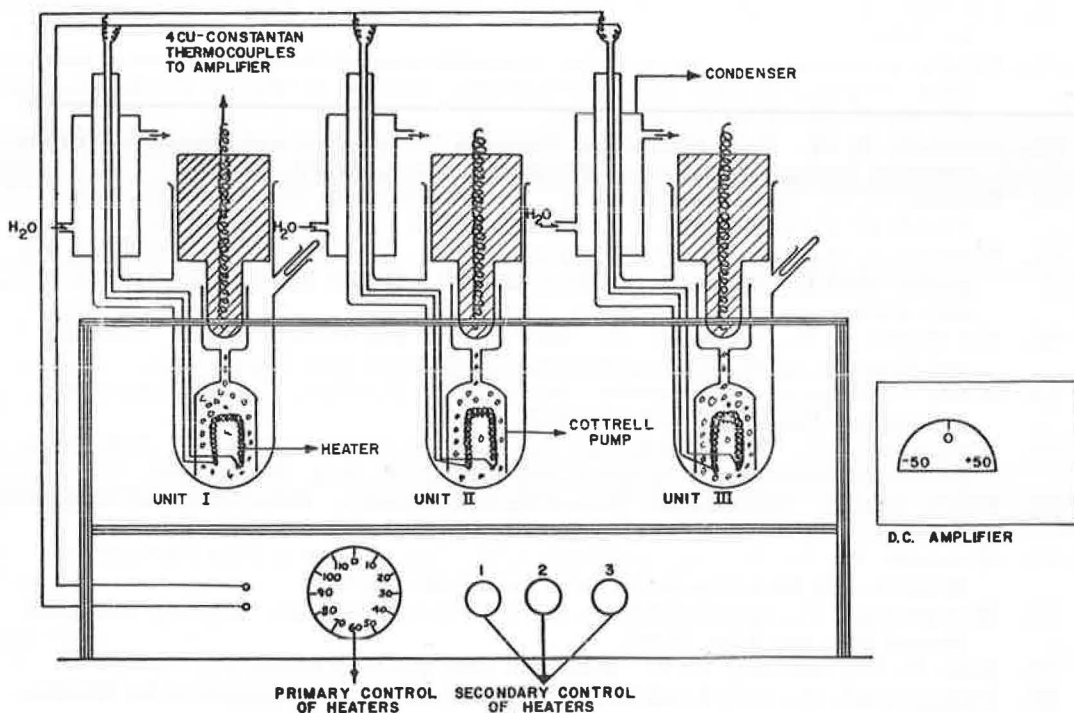


Figure 26. Schematic diagram of apparatus for the ebullioscopic method of molecular weight determination.

To calculate the molecular weight, the apparatus constant, k , is found as

$$k = \frac{Mx \cdot wG}{1,000} \quad (8)$$

where Mx is the molecular weight of benzoic acid, w is the weight of sample, and G is found from

$$G = \frac{n \sum w_i \theta_i - \sum w_i \sum \theta_i}{n \sum w_i^2 - \sum w_i \sum w_i} \quad (9)$$

where n is the number of sample additions, w_i are the weights of sample, and θ_i are the differences in boiling points. A zero point error calculation:

$$\theta_0 = \frac{\sum \theta_i - G \sum w_i}{n} \quad (10)$$

should be such that θ_0 does not exceed θ_1 , the boiling point elevation for the first sample addition. Using the apparatus constant, similar calculations using the data obtained for asphalt samples can be made to determine the molecular weight of the asphalt sample.

The second method involves using a vapor pressure osmometer (Mechrolab Osmometer). This instrument determines the concentration of solute particles in a solution by accurately comparing the equilibrium temperatures of a drop of solution. Two thermister beads in a thermostat are the key parts. The difference in the temperatures of the two beads is measured by means of a built-in resistance bridge and is read by use of four decade dials.

Syringes are used to place drops of solvent or solution on the thermister beads. One of the thermister beads is used exclusively with the solvent. The apparatus has provision for loading two syringes containing the solvent and four syringes containing solutions.

For operation of the osmometer, the following steps are necessary for any given solvent.

Once temperature equilibrium has been attained in the chamber, two syringes with solvent are placed in the holders. The unused holders are closed with corks. Temperature equilibrium was attained in about 15 minutes after insertion of the syringes.

One drop of solvent was placed on each thermister bead by proper operation of the syringes. The drops were made as nearly the same size as possible. The indicator needle of the resistance bridge was zeroed. About three minutes after the drops were placed the indicator needle was adjusted to the needle point by operating on the decade dials. The balance measurement was repeated by placing fresh drops of solvent until the needle point can be reproduced consistently at the appropriate time interval. The acceptable readings are averaged and the value represents the T for the solvent.

To determine the calibration curve when benzene is used as the solvent, different solutions of benzoic acid in benzene having the concentration range 0.015 to 0.062 moles/liter are made.

The procedure for determining the T of any one of the standard solutions is the same as described for the solvent, with the exception that a drop of solution is placed on the sample thermister after cleaning it thoroughly with the solution. The calibration curve is obtained by plotting the difference in the T 's of the solution and solvent against the molar concentration of the solution.

The T 's for the asphalt solutions are determined as described earlier. From the calibration curve the concentration of the asphalt solutions in gm-moles/liter are then obtained. Since the concentration in gm/liter is known, the molecular weight of the asphalt can be easily obtained.