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THE CHEMICAL AND PHYSICAL PROPERTIES OF ASPHALT-RUBBER MIXTURES

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Prepared by:
E.L. Green
William J. Tolonen
Materials Services
Arizona Department of Transportation

Prepared for:
Arizona Department of Transportation
206 South 17th Avenue
Phoenix, Arizona 85007

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16. Abstract

The properties of asphalt-rubber mixtures composed of paving grade asphalt and ground automobile tire rubber are examined. The mechanism of swelling of the rubber in asphalt and asphalt-like materials is proposed and the effect of variables which affect the swelling is discussed. Experiments determining the swelling of tire rubber in selected oils are related to the swelling of tire rubber in asphalt. Several test methods are presented which measure the properties of the asphalt-rubber mixture. Data concerning the properties of a commercially available asphalt-rubber mixture and the effects of processing variables on these properties are presented. Techniques useful for the quality control of this material as well as suggestions for research into the theoretical aspects of the unique characteristics of this material are discussed.

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THE CHEMICAL AND PHYSICAL PROPERTIES OF ASPHALT RUBBER MIXTURES

(PART I - BASIC MATERIAL BEHAVIOR)

March 1977

Final Report HPR-1-14(162)

E. L. Green
&
William J. Tolonen
Arizona Department of Transportation
1745 West Madison Street
Phoenix, Arizona 85007

Robert L. Dunning
Special Consultant

Under the Direction of
Gene R. Morris
Engineer of Research

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PREFACE

Interest in the use of hot asphalt rubber binder systems for highway construction and maintenance is growing as reports of the advantages of this system are circulated. Experimental test sections of hot asphalt rubber seal coats and stress absorbing membrane interlayers have been applied in the State of Arizona in recent years to evaluate the construction potential of this system. The results have been promising enough to promote a research effort to investigate the properties of the system and to develop test procedures to evaluate field samples. This report is the beginning of what appears to be a long term effort to understand and utilize this new construction material.

A special acknowledgement is given to Professor C. W. Macosko at the University of Minnesota for testing samples of hot asphalt rubber seal on his Rheometrics Mechanical Spectrometer. The authors gratefully acknowledge the assistance of the following companies for supplying the materials used in this study: Atlos Rubber Co., Inc., U.S. Rubber Reclaiming Co., Inc., Douglas Oil Co., Edgington Oil Company, Golden Bear Division of Witco Chemical, Shell Oil Co., and Crowley Tar Products Co.

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INTRODUCTION

Asphalt concrete pavements have been a major component of this country's road system for many years. Although they have performed well, for the most part, their lifespan has been limited by the tendency of the asphalt cement to become brittle with age. When the asphalt cement cannot yield to stress without fracturing, it cannot hold the aggregate in its place on the roadway. Today there are many ways of attempting to restore old pavement to its original softness and many highways are simply being resurfaced or reconstructed to overcome the aging problem. One approach to extending the life of the roadway is to use asphalt with special modifiers on projects requiring resurfacing.

The addition of rubber to asphalt is an attempt to extend the life of an asphalt cement by imparting rubber like properties to the asphalt. This technique gives the asphalt greater flexibility over its life span and imparts unique properties to a pavement. The major work underway in this field is in the use of asphalt rubber mixtures in seal coat overlays and interlayers between asphalt concrete overlays. The rubber like resilience of the mixture has the ability to yield to pavement deformations without fracturing and to bond tenaciously to aggregate chips. The properties of this system are markedly different from asphalt cement and a different system of tests are necessary to define these properties.

RHEOLOGICAL STUDIES OF THE HOT ASPHALT-RUBBER BINDER

The purpose of these studies was to develop test methods which may be used in the production control of hot asphalt rubber membranes placed as seal coats or interlayers. The rheological factors which must be evaluated include the effect of the swollen rubber particles on the viscosity of the hot asphalt rubber. The swelling of the rubber particles is a function of the temperature, the particle size, the relative compatability of the rubber and asphalt, and the type of rubber used.

The hot asphalt rubber seal coat, which was developed by Charles H. McDonald while he was Engineering Supervisor for the City of Phoenix, Arizona, has been especially successful in providing a durable wearing surface for severely fatigued and "alligatored" pavements. A description of the process may be found in the Implementation Package prepared by Robert E. Olsen[1] for the Federal Highway Administration. Mr. McDonald has done considerable work studying the effect of temperature, and the addition of solvent to the hot asphalt rubber system. The studies here are aimed at continuing the work initiated by Mr. McDonald, and, as mentioned above, to develop test procedures for production control. The specific system being evaluated is comprised of a paving grade asphalt and a quantity of 16-25 mesh size ground automobile tire rubber which are mixed and heated together until the mixture possesses properties related to each component. The rubber is primarily a SBR Type and is utilized at a concentration of approximately 25% in the mixture. Other systems, not included in this study, typically contain 5-10% ground tire rubber or natural latex rubber. It is the high concentration of rubber which makes this system possess its particular desirable quality of reflective crack prevention.

The rheology of mixtures of asphalt and rubber is very complex, and cannot be completely described by the viscosity, which is the ratio of shearing stress to shear rate. Indeed, the rheology of asphalt, even in the absence of rubber, often cannot be completely described by the viscosity. Asphalt rubber mixtures are strongly viscoelastic, which must be taken into account in describing their behavior. This complex nature becomes readily apparent when such mixtures are stirred hot. They climb the stirrer, moving against gravity and centrifugal force. This phenomenen is called the Weissenberg effect and was reported by Herzog and Weissenberg[2] in 1928 as the development of normal (ie perpendicular) forces in polymers undergoing shear stress. These normal stresses will be discussed in more detail later.

In working with the hot asphalt rubber seal, interest lies not only in the properties of the final product on the ground, but also in the properties of the mixture as it is made and applied, as there are severe time and rheological limitations in applying it through a spreader truck. As this process is reviewed, the need for proper testing tools at each step will become obvious.

There appears to be a distinct difference between the asphalt rubber binder and other types of rubber in asphalt mixtures. In order to avoid confusion, asphalt rubber is defined to mean mixtures of rubber and asphalt whose response is primarily rubberlike although those responses are modified by the presence of asphalt, such as a system of asphalt containing 25% ground SBR rubber. A rubberized asphalt, on the other hand, is a mixture of rubber in asphalt whose response is primarily asphaltlike, although those responses are modified by the presence of rubber, such as a system of asphalt containing 5% natural latex rubber.

CONCLUSIONS

1. The viscoelastic properties of the hot asphalt rubber binder differs so greatly from asphalt, that normal asphalt test procedures are of little value in describing its behavior.

2. A test procedure has been developed by which the ability of asphalts from differing sources and of differing viscosities to swell rubber may be compared. This procedure consists of comparative swelling experiments using standardized, specially compounded rubber specimens. An empirical equation has been fitted to the swelling data obtained which contains two significant constants; the rate of swell, and the maximum swell attainable.

3. A test procedure has been developed to measure the viscosity of the hot asphalt rubber binder at 60°C (140°F) using vacuum capillary viscometers. The procedure differs from that used on asphalt in various details, with the largest difference being that tests may be conducted at vacuums less than the 30 cm of Hg as used for asphalt. This test procedure may be used with the binder with or without kerosene.

4. Viscoelastic measurements conducted on the Rheometrics Mechanical Spectrometer has demonstrated the differences between asphalt and asphalt rubber. The latter responds more elastically than does asphalt, and has a higher elastic modulus above 10°C and a lower elastic modulus below 10°C. While asphalt responds either as a liquid or a brittle solid over all except a very limited range of temperatures, the asphalt rubber binder responds both elastically and viscously over a large range of temperatures.

5. A test procedure has been developed which may be used to measure the viscoelastic nature of the asphalt rubber on a routine basis. It

is based upon strain recovery of that binder after removal of a preload. The data has been fitted with an empirical equation containing three constants, one of which is sensitive primarily to the elastic nature of the binder, while the other two are primarily responsive to the viscous nature of the binder.

6. The reaction between the asphalt and the rubber in the asphalt rubber binder continues, although at a greatly reduced rate, when the binder is stored at ambient temperatures. For the test procedures which have been developed to be of value as control tests, field samples must arrive in the laboratory essentially the same as when sampled. A sampling technique which rapidly chills the asphalt rubber binder after sampling and maintains a low temperature during shipment to the laboratory must be utilized. A suggested sampling procedure has been developed which will essentially halt the asphalt rubber reaction during transport to the testing laboratory.

DESCRIPTION OF PROCESS

The hot asphalt rubber seal is prepared as follows: The rubber particles of a selected size range are added to asphalt with mixing at 175° - 200°C (350° - 400°F). The rubber particles immediately begin to swell, increasing the volume fraction of the dispersed rubber phase, and increasing the viscosity of the asphalt continuous phase as light oils are absorbed by the rubber. 5-7% Kerosene is then added to reduce the viscosity to the point where the resulting mixture may be readily placed by a spreader truck. Because of its lower viscosity, the kerosene may also increase the rate of swell as well as decrease the viscosity of the continuous phase.

The ultimate percent swell may also be increased by the kerosene.

The process of swelling is a crucial factor in the hot asphalt rubber binder. As the rubber particles swell, there is less free space between them with the result that the viscosity of the mixture increases. The equation which relates the viscosity of a two phase system may be expressed in this form.

$$\eta = \eta_o \ (1 + \alpha_1\phi + \alpha_2\phi^2 + \alpha_3\phi^3)$$

η is the measured viscosity

η_o is the viscosity of the continuous phase

ϕ is the phase volume of the dispersed phase

α are constants with $\alpha_1 = 2.5$

In most studies where the above equation is applied, η_o is a constant. This is not the case with the hot asphalt rubber seal since the lighter fractions of the maltene phase of the asphalt would be absorbed by the rubber particles, which would result in an increase in η_o. We will be examining that in a later section.

MECHANISM OF SWELL

As mentioned above, the placing of the hot asphalt rubber seal consists of adding ground tires of a controlled gradation to hot asphalt, adding kerosene to provide pumpability and spreading the mixture before the particles swell to the point of gelling. The particle size of rubber is carefully controlled to #16 - #25 mesh, the temperature is carefully controlled, and the binder is spread within a time limit of about two hours. All of these

control measures were arrived at empirically by Mr. Charles McDonald[3] [4]. A state of the art summary may be found in a recent paper by Morris and McDonald[5].

Ground tires have been used to provide a measure of protection from the cracks in pavements in other systems, an example of which is The Stress Relieving Interface (SRI) reported by Gallaway[6]. This system, which consists of a blend of tire buffings, sand and asphalt emulsion, has performed well in reducing crack reflection. A significant difference between the McDonald formulation and the SRI is that in the McDonald system, the rubber is swollen prior to applying. The SRI is applied cold, and the time required for asphalt to swell rubber at ambient temperatures is considerable, perhaps approaching several years. The mechanism of swelling is therefore a crucial part of this project. It is desirable to gain an understanding of the mechanism so that, by measuring the properties of the asphalt, a relatively trouble free job could be assured. Additionaly, it would be desirable to place the hot asphalt rubber binder without the necessity of adding kerosene. However, that subject is beyond the scope of this report.

The asphalt rubber seal differs markedly from conventional rubberized asphalts, whose properties, although changed by the presence of rubber, are essentially those of an asphalt. The asphalt rubber seal acts like a rubber. Morris and McDonald[5] described it this way:

> *"...it is postulated that the asphalt is serving to modify the elastic properties of the rubber rather*

than the rubber serving to modify the ...asphalt. This difference from previous past research into ...asphaltic concrete utilizing low percentages of rubber is basic....."

They further state that 25% rubber is required, and show that the rubber gradation must be carefully controlled.

The rubber swells at a rate determined by the temperature, rubber particle size, interaction constant between the maltene fraction of the asphalt and rubber, the activity of the maltenes (as affected by a partitioning of the solvent between the rubber and asphaltenes) and the absorption of oil by the rubber, which causes the concentration of the asphaltenes to increase. The viscosity is a function of the volume fraction of the dispersed phase, which increases with time, the viscosity of the continuous phase, which increases as the lighter maltene phase is absorbed by the rubber, and possibly the precipitation of asphaltenes, if the asphalt is metastable. All these tend to increase the viscosity of the mixture. While this process is occurring, the material must be applied. The maximum amount of swell which takes place (at equilibrium) decreases as the temperature increases, and depends on the interaction of the asphalt with the rubber, and the crosslink density of the rubber. A detailed study of the swelling mechanism in the individual particle is outside the scope of this work. What we are interested in is the variation of swell with time, temperature, radius, etc. as caused by changes in the volume flux of oil (or asphalt) entering into the sum of particles. Once the volume of the rubber has

expanded to the point of interfering with pumping and spreading in a truck, the maximum time the sample may be kept in a truck prior to application to the road has been reached.

EFFECT OF TEMPERATURE

Temperature has two effects on swelling. The first effect is on the rate of swelling. As the temperature increases, the rate of swelling greatly increases. The second effect is on the extent of swelling. As the temperature increases, the extent of swelling decreases.

The equation expressing the relationship between the extent of swelling and temperature as derived by Flory and Rehner[7] is as follows:

$$d \ln v_2 = \frac{K}{2\,[5/6\,(K-1) - 8/9\,v_2 - 11/12\,v_2^2]} \qquad 1$$

where v_2 = volume fraction of the polymer

$K = A + \frac{2BV_1}{RT}$ A and B are constants, V_1 volume of solute, T is the absolute temperature and R is the gas constant.

For small values of K and high degrees of swelling,

$$\frac{d \ln v_2}{d \ln T} \simeq \frac{-3K}{5\,(1-K)}\,(1-v_2) \qquad 2$$

As may be seen in equation 2), the absolute extent of swelling would be expected to decrease with increased temperature (the negative sign). The reason for the negative sign in equation 2) (i.e., why the rubber network is harder to expand as the temperature increases) is because the elastic energy is stored as entropy, not enthalpy (heat content). Consider the following equation:

$$\Delta F = \Delta H - T\Delta S \qquad 3$$

where ΔF = change in free energy

ΔH = change in enthalpy

ΔS = change in entropy

T = absolute temperature

Under isothermal conditions, ΔH is virtually zero in a rubber material. As may be seen, adding energy to the system by stretching the rubber (positive ΔF), the entropy must decrease, thus energy is stored in the $-T\Delta S$ term. As the temperature increases, it is obvious that an increased amount of energy must be added to achieve an equivalent change in entropy. Thus the network becomes stiffer as temperature increases.

The fact is emphasized that the extent of swelling would be predicted to decrease with temperature because, should experimental data show an increase in swelling with temperature, it would indicate that some other reaction is taking place. In other words, whenever there is a greater ultimate swelling at a higher temperature, something is happening to the rubber. It may be devulcanizing, detaching itself from the carbon black particles or undergoing some other process which decreases the crosslink density.

The rate of swell is related to the ability of the asphalt to diffuse into the rubber. Oliver[8], in discussing diffusion of oils into asphalt, found that the diffusion coefficient was related thusly:

$$D = A\ e^{-E/RT}$$

where D is the diffusion coefficient

A is a constant

E is an activation energy

R is the gas constant

T is temperature

That is, an exponential equation. As the asphalt diffuses into the rubber and interacts with it, energy is given up, which is absorbed by the work of expanding the rubber network. At equilibrium, the energy of solution equals the energy stored in the network. Because of the exponential nature of the diffusion equation, with T in the denominator of the exponent, the rate of swell is very sensitive to temperature.

Evidence for this release of energy has been observed in the experimental work. In preparing asphalt rubber samples from paving grade asphalt and ground, reclaimed tire rubber, a rise in mixture temperature is observed 5-15 minutes after adding the rubber to the hot asphalt. This causes difficulties in maintaing a constant mixture temperature during the sample preparation and in achieving good repeatability on duplicate preparations. It is felt that this temperature rise is caused by an excess of energy released during the diffusion of the asphalt into the rubber.

EFFECT OF PARTICLE SIZE ON RATE OF SWELL

Backley and Berger[9] have studied the rate of swelling of rubber. From their work, and other work on diffusion, the relationship that the time required to swell the 1/2 the equilibrium value will increase with the radius squared can be derived.

Crank[10] in discussing diffusion into a sphere from a well-stirred solution of limited volume arrived at the equation:

$$\frac{M\tau}{M\infty} = 1 - \Sigma_{n=1}^{\infty} \frac{6\alpha(\alpha+1)e^{-Dq_n^2\tau/a2}}{9 + 9\alpha + q_n^2\alpha^2}$$

where $M\tau$ = amount of solute in sphere at time = τ

$M\infty$ = total amount of solute at time = ∞

τ = time

a = radius of the sphere at time = τ

D = diffusion coefficient

q_n = non zero roots of Tan $q_n = \frac{3q_n}{3 + \alpha q_n^2}$

$\alpha = \frac{3V}{4\pi a^3}$ (ratio of the volume of solution to volume of sphere)

To assess the inter-relationship between τ and a, one might run a mental experiment of swelling at constant $M\tau/M\infty$ and constant α. Under these conditions, $M\tau/M\infty$ can remain constant only if the ratio τ/a^2 remains constant, i.e. τ proportional to a^2. Decreasing the radius by a factor of 2 decreases the time to swell be a factor of 4.

EXPERIMENTAL

SWELLING EXPERIMENTS

The purpose of these experiments was to evaluate the rate and extent of swelling of rubber samples at various temperatures in order to develop a test method for specifying and designing the hot asphalt rubber seal. The first series of experiments consisted of determining the rate of swelling of samples of ASTM E-501 rubber stock in four selected oils and one asphalt

at temperatures ranging from 52°C (125°F) to 191°C (375°F). This rubber is an oil-extended styrene-butadiene rubber (SBR) conforming to the specifications listed in ASTM E 501-73. Rubber samples were obtained from the tread of an ASTM skid testing tire. 6-9 gram rubber samples, cut from the tire tread and measuring approximately 40mm x 20mm x 12mm, were placed in ten times their weight of oil or asphalt and placed in an oven to soak at a constant temperature. The samples were removed daily and their weights and volumes recorded. Volume determinations were made by weighing in water and calculating the volume of displaced water. The oils used were Dutrex 739 (Shell), Califux G.P. (Golden Bear), XPD 8181 (Shell) and Docal 166 (Douglas Oil). An AR-1000 asphalt from Edgington Oil Company was used to determine swelling in asphalt. The properties of the oils and asphalt are shown in Table I.

TABLE I

Characterization of Oils and Asphalts

Material	Viscosity 60°C (140°F), p	Viscosity 135°C (275°F), cs
Dutrex 739	2.12	
Califlux GP	1.55	
XPD 8181	10.47	13.4
Docal 166	5.53	
AR-1000	638	151
AR-4000	1908	
200/300	284	
AR-1000 Maltenes	74.5	

The second set of experiments was made with specially formulated and prepared rubber buttons. These samples were uniform in size and weight, which made it easier to standardize a test method for evaluating the ability of asphalts and oils to swell rubber. The same oils and asphalt used in the ASTM tire tread swelling experiments were used in the second set of experiments.

A standard test method was developed from these experiments which can be used to determine the ultimate percent swell of a particular rubber formulation in a given asphalt or oil. This method is included as Appendix I.

VISCOSITY TESTS

Determining the viscosity of the hot asphalt rubber mix, with and without the addition of solvent, is quite difficult. The swollen rubber particles are too large to pass through a standard vacuum capillary viscometer. Methods involving the use of rotating spindles to determine viscosity fail when the spindle developes a channel between the rubber particles and effectively measures only the asphalt viscosity. The asphalt rubber mix generally has a very high viscosity after the rubber has swollen. This requires a driving force to make the sample flow, such as is found in a vacuum viscometer.

In this study, viscosities were determined with Asphalt Institute size 400 viscosity tubes. Initial attempts to run viscosities by ASTM Method D 2171-66 at 30 cm of Hg applied vacuum resulted in the column of sample tearing or cavitating in the capillary. Plug flow was also observed in some samples. It was found that the samples could be run successfully at

lower applied vacuums, generally between 3 cm of Hg and 10 cm of Hg. An appropriate correction was applied to the viscometer constants to compensate for the lowered vacuum. Asphalt rubber mixes, with and without added solvent, were run at 60°C (140°F) by this method. Details of this method are shown in Appendix II.

The precision of this modified vacuum viscometer method differs from the standard procedure using 30 cm of Hg. Replicate samples vary by as much as 10% of the mean value, however, it has been noted that the measured viscosity changes with the order that the viscometer tubes are filled. The last tube filled from a given sample container generally has the highest viscosity. The hot asphalt rubber mix is apparently reacting in the sample container during the time it takes to fill the viscometer tubes. This emphasizes the need to keep the samples cool until just before testing in order to achieve reproducible results.

DYNAMIC PROPERTIES OF THE HOT ASPHALT RUBBER BINDER

In order to obtain a better understanding of the differences between asphalt and the hot asphalt rubber binder, samples of AR-1000 asphalt and the hot asphalt rubber seal (containing 25% tire buffings) were sent to Professor C. W. Macosko at the University of Minnesota for testing on the Rheometrics Mechanical Spectrometer[11] [12]. This rheometer was operated in the eccentric roating disc (ERD) mode under dynamic conditions. In the ERD mode, a sample is positioned between two parallel discs which rotate (or vibrate) at the same angular velocity (or frequency). There would be no stress on the sample if the centers of rotation of the discs were in

the same axis. However, when the centers of rotation are offset by a given distance "a", a shearing action takes place. At a given angular velocity, offset distance "a", sample thickness "h", and temperature, a measure of the dynamic modulus of the sample can be determined. Variations in the angular velocity and sample temperature can reveal a "mechanical spectrograph" of the material under test. This can help to explain the effect of stress and temperature on the dynamic properties of asphalt rubber binders.

Tests were conducted on the asphalt and asphalt rubber binder submitted for evaluation over a temperature range of -20 to 50°C (-4 to 122°F) and a range of angular velocities of 1.0 to 100 radians per second. A detailed description of the Rheometrics Mechanical Spectrometer and its operating principles can be found in references (11), (12) and (13).

STRAIN RECOVERY EXPERIMENTS

The strain recovery experiments were conducted to develop a test procedure which might be used in a control laboratory to measure the viscoelastic response of the asphalt rubber binder. A high viscoelastic character to the mixture would indicate that the rubber particles had reached, or nearly reached, its ultimate percent swell and were adding their elastic properties to the asphalt. A low viscoelastic character would indicate that the rubber particles had not reacted fully with the maltenes and/or oils in the asphalt. In this case, the rubber would act simply as a filler. A strain recovery test would indicate the state of "cure" of the asphalt rubber binder and could be related to performance on the job, after appropriate correlation tests.

These experiments were conducted with a sliding plate microviscometer at a temperature of 25°C (77°F). Samples were prepared on glass microviscosity plates at a film thickness of 0.1 inch (2.54 mm) and an area of approximately 5 cm^2. After the sample was placed into the microviscometer and allowed to condition until all induced stresses were relieved, a 50 gram load (equivalent to about 981 pascals stress) was applied until a strain of 197 μm/mm was achieved, after which the stress was removed. In effect, a reverse load was applied to the sample. When the weight was removed, a strip chart recording similar to a microviscosity recording was obtained. This recording yielded information about how the sample responds to a given strain and how fully it recovers from its deformation. The complete test method may be found in Appendix III.

RESULTS AND DISCUSSIONS

SWELLING EXPERIMENTS

A critical property of the hot asphalt rubber seal is the manner in which the viscosity of the mixture increases with time as the rubber particles swell. Swelling is quite rapid at application temperatures, and if not well controlled, may occur too fast with the result that application problems will occur. The rate at which the rubber particles swell depends upon the interaction between the rubber and solvent (in this case, asphalt), temperature, viscosity of the solvent and particle size of the rubber.

The data obtained on the first set of swelling tests at 121°C (250°F) are shown in Figures 1 and 2. As may be seen, the increases in weight and

volume are plotted against time for the various oils and the asphalt. The weight gain data gave a smoother curve. The differences in precision (or smoothness of the curve) are attributed to the difficulty in determining volume of the rubber samples. A procedure was later developed to determine the volume with greater precision.

In the initial analysis of the data, a linear relationship was found by plotting ln (t + a) against % swell (weight gain), where "t" is time and "a" is an arbitrary constant. Those equations are shown in Figure 3. All data obtained with the oils were found to fit the following equation:

$$\text{where } s = m \ln (t + a) - 200 \qquad \underline{4}$$

s = % swell

m = slope of plot

a = constant

The values for m and a are shown in Table II.

TABLE II

Oil	m	a
Dutrex 739	67.41	22.0
Califlux GP	64.81	28.8
XPD 8181	57.25	43.0
Docal 166	49.70	71

The formula for swelling with AR-1000 was of the same type, except that the intercept was considerably lower:

$$s = 25.42 \ln (t + 100) - 112.0 \qquad \underline{5}$$

The slope, m, for the equation for the swelling of the oils was found to be related to "a" by the following equation:

$$m = 163\ a^{-0.277} \qquad 6$$

Interesting enough, if the equation for the swell in asphalt is multiplied by a factor which would make the incercept 200, then:

$$1.786\ s = 45.4\ \ln\ (t + 100) - 200 \qquad 7$$

and equation 6) would predict a value of m of 45.5, which is within experimental error of that found with the oils.

In the function f (s,t) shown as equation 4), both the domain and range of f map onto an infinite set;

$$\text{Dom } f = \{s:(s,t)\varepsilon S\rightarrow[0,\infty]\}$$

$$\text{Range } f = \{t:(s,t)\varepsilon T\rightarrow[o,\infty]\}$$

This is obviously incorrect for the domain, as experience has shown that $s\ \varepsilon\ S \rightarrow[0,s_m]$ as the swell reaches a finite maximum s_m. The mapping of the range is correct, however.

In other words, while equation 4) will fit the data, it must be limited to the extent of that data and may not be extrapolated, since that equation predicts the swelling would continue to increase with time, while in fact, it reaches a limit.

It is therefore postulated that a relationship which would more closely describe the swelling mechanism should be in the form of equation 8) below:

$$\text{where} \quad s = s_m\ (1-Ce^{-kt}) \qquad 8$$

$$s = \text{percent swell}$$

s_m = maximum swell possible at time = ∞

k = rate of swell

C = constant

t = time

This equation allows the prediction of the maximum possible swell, a clear advantage over equation 4) since, as time increased, s approaches s_m as a limit; ie $s \in S \rightarrow [0, s_m]$ for all $t \in T \rightarrow [0, \infty]$. This equation was found to fit the data very well.

For convenience of plotting, equation 8) was rearranged as follows:

$$\ln \left(\frac{s_m}{s_m - s}\right) = kt - \ln C \qquad \underline{9}$$

s_m was then adjusted until a straight line was obtained. The data found for the swelling experiments at three temperatures on the specimens of tire tread are shown in Table III and Figures 4-11. The experiments conducted at 191°C (375°F) were terminated sooner than those experiments at lower temperatures. The test specimens began disintegrating after about 72 hours at 191°C (375°F). In some cases, dramatic weight losses were noted as the samples lost surface rubber during the weighing operation.

Theoretically, the value of s_m should decrease as the temperature is increased, however, at 191°C (375°F), s_m was larger than at 135°C (275°F). This indicated that the network is loosening up, either by chain sission, or detachment of the rubber from the carbon-black particles. Kim[14] has shown how chain detachment can occur, resulting in a decreased modulus and greater elongation at break, while Crane and Kay[15] have shown that aromatic solvents can cause depolymerization of SBR polymers, although the

process may take 12-24 hours at a temperature of 250-275°C (482-527°F). k is the kinetic rate constant for the swelling operation. The effect of temperature on the rate of swelling are shown for the Califlux GP and AR-1000 data in Figure 12. As may be seen, these plots are curved, deviating from linearity at the higher temperatures.

It was expected that if the value of the intercept constant C deviated from unity, it would be above rather than below unity, the deviation reflecting the time lag required to get the samples up to temperature. This is not the case, however. It is considered that the most probable cause of the value of C being less than one is continued vulcanization. In the preparation of rubber compounds, vulcanization proceeds to what is termed the optimum cure, which may not be the state of vulcanization at which all of the sulfur has been used up. As an example, if it is assumed that an additional 1/2-1 hour of cure is needed at 150°C (302°F) to use up the remaining sulfur, and that the activation energy of SBR vulcanization is the same as that of natural rubber (about 23 K cal/mol [16-20]), then at 135°C (275°F) an additional 4-8 hours would be needed to complete the vulcanization. This would suggest that care must be taken in using early swell data at the lower temperatures as post-vulcanization may not be complete.

In order to establish the swelling test as a routine procedure, it was necessary to standardize the rubber compound used and the geometry of the specimens. A description of the rubber formulation is shown in Appendix I. The test specimens were Yerzley test buttons as described in ASTM D-945.

As has been mentioned earlier, the extent of swelling of the rubber specimens will depend upon the crosslink density of the rubber (ie state of vulcanization), the type of asphalt used, and the temperature. In our test procedure, the crosslink density of the rubber was controlled by carefully controlling the compounding and vulcanization of the rubber specimens, and by using a standard asphalt as a control asphalt. The extent of crosslinking of the rubber specimens is determined by swelling them in toluene at 38°C (100°F) as described in the method in Appendix I. This method yields a maximum swell (s_m) from the measured swell (s) data by a trial and error method of estimating a value of s_m for the sample and plotting $\ln \left(\frac{s_m}{s_m - s}\right)$ versus time. If a curved line results, a new s_m is estimated and replotted until a straight line is achieved. The value of s_m which yields a straight line is the maximum percent swell possible for the sample. In Table IV are compared the state of vulcanization of two separate sets of Yerzley specimens analyzed by this technique.

TABLE IV

Extent of Vulcanization of Yerzley Buttons

	Swelling Constants		
	s_m	k	C
Set #1	268.7	1.178	0.861
Set #2	278	1.025	0.861

The significant comparison is with the value of s_m, which measures the extent of the cure. These determinations were made on different batches of Yerzley buttons, in two different laboratories by different personnel.

As may be seen, the extent of swell differed by approximately 3.7%. In order to correct for differences in cure, the swelling of the rubber specimens in the asphalt may be expressed as a ratio to the swelling of specimens from different batches in toluene at 38°C (100°F). The swelling of the two batches of Yerzley buttons in different batches of Edgington AR 1000 asphalt are shown in Table V.

It is felt that the agreement between different runs is excellent, and that the use of the ratio of s_m in asphalt to s_m in toulene will work very well for specification criteria in determining the swelling ability of a given asphalt.

The swelling data obtained for the Yerzley buttons at 135°C (275°F) are shown in Table VI. Tests were run at 93°C (200°F) also, however, considerable difficulty was encountered in calculating that data. The accuracy of these values may be in question, as the samples did not swell sufficiently during the nine day duration of the tests to establish sufficient sensitivity to changes in s_m. Thus those data are not included in Table VI. Also, we suspect that some post vulcanization may be taking place over the initial 24-48 hours. In the use of a swelling test to evaluate asphalts with respect to their ability to swell the rubber particles in the hot asphalt rubber seal, the following criteria must be observed. The temperature of the test must be high enough so that the test may be concluded in a reasonable time, yet not sufficiently high to cause the disruption of the network of the rubber-carbon-black matrix. A reasonable temperature for the test is 135°C (275°F). A strict control of the temperature, and keeping

the time required to weight the specimens to a minimum should be observed in order to reduce the variance of the data. In these tests, data was gathered on both weight change and volume change, which required that the specimens be out of the oven for an hour for each measurement. If only weight changes are followed, the samples will be out of the oven only 5 minutes at a time. Since we are attempting to detect linearity, and test for curvature on either side of the plot in which the assumed value of s_m gives a straight line, a scatter in data will cause difficulty in selecting the proper value of s_m. Also, the duration of the test should be long enough so that the measured swelling is close enough to s_m for small changes in the assumed value of s_m to cause large changes in the calculated value of $\ln \left(\frac{s_m}{s_m - s}\right)$ for the last points of the plot. A good time interval of test at 135°C (275°F) might be to start on Wednesday, and end on Friday of the following week. Tests run at lower temperatures would have to be correspondingly longer.

SWELL TEST IN ASPHALT CUT WITH KEROSENE

The hot asphalt rubber membrane is usually prepared by adding kerosene to the mixture to reduce viscosity, thus aiding in spreading of the material. In addition to reducing the viscosity of the asphalt, the kerosene would be expected to reduce the solubility parameter of the asphalt. While a reduction in viscosity should increase the extent of swelling, the reduction in solubility parameter of the asphalt should work in the opposite direction with respect to swell.

The results of tests with kerosene addition are shown in Table VII.

TABLE VII

Swelling of Yerzley Buttons by Addition of Kerosene to the Asphalt

	Kinematic Viscosity at 135°C (275°F)	Absolute Viscosity at 60°C (140°F)	s_m	k	C
Asphalt	153 cp	647.6 poises	86	0.166	0.852
Asphalt + 7% Kerosene	-	101.4	93	0.237	0.861

The viscosity of the blend of asphalt and kerosene was 101.4 poises. If it is assumed that the viscosity of the kerosene was about 2 cp at 60°C (140°F), and that the viscosity of the blend of asphalt and kerosene could be calculated from the relationship described in ASTM D-341, we obtain a theoretical viscosity of 107 poises. The equation used was:

$$\log(\log \eta) = [11.69851 \log(559.7-po)-32.14699] \quad \underline{10}$$

$$[\log(\log \eta_\alpha) - \log(\log \eta_o)]$$

$$+ \log(\log \eta_\alpha)$$

where η = desired viscosity in cp

η_α = asphalt viscosity in cp

η_o = kerosene viscosity in cp

po = % kerosene

This excellent agreement implies that the kerosene acts only as a diluent, and doesn't aid in dispersing of the asphaltenes as an aromatic oil would do. Unpublished data available to the authors have shown that the viscosity of a blend of asphalt and solvent (or oil) will be considerable lower than that predicted by equation 10) if an aromatic oil is used.

The addition of the kerosene actually had an inhibiting effect on the

swelling if the much lower viscosity of the asphalt-kerosene mix is taken into consideration. This is shown graphically in Figure 13 where the effect of viscosity and oil composition on swelling is shown. Plotted on this graph also is unpublished data of the swelling in asphalts other than AR-1000 from the same source as the AR-1000. Notice that the point representing the blend of asphalt and kerosene is displaced beneath the line. An asphalt with that same viscosity should have caused the sample to swell to about 113% rather than the measured 93%, nearly 18% less. On the plot also are compared the effect of viscosity of the asphalt on swelling, and the effect of blends of asphalt and Dutrex 739. As may be seen, the plots for the asphalts (of different viscosities but the same source) and plots for the blends of asphalt and Dutrex 739 fall on the same line. This implies that the oils that remain by distilling to a lighter asphalt is compositionally similar to Dutrex 739. This would also imply that an asphalt run directly off of a vacuum tower may be of different composition than an asphalt made by blending a hard asphalt with a heavy gas oil (or lube stock), which is commonly done.

VISCOSITY OF THE ASPHALT RUBBER BINDER

When the particles of rubber swell to such an extent that they interfere with one another, the hot asphalt rubber seal gels and cannot be pumped and placed easily. This gel state is the eventual desirable consistency of the in place material. The tendency to gel and the length of time it takes for gelling to occur depends upon the temperature of mixing, the phase volume of the swollen rubber, the viscosity of the asphalt

phase and the gradation of the rubber particles. To aid in application and proper seating of the chips, kerosene is added which lowers the viscosity of the asphalt and reduces the phase volume of the rubber particles. In developing specifications for the hot asphalt rubber membrane we need to specify the properties of the final end product, and the properties of the product when diluted with kerosene.

The purpose of this section is to obtain viscosity data on the hot asphalt rubber binder with and without the addition of kerosene and to develop a basis for test procedures which could be used in specifications. The relation between viscosity and phase volume is quite complicated, as the viscosity of the asphalt continuous phase will increase as the rubber absorbs oils. If the rubber preferentially discriminates against the asphaltenes, we can have a situation where the asphaltenes in the asphalt become metastable and cause the asphalt viscosity to rise abruptly. Kalbanovskaya[21], has shown that the viscosity of certain asphalts rises abruptly at a lower asphaltene concentration than in other asphalts. Altgelt and Harle[22] have demonstrated the same effect and were able to relate this effect to molecular weight of the asphaltenes and the solvent power of the maltene fraction of asphalt.

In our system, the second phase is not composed of spheres which are commonly used for the theoretical analysis of the viscosities of solid-liquid mixtures, but rather, shreads of rubber in the dispersed phase which are swelling while the continuous phase is an asphalt whose viscosity is changing with time. The asphalt rubber system is more complex than

those systems reported in the literature, thus what is calculated will not be accurate in an absolute sense. However, it should be sufficiently precise to show relative differences between systems and maybe used in describing various systems.

The first equation proposed for evaluating the bodying effect of a dispersed phase was that presented by Einstein[23] for systems with small concentrations of a dispersed phase.

$$\eta_r = \frac{\eta}{\eta_o} = 1+k_i\phi \qquad \underline{11}$$

where η = measured viscosity

η_o = viscosity of the continuous phase

k_i = constant = 2.5

ϕ = volume fraction of the dispersed phase

For more concentrated systems, additional terms are required, and there have been numerous equations proposed, nearly all of which are based upon ridged spheres in a medium with a stable viscosity.

One such equation is that developed by Lewis and Nielson[24].

$$\eta_r = 1+2.5\phi + 7.031\phi^2 + 37.37\phi^3 \qquad \underline{12}$$

and another is an exponential equation presented by Lee[25].

$$\eta_r = \frac{1}{(1-\phi)^{(2.5 + 1.95\phi + 7.739\phi^2)}} \qquad \underline{13}$$

None of these equations can be expected to give an exact fit. However, they do give us a starting point to study what is happening in the hot asphalt rubber mixture, which is much more complicated than a rubber latex or a dispersion of glass spheres.

As mentioned earlier, with certain asphalts, when a critical asphaltene concentration has been reached, the viscosity will increase sharply. Hillyer and Leonard[26] have discussed the mechanism of such viscosity rises of polymers in relatively poor solvents, while Atlgelt and Harle[22] have shown the same effect of asphaltenes in asphalts. There are, therefore, two viscosity effects; that of the rubber particles, and that in the asphalt itself as a result of a change in the asphalt composition as fractions of the asphalt are absorbed by the rubber.

Experiments were conducted in which viscosities were run on mixtures of the rubber at various concentrations in the various oils, and in asphalt. Those data are shown in Figure 14. The data for the rubber in asphalt was analyzed using the cubic equation of Lewis and Nelson[24] shown above and back calculated what the change in viscosity of the asphalt (not the asphalt rubber mixture) would be if it was assumed that the rubber swelled by a factor of 1.5. The results are shown in Table VIII below.

TABLE VIII

Measured Viscosity poises	Rubber Weight %	Rubber Volume: Unswollen	Rubber Volume: Swollen, 1.5x	Calculated Asphalt Viscosity
460	0	0	0	460
570	5	4.35	6.53	474
1120	10	8.70	13.05	733
3650	15	13.04	19.56	1791
7900	20	17.30	25.95	2846
15500	25	21.65	32.48	4043

A factor of 1.5 was used because the swell data in a previous section showed that, a 121°C (250°F), the tread stock would be expected to swell by a factor of 50%. These data are presented only on an exploratory basis and this phase of the studies will not be pursued further. However, it is clear that, if it were possible to recover the asphalt and determine its viscosity, it might be possible to determine what the proper equation would be. Of course, the rubber acts as more than an inert filler in the asphalt rubber mixture. Its presence alone can cause the asphalt to increase in viscosity by its absorption of maltenes, but it also interacts with the asphalt to produce viscosities much higher than that which is predicted by these equations, as can be seen in Table VIII. In Figure 15 is shown a plot of the calculated asphalt viscosity vs the swollen rubber volume. As may be seen, the asphalt viscosity starts to increase sharply at about 16% swollen rubber volume. This point of rapid increase might be expected to depend upon asphalt type since the rubber should compete with the higher molecular weight asphaltenes, resulting in an increase in asphaltene concentration. As mentioned before, certain asphalts are "bodied up" by asphaltenes at a faster rate than are others. Thus, some asphalts may increase in viscosity at a faster rate than others from the loss of maltenes into the rubber particles.

It was noted during the course of the sample preparations for the viscosity determinations that sample handling can have an effect on viscosity. Duplicate formulations prepared with and without agitation yielded materials with greatly differing viscosities. Samples prepared by oven digestion

with occasional hand stirring had viscosities five times higher than samples prepared with continual high speed mixing (500 RPM stirring). It is thought that the shearing action of the mixer is tearing the softened rubber particles in the mixture and reducing the particle-particle interaction. This tends to lower the viscosity of the mixture. Field sample viscosities fall roughly midway between laboratory samples with intermittent and continual stirring, suggesting an intermediate mixing rate is occuring in production equipment.

EFFECT OF TEMPERATURE ON VISCOSITY

The viscosity at 60°C (140°F) mixes of 75% AR-1000 and 25% TP 044 rubber was determined after being digested at 177°C (350°F), 191°C (375°F), 204°C (400°F) and 218°C (425°F) and at various time intervals. The data obtained are shown in Figures 16, 17, 18, and 19. As may be seen, the viscosity decreases as the temperature of heating increases. This is in agreement with theory which would predict that swelling would decrease as the temperature increased, although the rate of swell would increase with temperature. As may be seen in Figure 20, the amount of swell decreases with increased temperature. These data are in agreement with field observations that the asphalt rubber changes with time under ambient conditions. At 25°C (77°F) one would expect that the equilibrium viscosity would be considerably higher than that at 204°C (400°F), however, it would take much longer for equilibrium to be reached at the colder temperatures.

RHEOLOGICAL PROPERTIES OF THE HOT ASPHALT RUBBER BINDER

The rheology of rubberized asphalt differs from that of asphalt in ways which are not obvious from simple viscosity measurements. We have become accustomed to using a single number to characterize the response of a material to stress. If the material is elastic, the ratio of stress to strain is used, which is called modulus. If the material is a fluid, the ratio of stress to rate of strain, is used, which is called viscosity. Most common liquids we deal with are Newtonian, which means that the ratio of stress to rate of strain is affected only by temperature and is independent of rate of shear or length of time of application of shear. When deviation from linearity of the relationship between stress and rate of strain occurs, a simple empirical equation often may be used to again get a straight line, such as defining the viscosity as the ratio of stress to strain rate raised to some power other than 1. At any one temperature, oil products, including asphalt, have therefore been characterized by using one number, which we call viscosity.

With asphalt rubber, a different situation exists and a single number isn't sufficient to describe the stress-strain behavior. According to Lodge[27], in order to provide fundamental information to test the applicability of proposed constitutive equations for a given viscoelastic material, the first and second normal stress differences as well as the viscosity must be measured.

The normal stress differences are forces which develop normal (ie perpenidcular) to the direction of shear. These normal stress differences

are not abstract mathematical concepts, but rather real phenomena which must be taken into account in predicting how a material will behave. As an example, the hot asphalt rubber binder, when stirred, climbs the stirrer shaft, moving in a direction opposing gravity and centrifugal force. This phenomena, called the Weissenberg effect, is a manifestation of the normal stress differences. Hoffman & Gollengerg[28] have used this effect to determine the normal stress function. The swelling of viscoelastic materials when being extruded through a die is also caused by the normal stress differences, which is caused in turn by the presence of an elastic as well as viscous response when a material is under stress. Blyler[29] has related the primary normal stress differences with the elastic component of the dynamic modulus, showing that its occurence is related to the presence of elasticity.

MECHANICAL SPECTROGRAPH

In order to obtain a better understanding of the differences between the asphalt rubber and asphalt, samples of Edgington AR 1000 asphalt and an asphalt rubber mixture of Edgington AR 1000 asphalt containing 25% TP 044 rubber were sent to Professor C. W. Macosko at the University of Minnesota for testing on the Rheometrics Mechanical Spectrometer, as described in the Experimental section. Through the use of the mechanical spectrometer, it is possible to measure separately the influence of the elastic and viseous components of the dynamic modulus, and determine the ranges of temperature and frequency over which both are a significant factor in evaluating the response to stress. The data obtained by Professor Macosko are shown

in Tables IX and X. Here the individual components of the dynamic modulus are shown for asphalt and an asphalt rubber mixture.

The dynamic modulus (G*) consists of an elastic (or real) component (G') which reflects the elastic response of a material and a viscous (or imaginary) component (G") which reflects the viscous response of a material. G' is also called the storage modulus, as the energy stored upon extension is a function of this component. G" is also called the loss modulus, as the energy dissipated upon extention is a function of this component. G" is 90° out of phase with G', and G* is the vector sum of G" and G', ie

$$G^* = \sqrt{(G')^2 + (G'')^2}$$

As may be seen, the rheological properties of the asphalt rubber was markedly different from those of pure asphalt. In Table XI and Figure 21 are compared the calculated dynamic viscosities of the asphalt and asphalt rubber. As may be seen, the asphalt rubber has a higher modulus or stiffness and a higher viscosity than asphalt above about $10^{o}C$ ($50^{o}F$) but a lower modulus or stiffness than asphalt below $10^{o}C$ ($50^{o}F$). Also, the ultimate maximum stiffness for the asphalt rubber is about one fifth of that of asphalt. If we assume that the tensile strength of the asphalt rubber is about the same as that of asphalt, we can conclude that, in cold weather, the asphalt rubber can undergo about five times the strain before rupture than can asphalt.

Although it hasn't been included in the scope of this project, future studies on the tensile strength and cold tear strength of the hot asphalt rubber binder might be interesting to conduct. The presence of the rubber

particles dispersed throughout the brittle asphalt should provide a means to stop crack propagation in the same manner as rubber does in high impact grades of polystyrene. As brittle materials (eg. asphalt in very cold temperatures) undergo tensile failure by crack propagation, the presence of the rubber might change the character of such failure. As an example, crystal grade polystyrene has a high tensile strength, but very low strain at failure. Impact grade polystyrene, on the other hand, while not having as high a tensile strength, goes through a yield point then elongates much further than does the crystal grade. Thus the energy required to cause failure (ie. the area under the stress-strain curve) in the impact grades, is much greater than with crystal grade.

At higher temperatures, the asphalt rubber is much stiffer and much more viscous. As an example, at 40°C (104°F), and 1 rad/sec, the elastic modulus of the asphalt rubber was 44,000 dynes/cm^2 while that of asphalt was only 200.

Professor Macosko, in his comments on these data stated:

"Based on (the) dynamic data at 30°C, I would expect the asphalt to be Newtonian and show low normal stresses. ...We would expect (the asphalt rubber) to have a higher but strongly pseudoplastic viscosity with significant normal stresses."

As mentioned earlier, the normal stresses are stresses which develop in a material in shear which tries to force the material in a direction normal (ie. perpendicular) to the direction of flow (the Weissenberg Effect). This would imply that those materials which manifest normal stress differences

would shrink in the direction of flow and expand in the directions normal to flow. This might explain why the hot asphalt rubber seal will cause cracks to heal under rolling traffic even though its viscosity is much higher than asphalt. Also, as mentioned earlier, the rubber particles probably act as a barrier to stop crack propagation.

The existance of normal stress differences may be deduced from the data as, at equivalent viscosity, the asphalt rubber has a higher G' modulus (elastic modulus) than does asphalt. As mentioned earlier, the cause of normal stress differences is the presence of elasticity. These tests are preliminary, however, they do show quite conclusively that the hot asphalt rubber binder differs from asphalt in ways other than simply differences in viscosity.

A portion of the data in Tables IX and X are shown graphically in Figures 22 and 23. The Tg shown in the estimated glass transition point at the frequency of 10 rad/sec. This data was developed at a single operating frequency of the Mechanical Spectrometer and its significance should be limited to indicating that this instrument has the potential of being a valuable tool in studying asphalt rubber systems. The slope of the curves suggests that the temperature susceptability of the asphalt rubber is less than that of the asphalt. Although the Tg is approximately the same for both materials, this might not hold if measurements were made at different frequencies. Detailed evaluations of asphalt rubber systems on this instrument might provide a means of further defining the visco-elastic properties of these systems.

STRAIN RECOVERY

The mechanical spectrograph is an excellent research took, however it is not one which exists in an asphalt control lab or which would be expected to appear in such a lab. Other rheometers on which the significant properties of asphalt rubber might be determined are of equal complexity and price ($30,000 - 50,000)[30]. To approach this problem in a manner which would provide data useful in theoretical viscoelastic equations would require the above complex equipment, and a rheologist and mathematician to use and interpret the data. It is therefore concluded that direct measurement of these fundamentally important properties would not suffice for a routine test procedure.

The goal is to develop a routine method which could be used for control purposes, thus the need to find a test procedure which reflects the presence of viscoelasticity on a comparative basis. It is not necessary to obtain exact data which would satisfy the theoretical rheologist in his task to construct constitutive equations, but rather only to obtain comparative data which would satisfy the construction engineer in this task to build roads and streets.

To do this, other manifestations of viscoelasticity such as creep, stress relaxation and strain recovery can be considered. These procedures are not complex to run, although the mathematics of trying to derive and fit the theoretical equations to the data is complex and more than one would expect to be done for control purposes by non-professional help. One approach in resolving this problem was to measure strain recovery

(rather than stress relaxation or creep) using the slide plate viscometer, an apparatus commonly found in an asphalt laboratory, and use an equation which, though not theoretically derived, fits the data and allows the operator to separate the viscous from the elastic response.

The procedure was to apply a load of 50 grams to a sample of the asphalt rubber sandwiched between two glass plates and deform the sample a given distance, then release the load and record the rebound (strain recovery). The strain recovers in a monotonically increasing manner, leveling off close to a maximum within approximately thirty minutes. We propose the use of an empirical equation in this form:

$$X = x_m (1 - e^{-Bt^n}) \qquad \underline{16}$$

$$f\ (x,t) \varepsilon F$$

$$\text{Dom } F = \{x:(x,t)\varepsilon X \rightarrow [o,Xm]\}$$

$$\text{Range } F = \{t:(x,t)\varepsilon T \rightarrow [0,\infty]\}$$

where x = strain recovery at time t in μm/mm

x_m = maximum strain recovery

t = time in minutes

B = constant

n = constant

This equation satisfied the conditions that $x = 0$ when $t=0$ and $x = x_m$ when $t=\infty$. The data obtained in our experiments was then plotted thusly.

$$\ln\ln \left(\frac{x_m}{x_m - x} \right) = n\ln t + \ln B$$

x_m is assumed to be equal to or at least close to the maximum recorded. t is the time from release of the weight. If there is some curvature in the plot at high values of t, x_m may be adjusted as needed.

x_m, which is zero with asphalt at 25°C (77°F), is a measure of the elasticity of the system, while the constant B and the exponent, n, are sensitive to the viscous nature of the material. The method is shown as Appendix III.

Strain recovery tests were run on a number of mixes, data for four of which are shown in Table XII. These tests were run in triplicate, which allowed the calculation of precision data.

As may be noted, two of the mixes contained kerosene, and two did'nt. It is interesting to note that the samples containing kerosene showed strong rebound, even with sample #1 in which the viscosity was so low that the prestress had to be reduced by 60%. The rebound per unit of stress applied were all between 1.30 and 1.91 x 10^{-4} P_a^{-1}.

An analysis of variance was conducted on the test data, using only those mixes in which 50 grams weight was used. A standard deviation of 5.97 about the individual means was found. Thus a 95% confidence level would be ±12.8 μm/mm of the mean and a 99% confidence level would be ±17.8 μm/mm of the mean. These were calculated using the Students *t* ratio with 14 degrees of freedom. The statistical analysis also indicated that the differences among the three sets of data obtained on mix #1 are not statistically significant. These samples were tested on three different days but were from the same mix. The difference between the means for mix #1 and mix #2,

which had been prepared with kerosene, are significant to a confidence level of 99%, using the Student t test with 13 degrees of freedom and pooling the variances. As the standard deviations of the two samples were 5.27 μm/mm and 5.46 μm/mm for mix #1 and #2 respectively, we can accept the null hypothesis of no difference between variances and felt safe to pool them.

Obviously the difference between mix #1 and mix #3 is significant. The precision of using the strain recovery (x_m) in the rebound test is quite adequate as a quality control test. The x_m measures the elastic qualities in rebounding while the constants n and B are related to the vicous retardation of that elastic rebound.

The standard deviation of the t_{90} values (time to 90% recovery of strain) for mix #1 was found to be 1.94 min, and an analysis of variance showed that the differences between the means for t_{90} on that mix are not statistically significant, using the F test.

The rebound tests appears to be an excellent tool for quality control of the asphalt rubber system, and a tool to separate the viscous and elastic effects. As a quality control method, there is no need to do an extensive analysis of the data, as was done here, but rather the rebound, or percent recovery, after 30 minutes may be used. Even though full recovery may not have occurred within that time, 90% recovery most probably will have occurred, especially when kerosene has been used.

For formulation studies, it might be well to determine x_m, n and B and use these parameters as guides for future work. However, it is convenient

to pool the effect of n and B and calculate a time at which 90% recovery may have occurred, since both n and B are related to the viscous response of the asphalt rubber material. As long as a fixed stress is used, the x_m is a handy parameter to use, or, especially for control work, the percent recovery. For more theoretically oriented studies, the rebound complicance together with x_m and the viscosity at 25°C (77°F) might be used to allow us to separate Equation 16 into parts representing the instantaneous rebound and viscous flow in a manner similar to that of Schweyer and Burns[31].

RECOMMENDATIONS

This study into the properties of asphalt rubber mixtures has revealed some of the many complex interactions which occur in these mixtures. There are many avenues of interest which could not be explored within the limited scope of this study, and the primary recommendation of this report is to continue other studies into theory, control and evaluation of asphalt rubber mixtures. Specific recommendations based on the results of this study are as follows:

1. The absolute viscosity at 60°C (140°F), 10 cm Hg, should be used to determine the viscosity of asphalt rubber and asphalt rubber-kerosene mixtures. The viscosity of the mixture is closely related to the handling and application of the mixture and may relate to field performance after field studies are performed.

2. The elastic rebound at 25°C (77°F) should be used to determine if the asphalt rubber mixture has been properly reacted. Performance evaluations will indicate the minimum rebound necessary to produce satisfactory results.

3. The test method for screening asphalts should be used for each different source and grade of asphalt if the ability of the asphalt to swell the rubber particles is in question. An asphalt with low swelling capabilities could then be modified with extender oils to more readily react with the rubber.

4. A chilling technique, such as is described in Appendix IV, should be used to assure that sample properties do not change during transit from the field to the laboratory.

5. Further work should be conducted to develop new test methods for determining the viscoelastic characteristics of asphalt rubber systems and how they relate to field performance.

6. The asphalt rubber system which gave desirable viscoelastic properties in this study is composed of an AR 1000 paving grade asphalt containing 25% by weight of #16-#25 mesh gradation SBR rubber from reclaimed tires. The mixture was digested with stirring for 60 minutes at 190°C (375°F) before testing or dilution with kerosene. Asphalt and rubber sources other than those used in this study may require a modification in the time-temperature-concentration parameters to achieve similar characteristics as the system under study here. The compatability of the various asphalt and rubber sources are expected to affect the properties of the mixture.

TABLE III

Constants for Swelling Equation, ASTM E-501 Tread Stock

$$s = s_m \left(1 - Ce^{-kt} \right)$$

	52°C (125°F)			121°C (250°F)			135°C (275°F)			191°C (375°F)		
Oils	s_m	k	C	s_m	k	C	s_m	k	C	s_m	k	C
DO 166	-	-	-	110	0.140	0.852	92	0.218	0.896	116	0.772	0.803
							105	0.219	0.852			
XPD 8181	-	-	-	140	0.184	0.878	144	0.227	0.795	189	0.950	1.000
Califlux GP	210	0.0557	0.954	170	0.226	0.819	164	0.252	0.811	213	1.258	1.000
Dutrex 739	-	-	-	190	0.262	0.878	175	0.262	0.819	-	-	-
							185	0.299	0.756			
AR 1000	70	0.0358	0.970	50	0.121	0.899	51.3	0.191	0.861	66	0.624	0.835
	70	0.0119	0.994	50	0.0992	0.886	-	-	-	-	-	-
AR 1000 Maltenes	-	-	-	-	-	-	57	0.201	0.838	-	-	-

s_m = maximum percent swell at $t = \infty$

k = rate of swell

C = constant

TABLE V

Comparison of Swelling of Different Barches of

Yerzley Buttons in Asphalts at 135°C (275°F)

Batch #1 in Asphalt #1	Swelling Constants s_m	k	C	Ratio of s_m in Asphalt to s_m in Toluene at 38°C (100°F) s_m(asphalt)/s_m(toluene)
Run #1	85	0.168	0.835	0.316
Run #2	82	0.166	0.861	0.305
Batch #2 in Asphalt #2	90	0.188	0.951	0.323
Adjusted for Viscosity[1]	88.7	-	-	0.319

	Asphalt Viscosities 60°C (140°F) poises	135°C (275°F) cs
Asphalt #1, Run #1	712	160
Asphalt #1, Run #2	692	158
Asphalt #2	Approx. 600	151.4

1 s_m adjusted to that expected at a viscosity of 160 cs at 135°C (275°F). It was assumed that swelling was proportional to the viscosity at 135°C (275°F) raised to the -0.3 power.

s_m = maximum percent swell at $t = \infty$

k = rate of swell

C = constant

TABLE VI

Constants for Swelling Equation for Yerzley Buttons, 135°C (275°F)

$$s = s_m (1-Ce^{-kt})$$

Oils	s_m	k	C
DO 166	190	0.173	0.923
XPD 8181	320	0.159	0.923
Califlux GP	320	0.226	0.942
Dutrex 739	370	0.210	0.905
AR 1000	90	0.188	0.951

s_m = maximum percent swell at $t = \infty$

k = rate of swell

C = constant

TABLE IX

Mechanical Spectrograph of Asphalt

Dynamic Data

Temp	Elastic Component G'					freq.	Viscous Component G"				
(°C)	1.0	3.0	10	30	100	(rad/sec)	1.0	3.0	10	30	100
		($\times 10^6$ dyne/cm^2)						($\times 10^6$ dyne/cm^2)			
50			~ 0						.01		
40	.0002						.005				
30	.0024		.04				.028		.29		
20	.04		.8	1.8	6.8		.26		2.1	5.7	16.3
15	.2		2.5				.91		7.5		
10	2		12	~ 50	~100		9.9		26	~60	~30
0	63	~ 120	~170	~200	~300		> 100	→			
-10	~ 300	~ 500	>500	→			> 100	→			
-20	> 500	→					> 100	→			

TABLE X

Mechanical Spectrograph of Asphalt-Rubber

Dynamic Data

Temp	Elastic Component G'					freq.	Viscous Component G"				
(°C)	1.0	3.0	10	30	100	(rad/sec)	1.0	3.0	10	30	100
		($\times 10^6$ dyne/cm^2)						($\times 10^6$ dyne/cm^2)			
50		.028	.089	.21	.41		.055	.064	.15	.27	.45
40	.044	.10	.25	.52	1.02		.15	.162	.33	.61	1.12
30	.204	.41	.78	1.45			.31	.43	.78	1.44	3.0
20	.70	1.32	2.44	4.4	9.6		.71	1.32	2.6	4.9	10.5
10	2.7	5.3	11	~30	~50		2.8	5.7	12	19	38
5	7.2	14	30	~50	~85		7.9	13	16	29	
0	32	~50	~75	~75	~90		24	29	10	< 10	→
-10	~70	~85	~90	~100	~110		< 10	→			
-20	> 120	→					< 100	→			

TABLE XI

Dynamic Viscosity, Kilopoises (G"/w)

	Asphalt					Asphalt Rubber				
Frequency, rad/sec	1.0	3.0	10	30	100	1.0	3.0	10	30	100
Temperature, °C										
50	-	-	1	-	-	55	21	15	9	4.5
40	5	-	-	-	-	150	54	33	20	11.2
30	28	-	29	-	-	310	143	78	48	30
20	260	-	210	190	163	710	440	260	163	105
10	910	-	750	-	-	2800	1900	1200	633	380
5	9900	-	2600	~ 2000	-	7900	4330	1600	970	-
0	*	*	*	*	*	24000	10000	-	-	-

*Response essentially that of a solid

TABLE XII

Data on Rebound of Asphalt Rubber

Sample	Made	Tested	Age Days @Room Temperature	x_m μm/mm	% Recovery	n	lnB	t90 min	t99 min	Stress Pascals	Rebound Compliance $x10^4$ Pa^{-1}
Neat											
Lab Mix #3	10/13/76	10/19/76	6	136	69.1	0.32	0.48	57.4	532	980.7	1.38
Lab Mix #3	10/13/76	10/25/76	12	138	70.1	0.29	-0.17	32.8	379	980.7	1.40
Lab Mix #1	9/13/76	10/14/76	31	183	93.0	0.23	0.40	6.6	130	980.7	1.83
Lab Mix #1	9/13/76	10/15/76	32	183	93.0	0.34	0.34	4.2	32	980.7	1.87
Lab Mix #1	9/13/76	10/21/76	38	187	95.0	0.28	0.38	5.3	65	980.7	1.91
With Kerosene											
Lab Mix #4 Sample 1	10/13/76	10/20/76	7	63	32.0	0.74	0.30	2.0	5.2	392.3	1.61
Sample 2	10/13/76	10/20/76	7	63	32.0	0.48	0.27	3.0	13.7	392.3	1.61
Lab Mix #2	9/13/76	10/18/76	35	172	87.4	0.34	0.41	3.5	27.1	980.7	1.75
Lab Mix #2	9/13/76	10/22/76	39	178	90.4	0.392	0.43	2.8	16.5	980.7	1.81

Notes: all are averages of triplicate data except #4
x_m is the strain recovery in μm/mm
n is exponent of equation below
lnB is intercept of $\ln\tau = 0$ in equation below
t90 is calculated time to 90% maximum recovery
t99 is calculated time to 99% maximum recovery
Strain at full scale = 196.7 μm/mm = plate movement ÷ sample thickness

Equation $\ln\ln\left(\frac{x_m}{x_m - x}\right) = n \ln t + \ln B$

FIGURE I

PERCENT INCREASE IN WEIGHT
E-501 TIRE TREAD RUBBER
AT 250° F

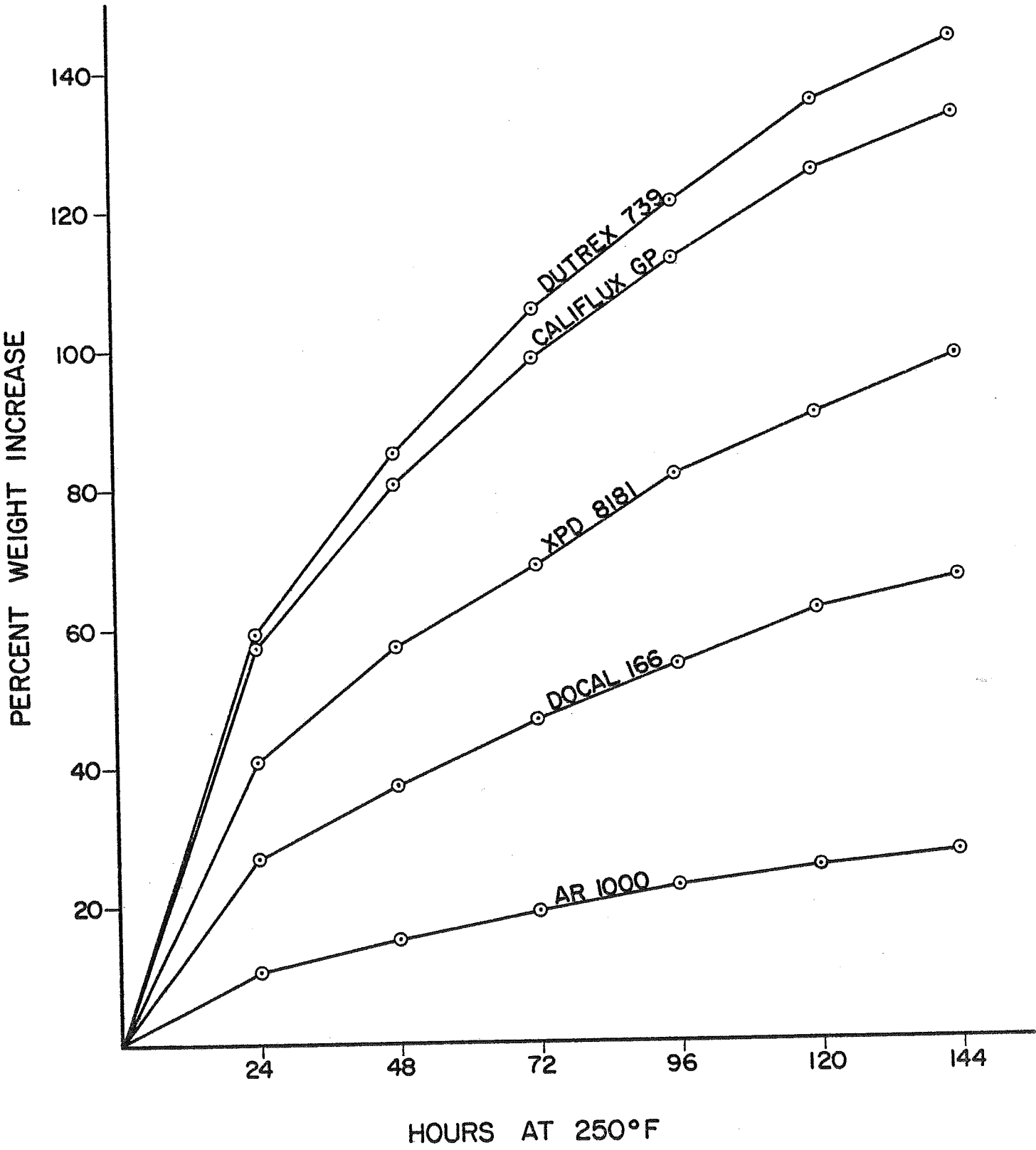
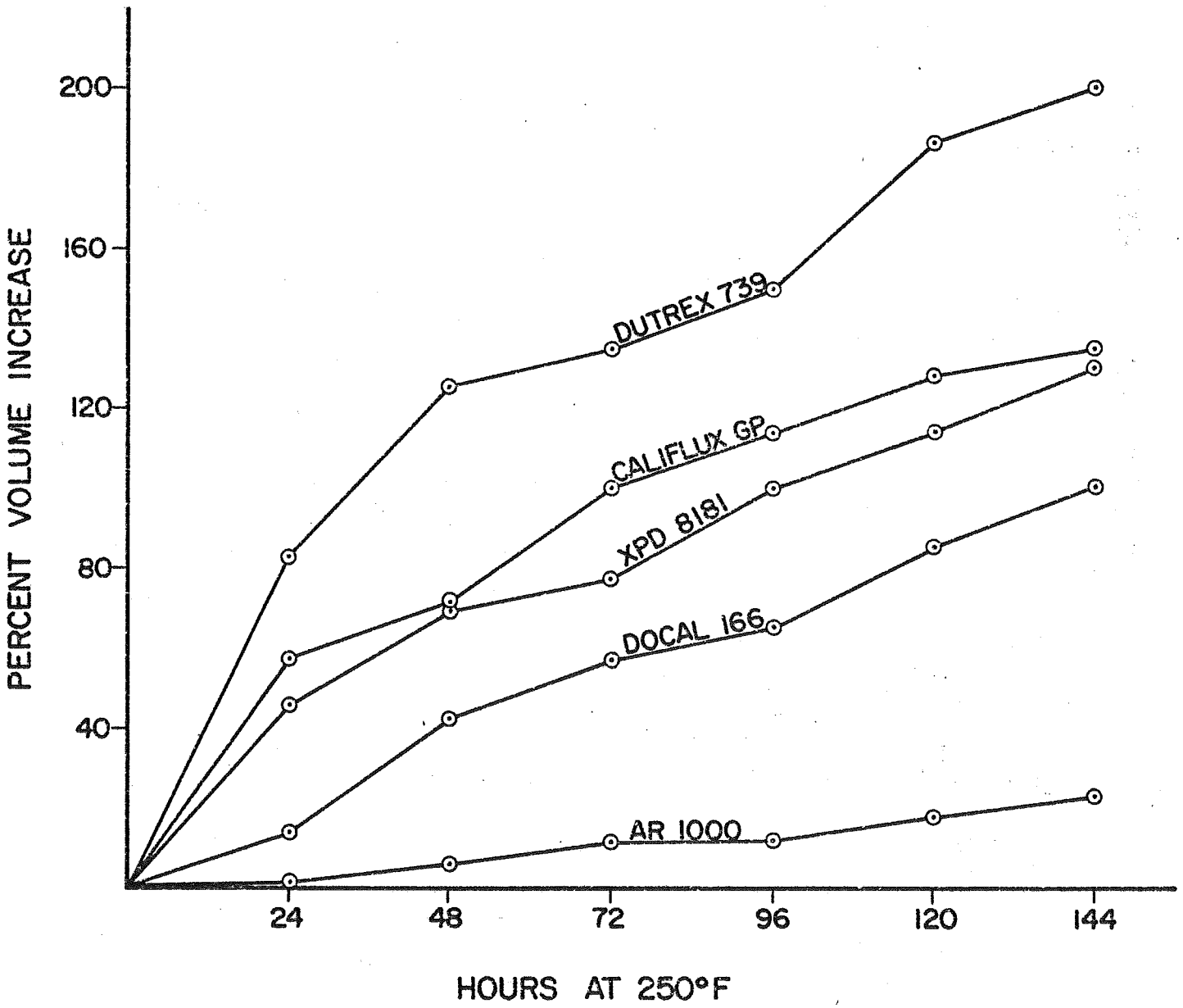


FIGURE 2

PERCENT INCREASE IN VOLUME
E-501 TIRE TREAD RUBBER
AT 250° F



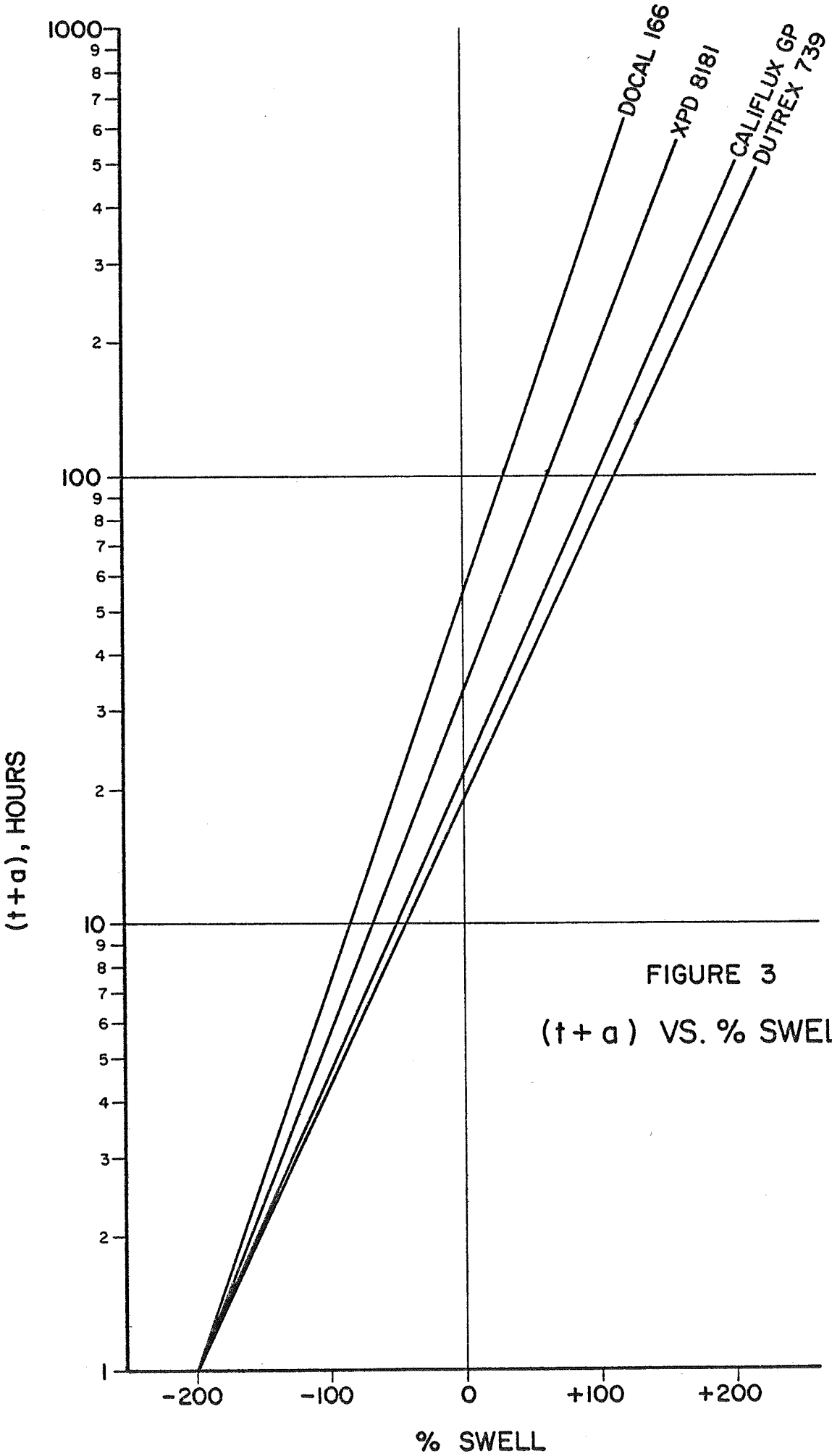


FIGURE 3

(t + a) VS. % SWELL

FIGURE 4

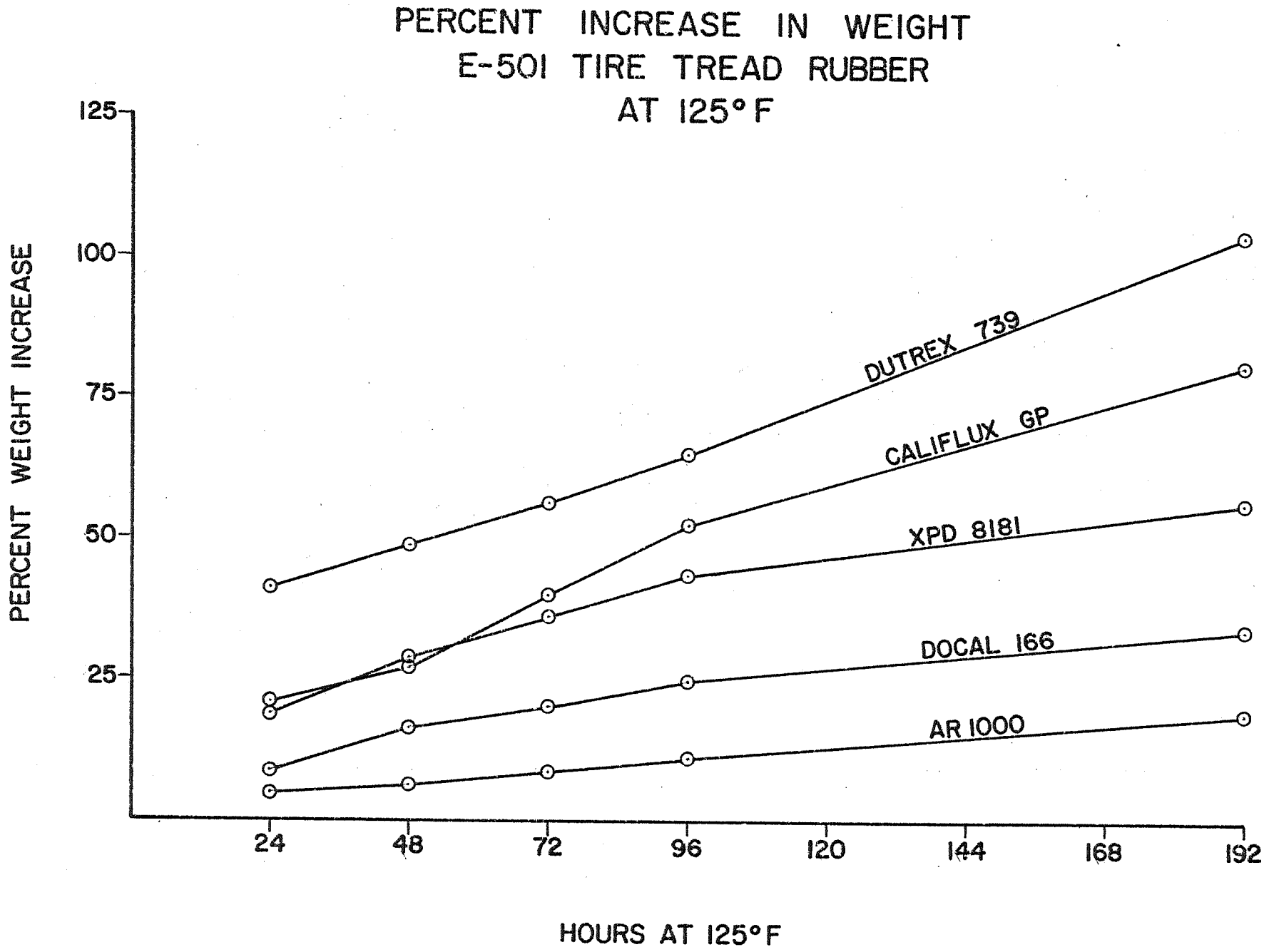

PERCENT INCREASE IN WEIGHT
E-501 TIRE TREAD RUBBER
AT 125° F
PERCENT WEIGHT INCREASE
125
100
75
50
25
DUTREX 739
CALIFLUX GP
XPD 8181
DOCAL 166
AR 1000
24
48
72
96
120
144
168
192
HOURS AT 125° F

FIGURE 5

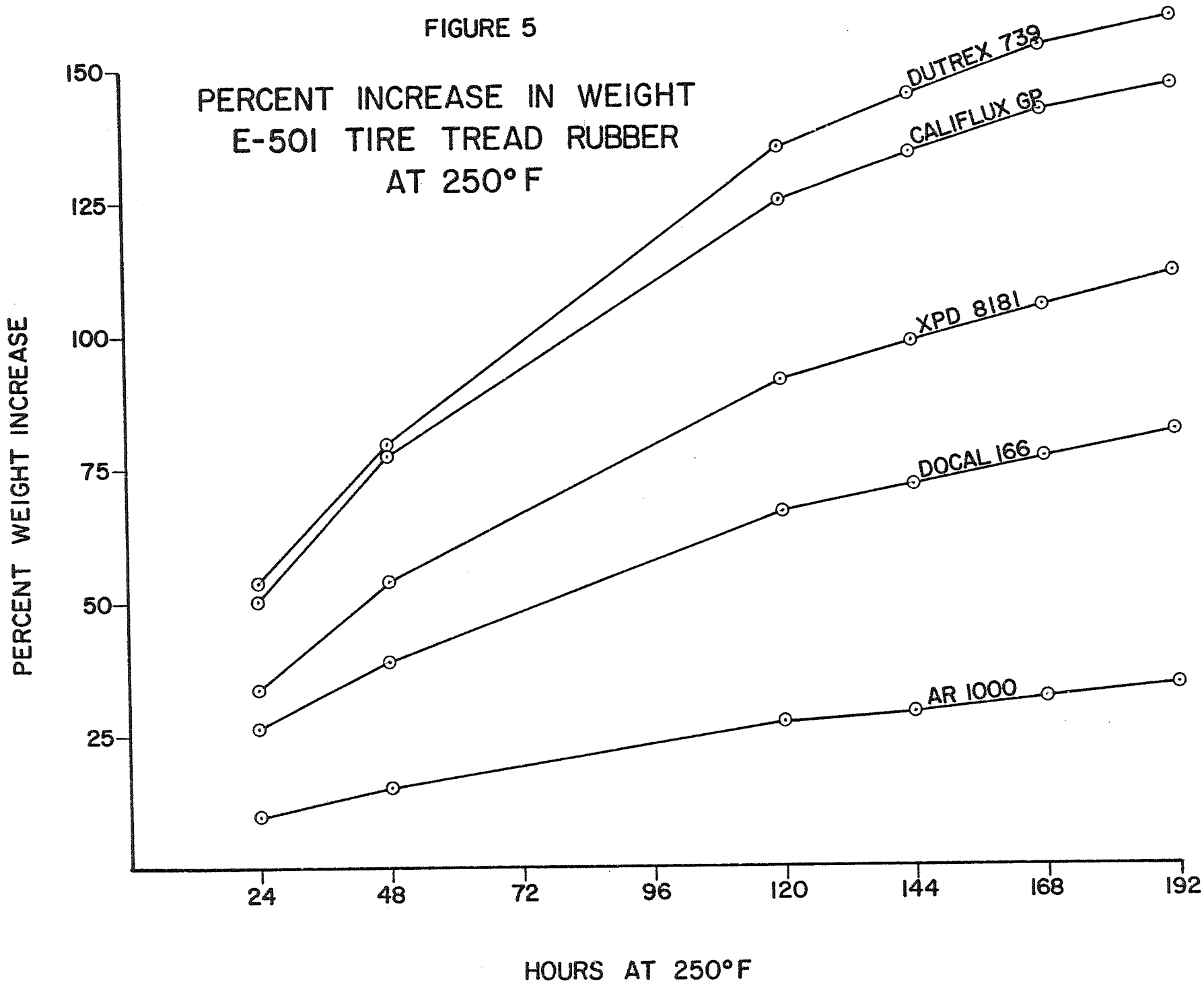

PERCENT INCREASE IN WEIGHT
E-501 TIRE TREAD RUBBER
AT 250° F
DUTREX 739
CALIFLUX GP
XPD 8181
DOCAL 166
AR 1000
PERCENT WEIGHT INCREASE
150
125
100
75
50
25
24
48
72
96
120
144
168
192
HOURS AT 250° F

FIGURE 6

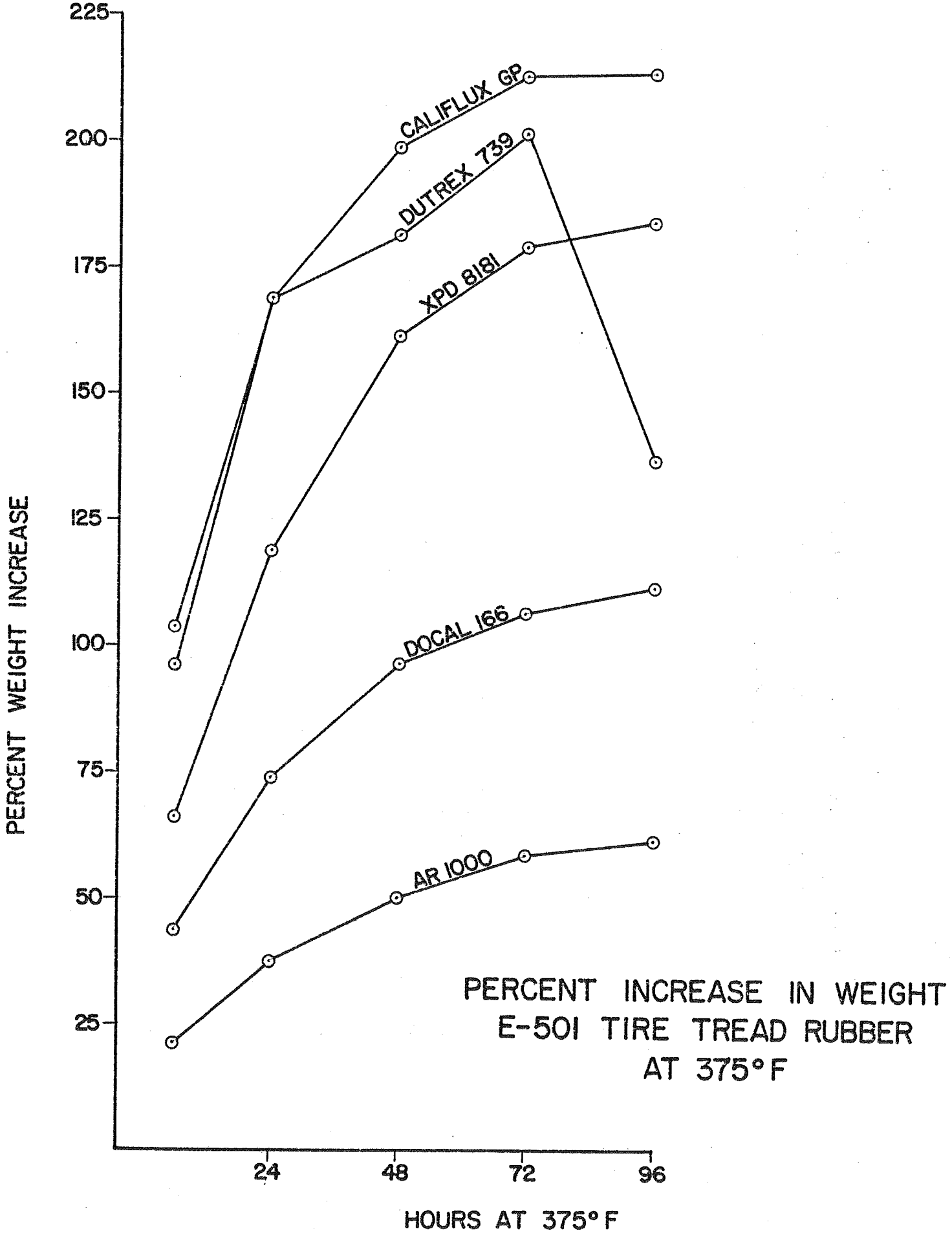

225
200
175
150
125
100
75
50
25
PERCENT WEIGHT INCREASE
CALIFLUX GP
DUTREX 739
XPD 8181
DOCAL 166
AR 1000
PERCENT INCREASE IN WEIGHT
E-501 TIRE TREAD RUBBER
AT 375° F
24
48
72
96
HOURS AT 375° F

FIGURE 7

PERCENT INCREASE IN WEIGHT
E-501 TIRE TREAD RUBBER IN DUTREX 739
AT 125°, 250°, 375° F

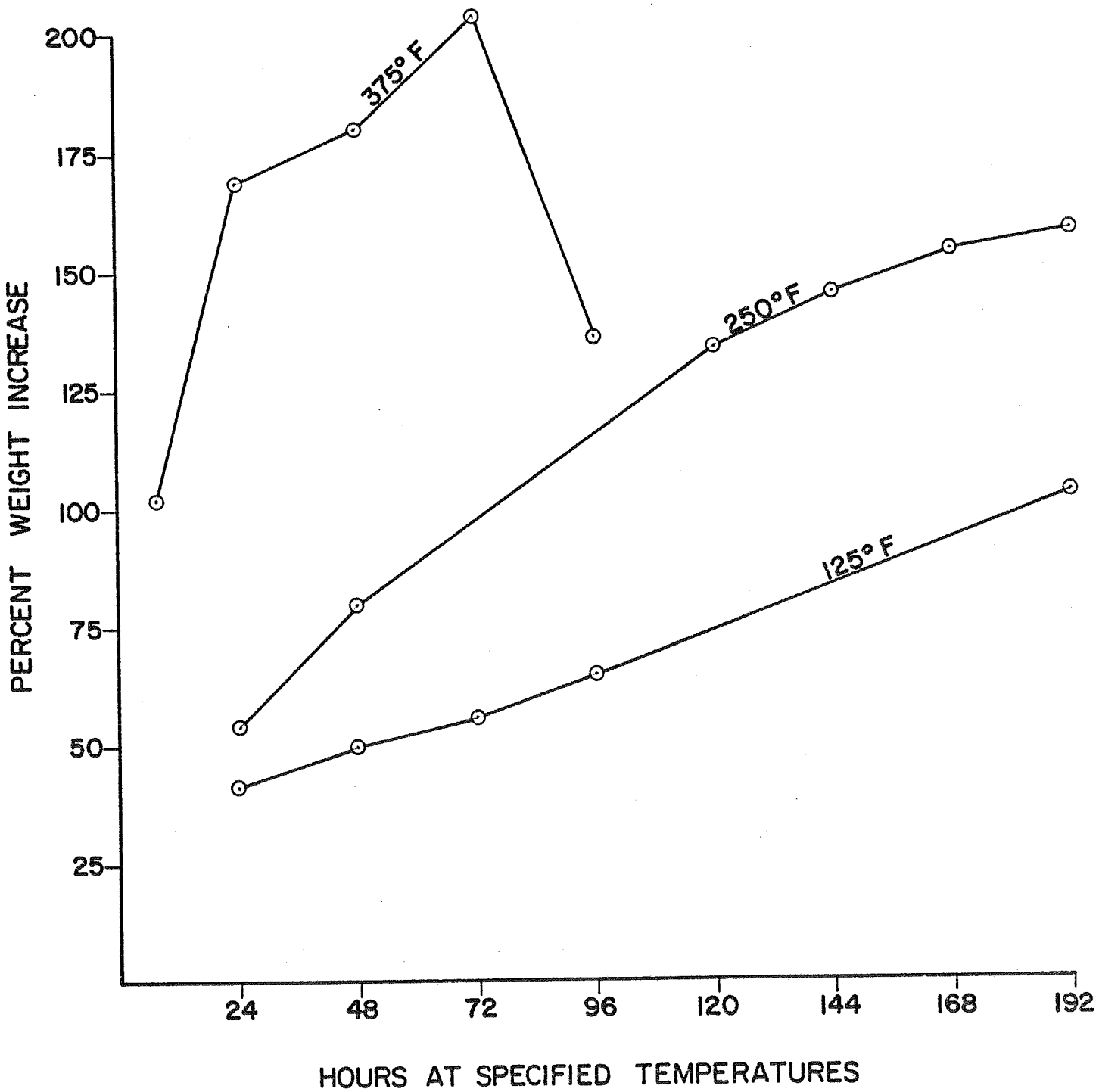


FIGURE 8

PERCENT INCREASE IN WEIGHT
E-501 TIRE TREAD RUBBER IN XPD 8181
AT 125°, 250°, 375° F

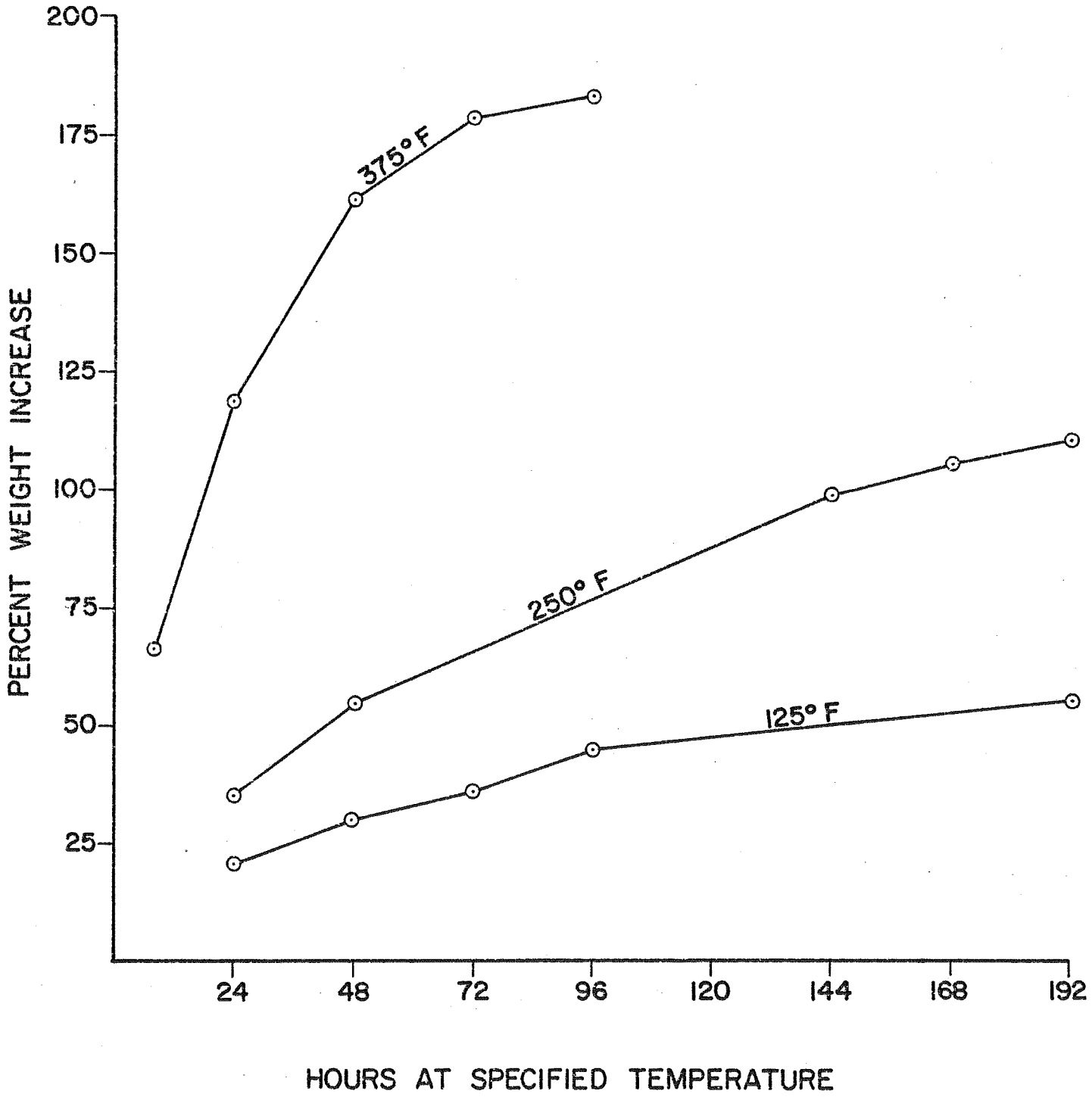


FIGURE 9

PERCENT INCREASE IN WEIGHT
E-501 TIRE TREAD RUBBER IN CALIFLUX GP
AT 125°, 250°, 375° F

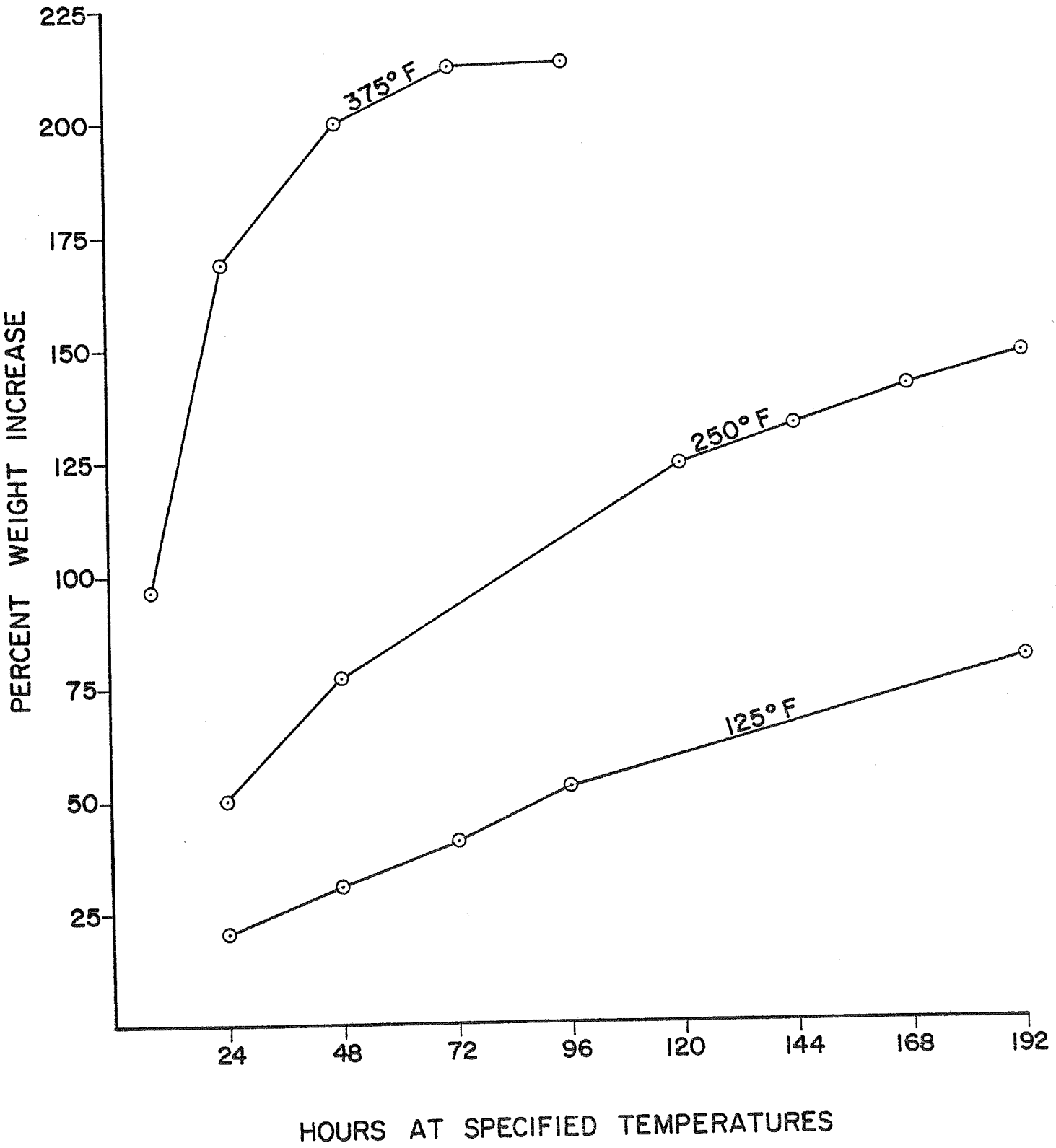


FIGURE 10

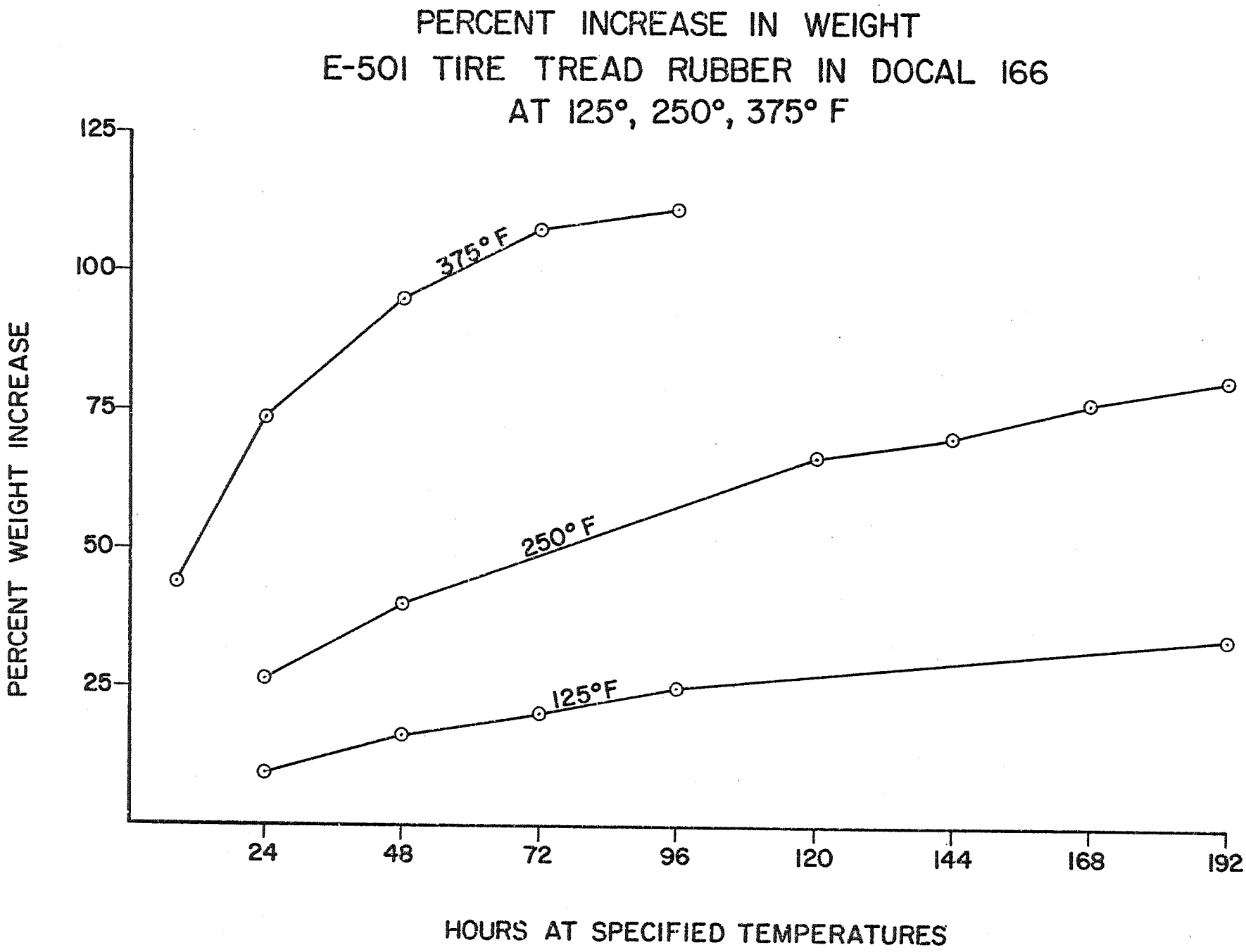

PERCENT INCREASE IN WEIGHT
E-501 TIRE TREAD RUBBER IN DOCAL 166
AT 125°, 250°, 375° F
PERCENT WEIGHT INCREASE
125
100
75
50
25
375° F
250° F
125°F
24
48
72
96
120
144
168
192
HOURS AT SPECIFIED TEMPERATURES

FIGURE 11

PERCENT INCREASE IN WEIGHT
E-501 TIRE TREAD RUBBER IN AR 1000
AT 125°, 250°, 375° F

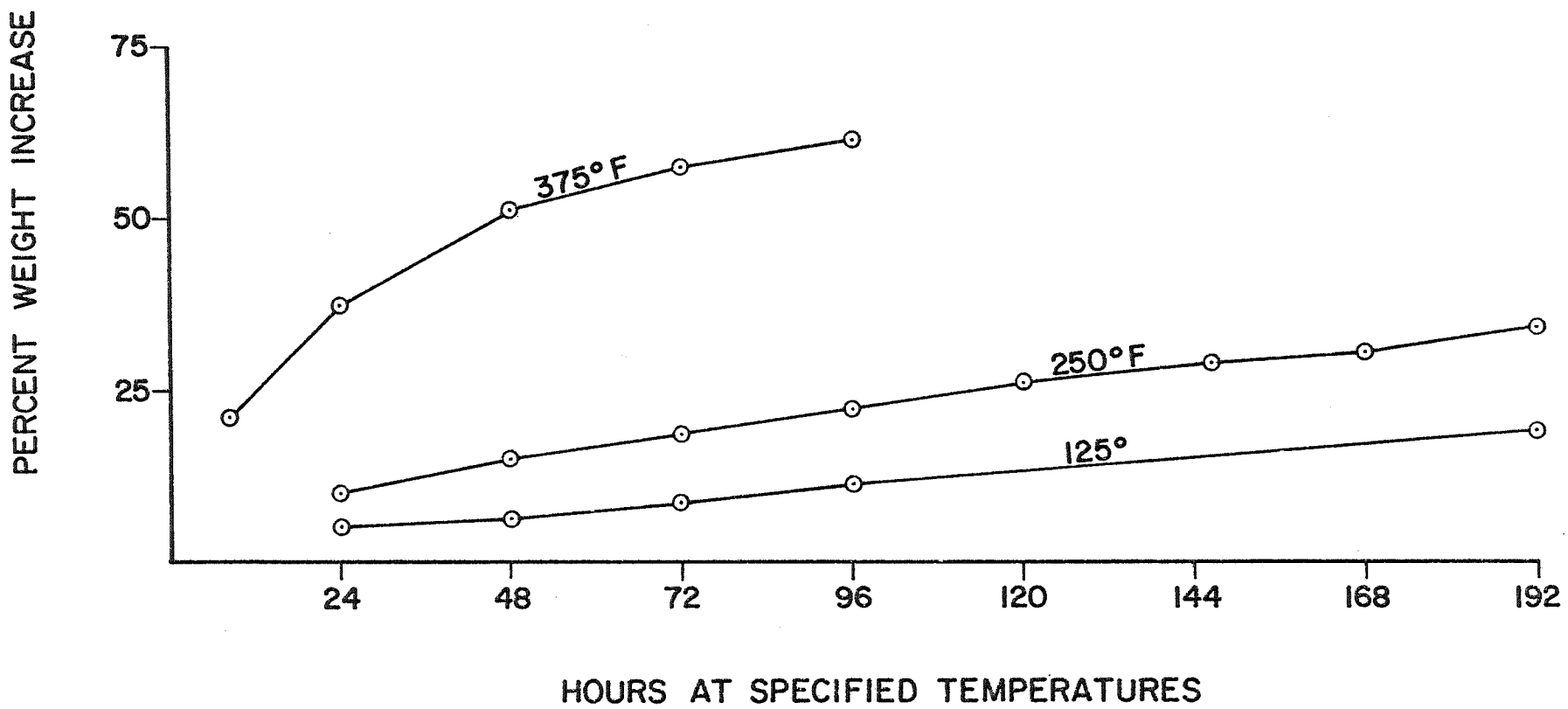


FIGURE 12

PLOT OF Ln KINETIC RATE CONSTANT OF SWELLING vs. 1/T (ARRHENIUS PLOT)

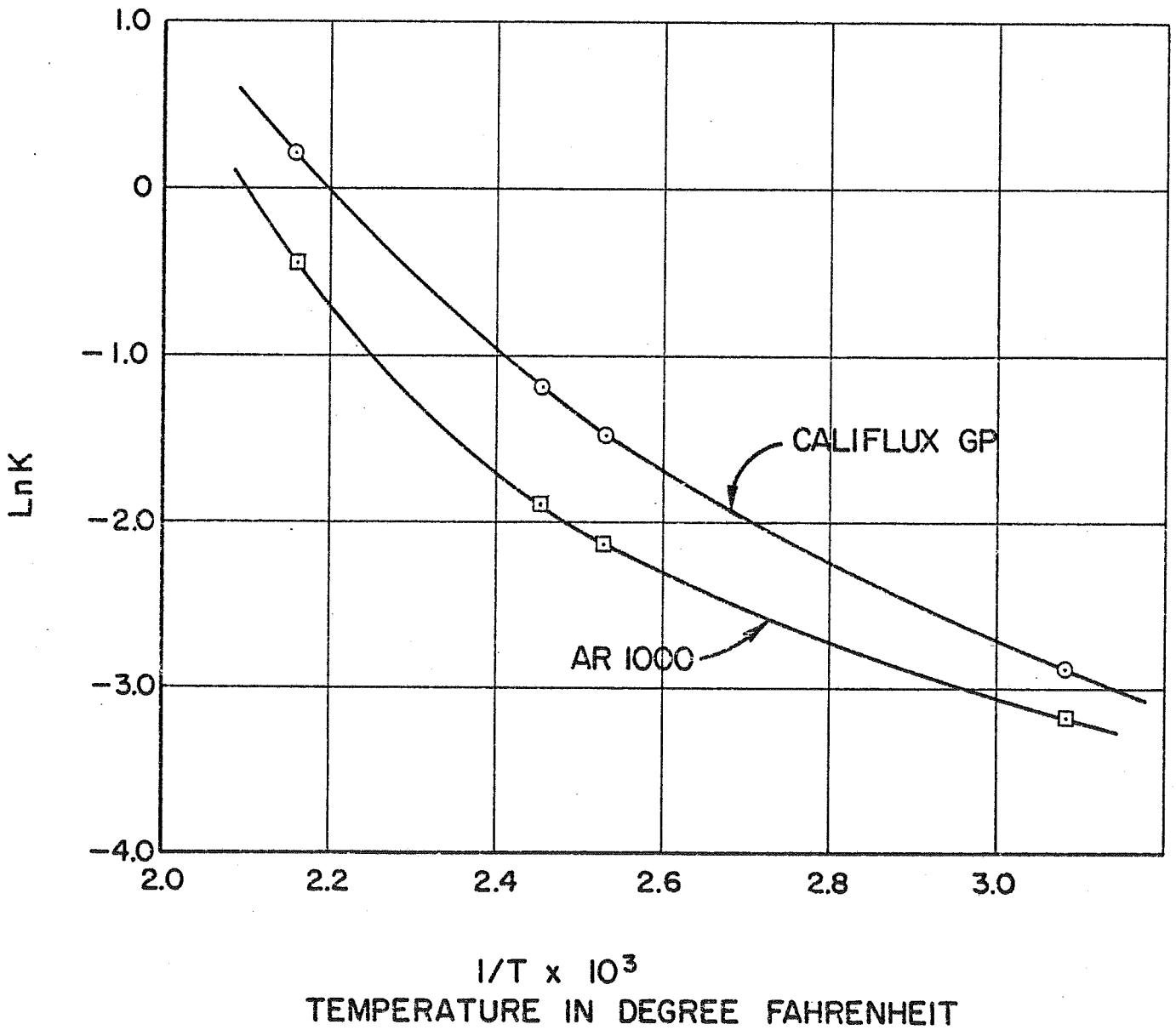
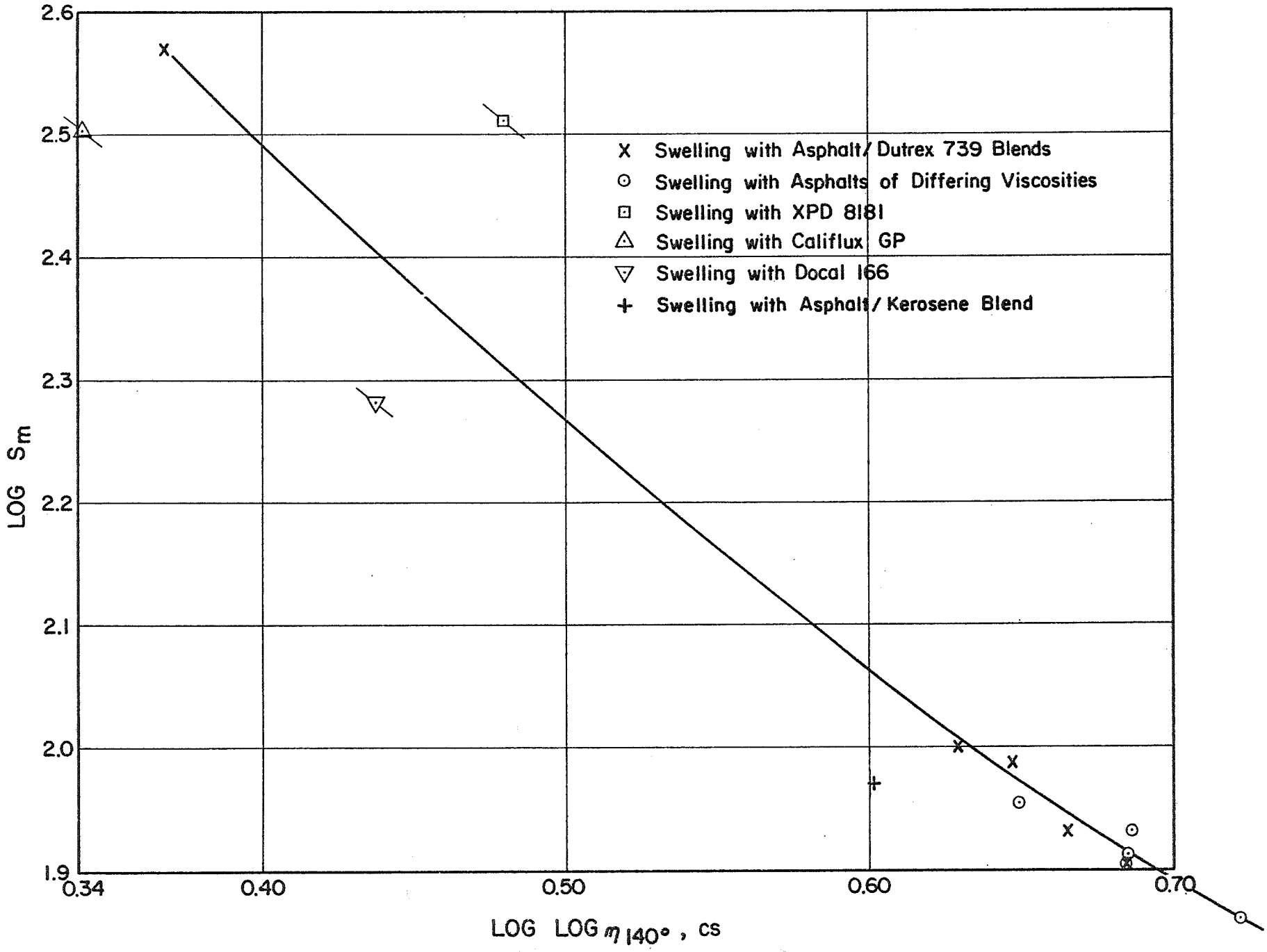


FIGURE 13

EFFECT OF VISCOSITY AT 140° F AND OIL COMPOSITION ON EXTENT OF SWELLING



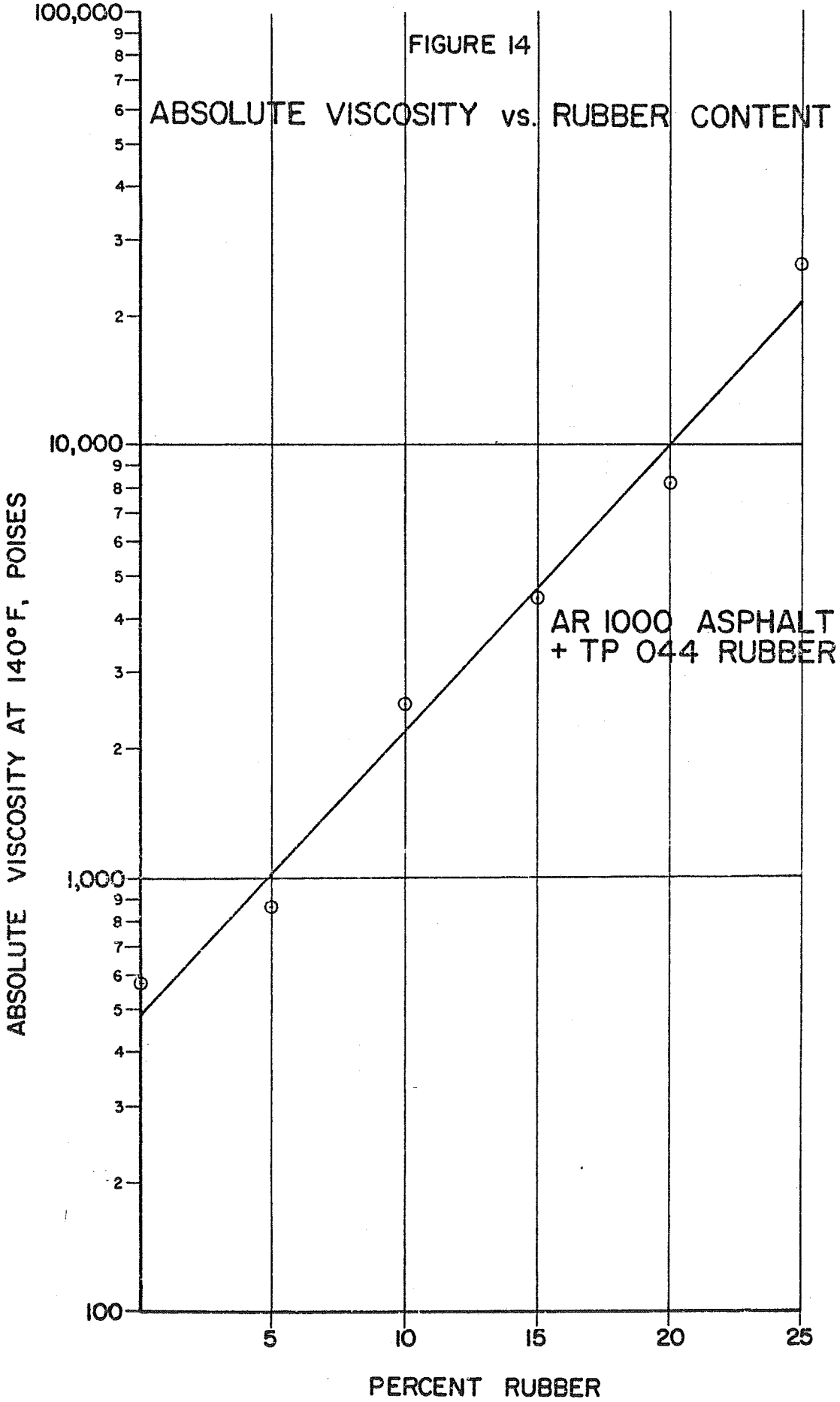


FIGURE 14
ABSOLUTE VISCOSITY vs. RUBBER CONTENT
AR 1000 ASPHALT
+ TP 044 RUBBER
ABSOLUTE VISCOSITY AT 140°F, POISES
100,000
10,000
1,000
100
5
10
15
20
25
PERCENT RUBBER

FIGURE 15

CALCULATE VISCOSITIES vs. SWOLLEN RUBBER VOLUME

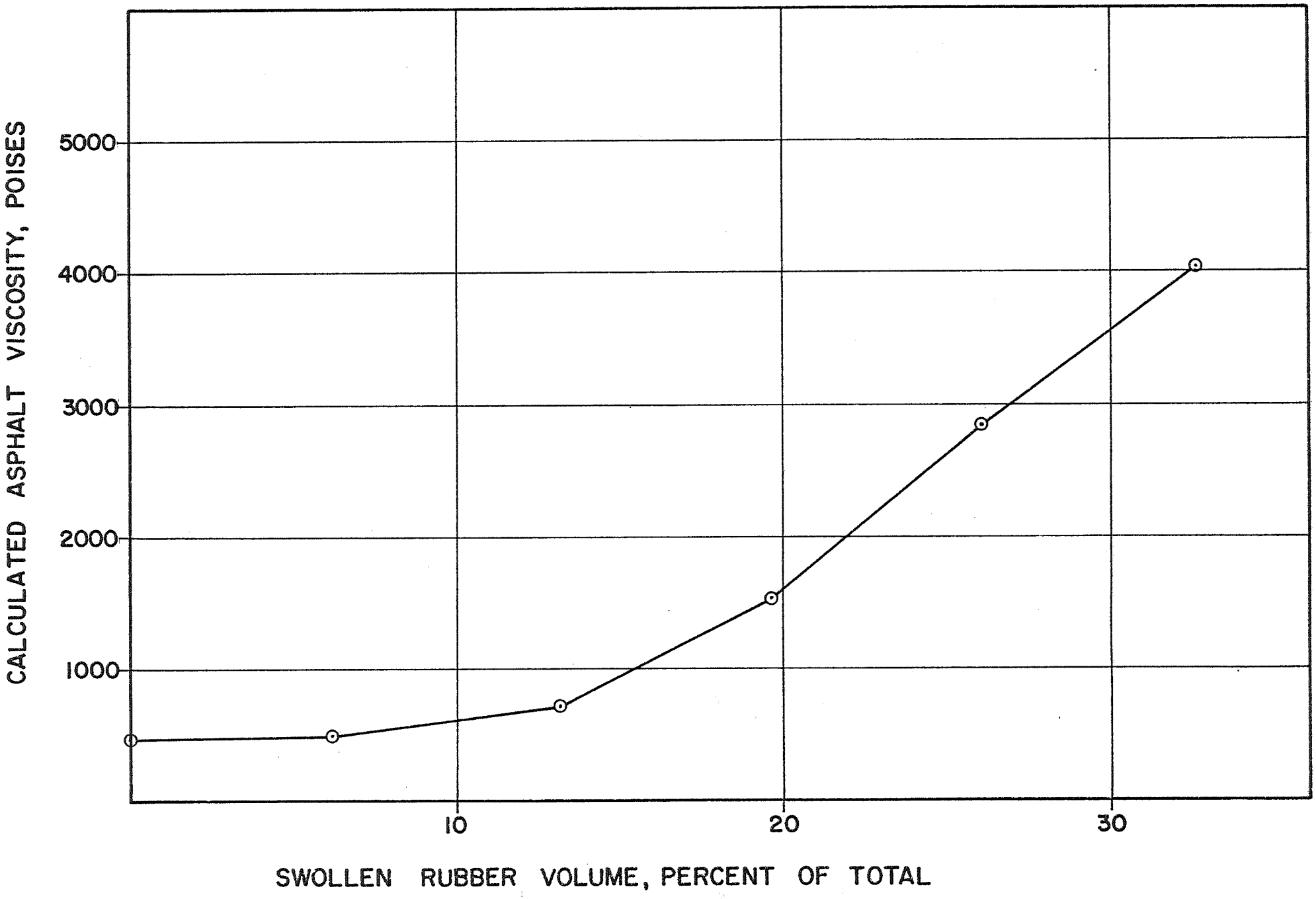


FIGURE 16

75% AR1000 + 25% TP044 RUBBER
ABSOLUTE VISCOSITY AT 140°F, 10CM Hg vs. MINUTES AT 350°F

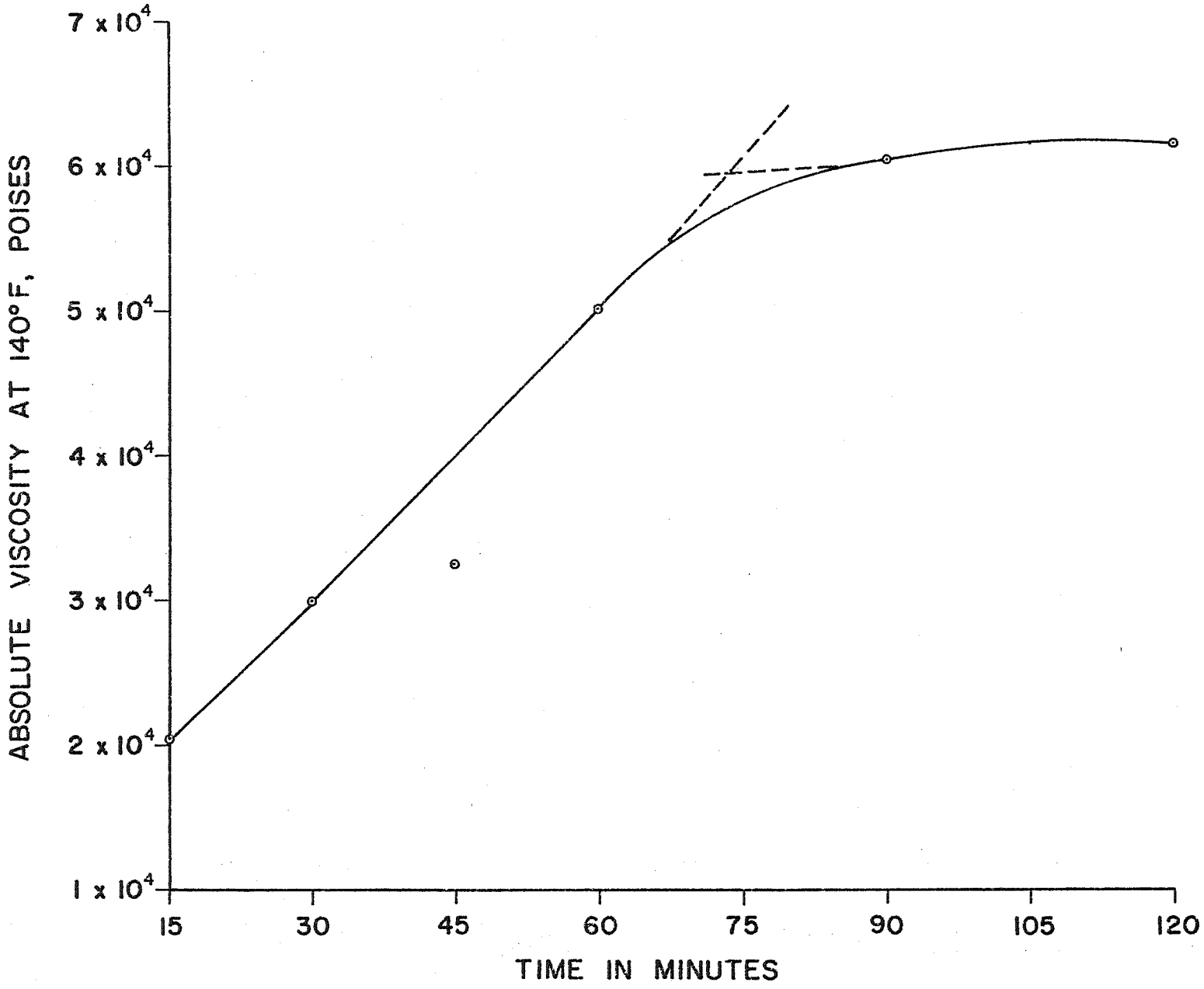


FIGURE 17

75% AR1000 + 25% TP044 RUBBER
ABSOLUTE VISCOSITY AT 140°F, 10CM Hg vs. MINUTES AT 375°F

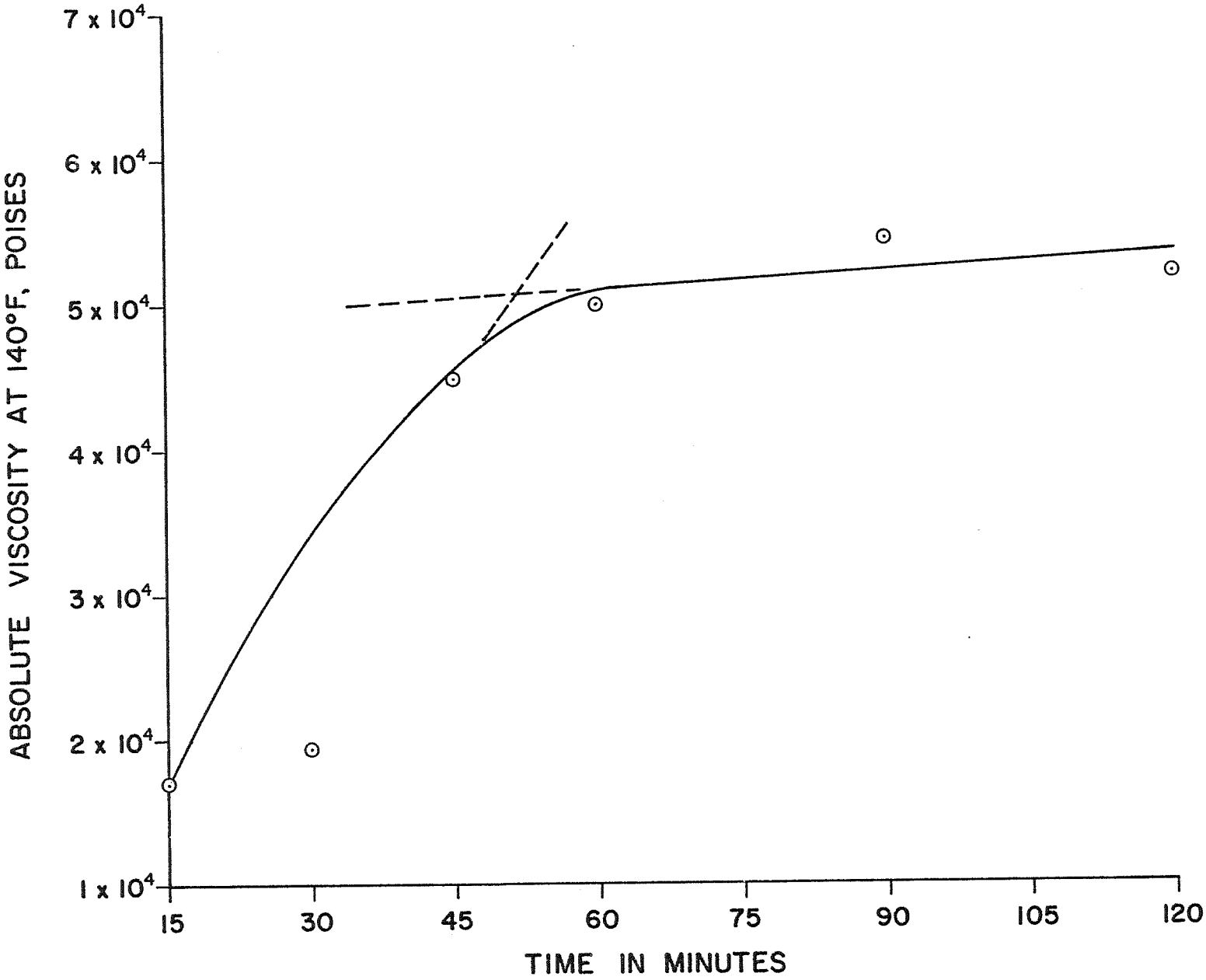


FIGURE 18

75% AR1000 + 25% TP044 RUBBER
ABSOLUTE VISCOSITY AT 140°F, 10CM Hg vs. MINUTES AT 400°F

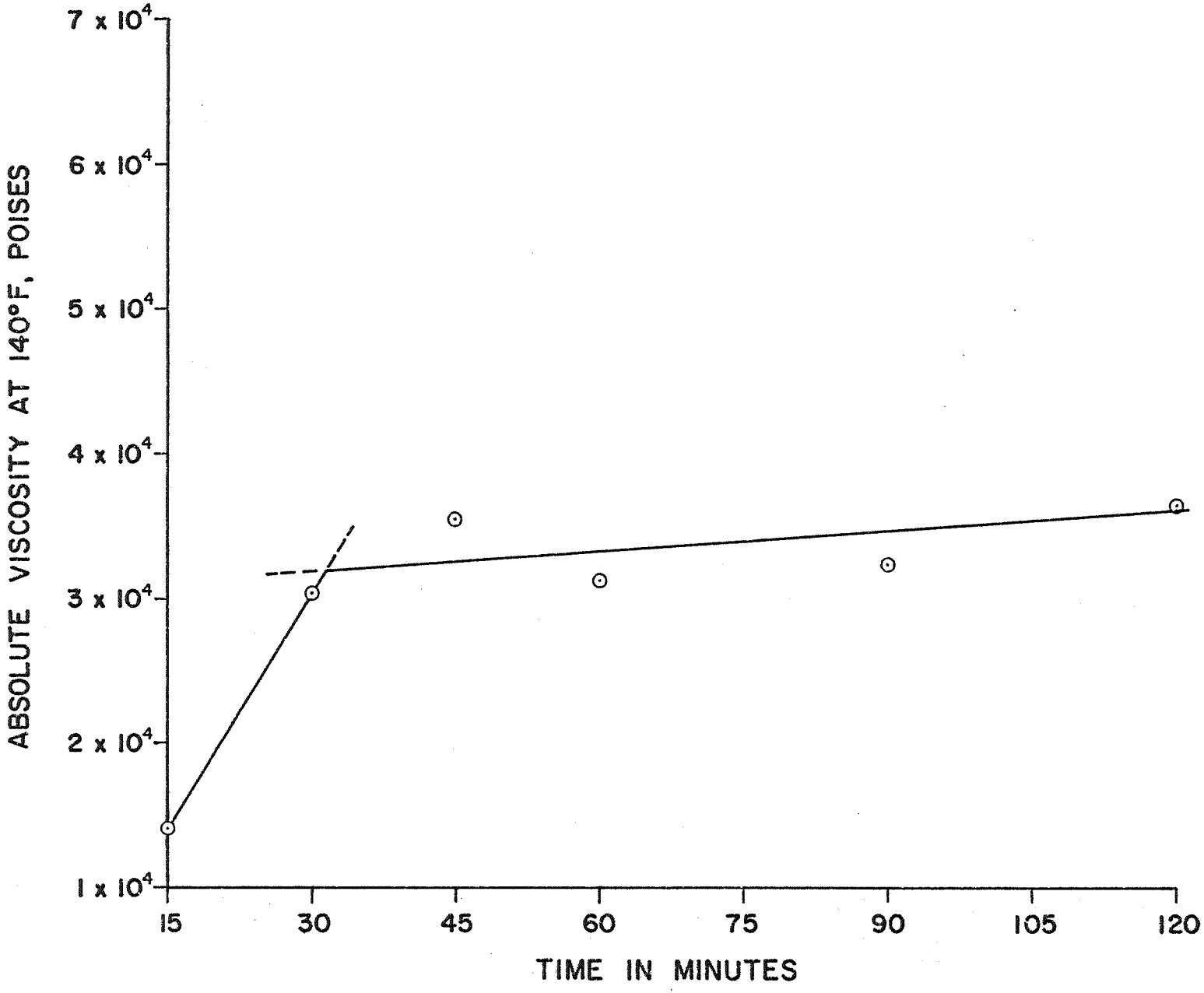


FIGURE 19

75% AR1000 + 25% TP044 RUBBER
ABSOLUTE VISCOSITY AT 140°F, 10CM Hg vs. MINUTES AT 425° F

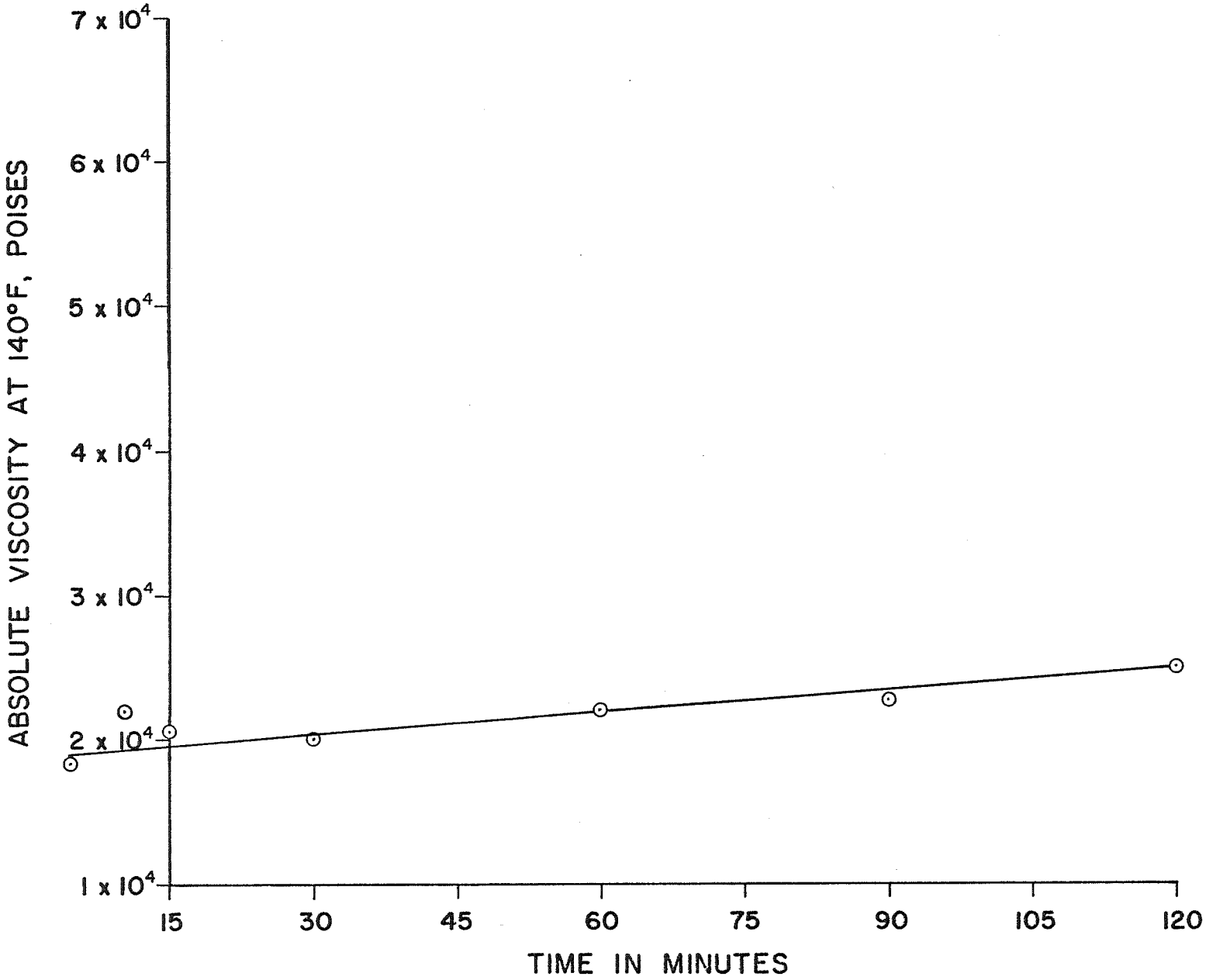


FIGURE 20

120 MINUTE ABSOLUTE VISCOSITY AT 140°F, 10CM Hg

VS.

REACTION TEMPERATURE

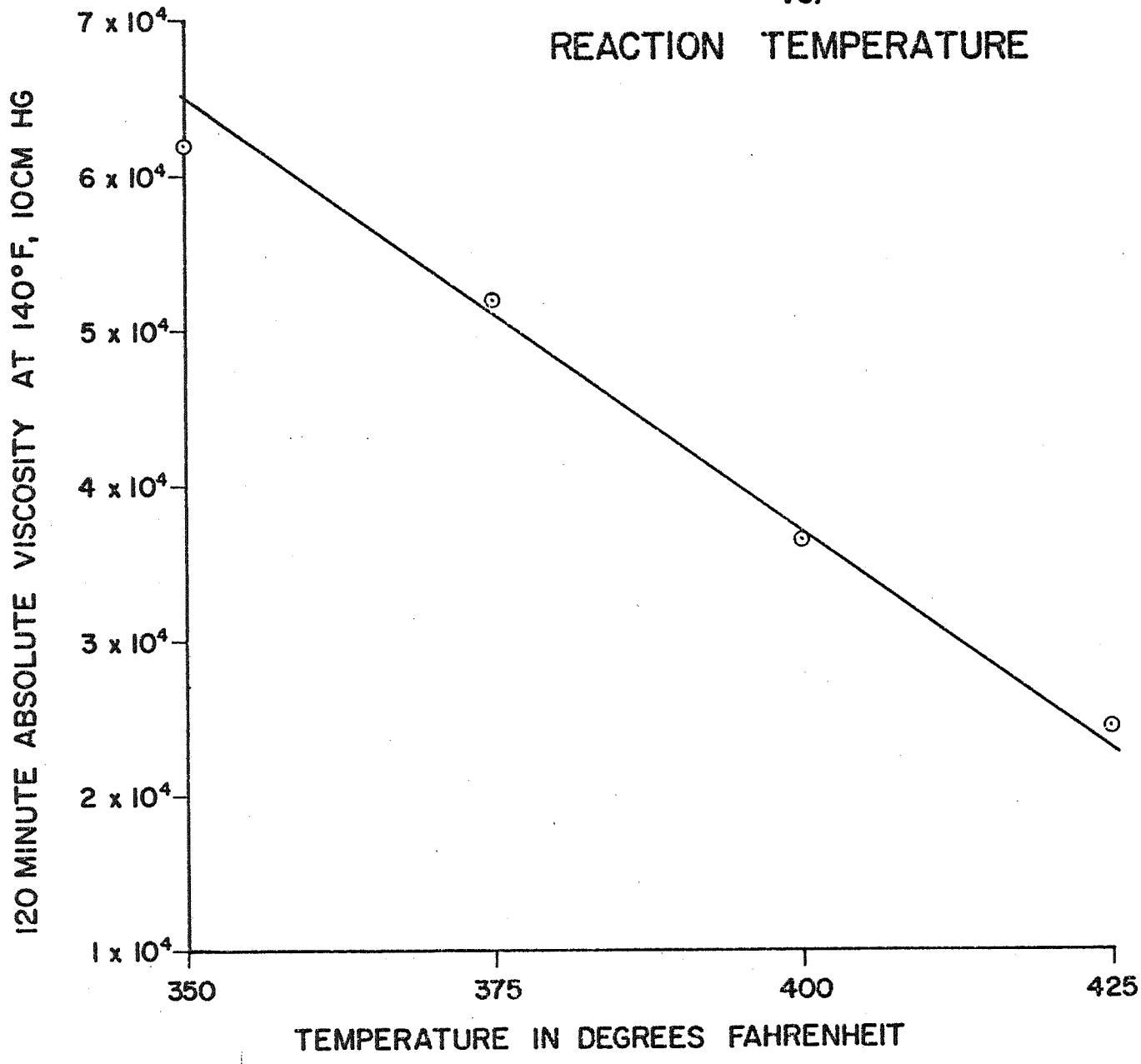


FIGURE 21

CALCULATED DYNAMIC VISCOSITIES OF ASPHALT AND RUBBER ASPHALT

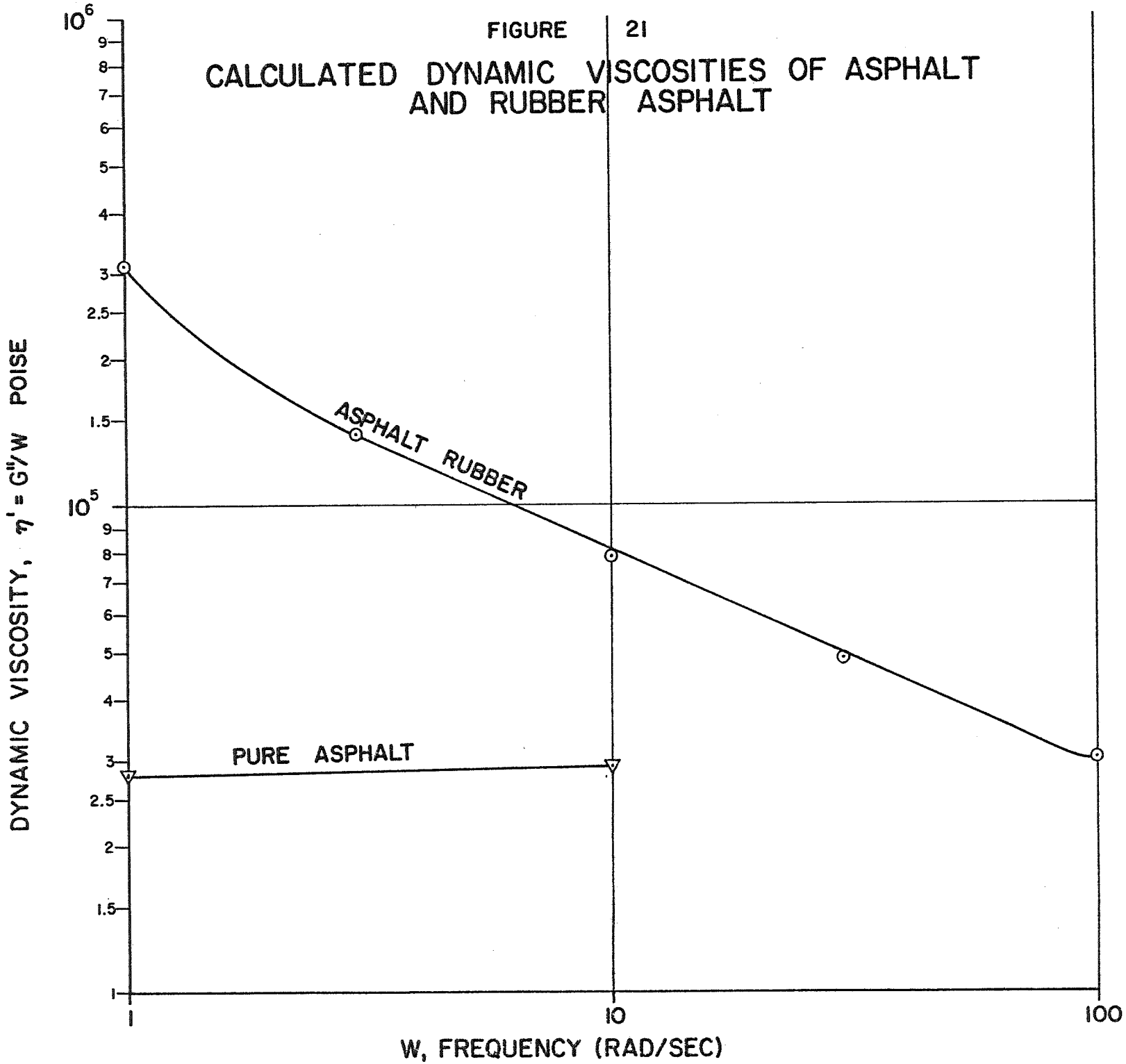


FIGURE 22

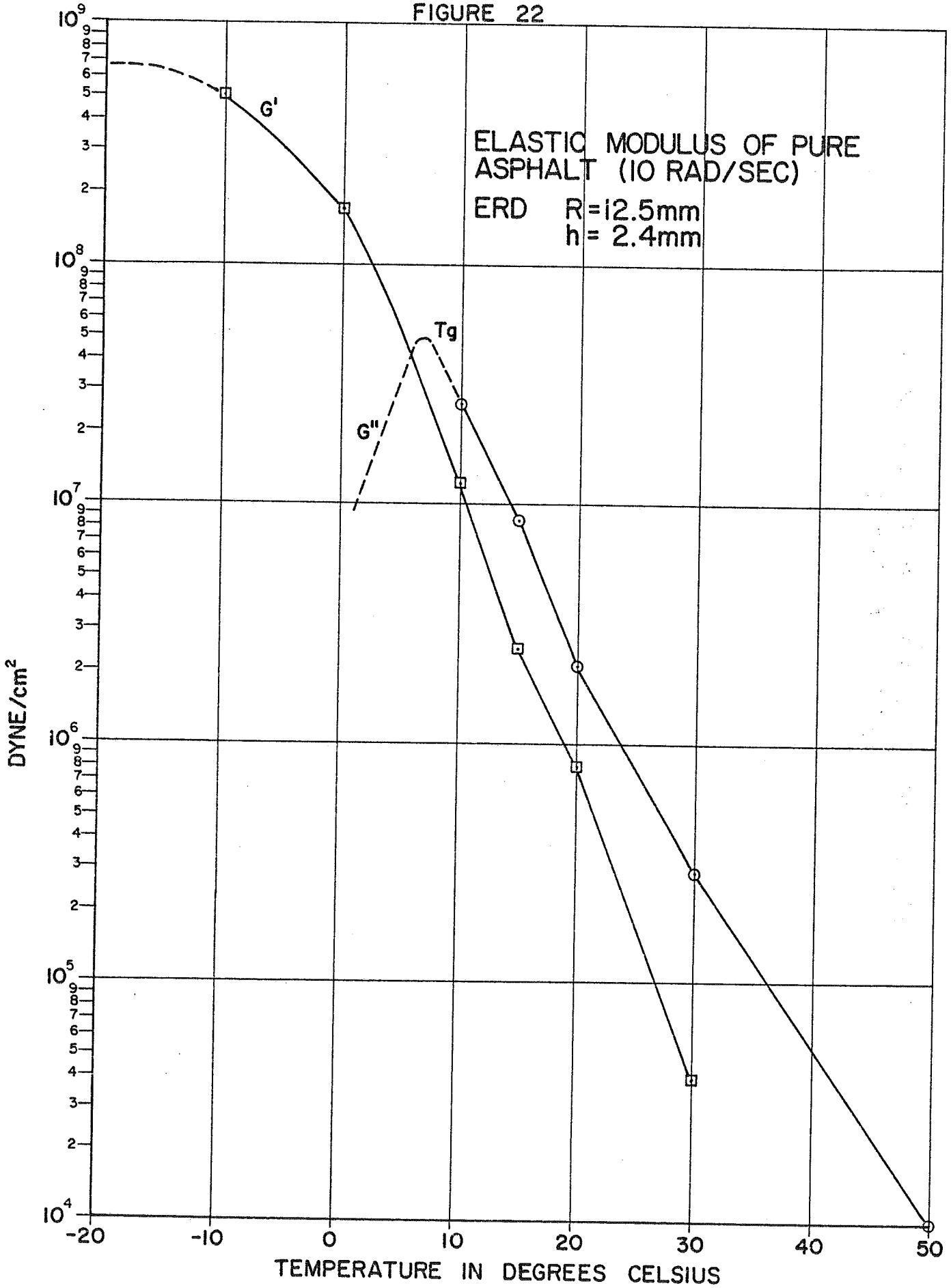
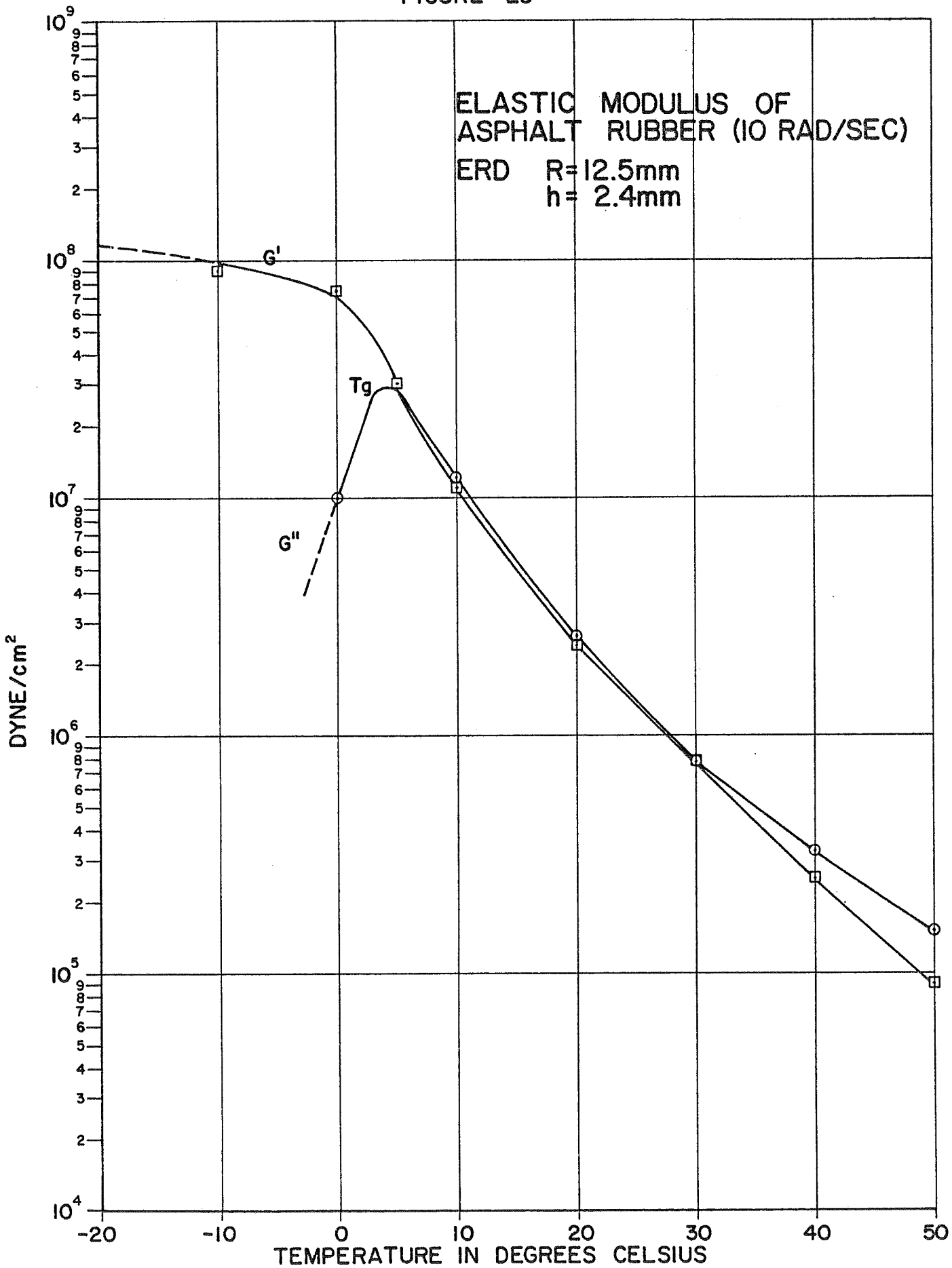

ELASTIC MODULUS OF PURE ASPHALT (10 RAD/SEC)
ERD R=12.5mm
h= 2.4mm
G'
G"
Tg
DYNE/cm²
TEMPERATURE IN DEGREES CELSIUS
10⁹
10⁸
10⁷
10⁶
10⁵
10⁴
-20
-10
0
10
20
30
40
50

FIGURE 23


ELASTIC MODULUS OF
ASPHALT RUBBER (10 RAD/SEC)
ERD R=12.5mm
h= 2.4mm
G'
G''
Tg
DYNE/cm²
TEMPERATURE IN DEGREES CELSIUS
-20
-10
0
10
20
30
40
50

APPENDIX I

Test Method for Screening Asphalts for Rubber Interaction

1.0 Scope

The purpose of this procedure is to measure the extent at which asphalt will swell rubber in order to obtain an estimation of the relative volume to which rubber particles would swell in the hot asphalt rubber mixture. The method consists of swelling specially prepared rubber specimens in a control asphalt and in the asphalt being tested.

2.0 Preparation of Rubber Specimens

2.1 - Prepare a compound of S-1500 rubber according to the following recipe:

	Parts
SRB 1500	100
PBNA (Agerite Powder)	0.5
Zinc Oxide (Kadox 15)	3.0
HAF Black (IRB#4)	50.0
Santocure	1.2
Sulfur	1.0

2.2 - From the compound, prepare Yerzley test buttons per ASTM D D-945.

2.3 - Cure the buttons for 30 minutes at 150°C (302°F). Typical test properties of a tensile sheet made from the same compound are:

Tensile Strength, psi	3380
Elongation of Break, %	630
Tensile Set, %	15

Modulus	
100%, psi	270
200%,	515
300%,	1235
Durometer A, 5 sec. rdg.	57

3.0 Determination of the State of Cure of the Rubber Specimens

3.1 - Weigh three rubber specimens to the nearest 10 mg.

3.2 - Prepare three screen stands for the rubber specimens and place those stands in 4 oz. capped bottles. The screen stands are prepared by cutting squares of window screen which approximately fit inside the bottles, then bending the corners to form legs which will lift the stands off of the bottom of the bottles, allowing solvent to enter the specimens from all sides.

3.3 - Place 100 ml of toluene in the bottles; put on the caps and place in a water bath at 38 + 0.5°C (100° ± 1°F) for one hour to equilibrate.

3.4 - After the hour has past, place each of the buttons into a bottle and place assembly in the water bath.

3.5 - Weigh the swollen specimens to the nearest 10 mg twice a day for two days, then once a day for a minimum lapsed time of five days. If the tests go over a weekend, end the test so that at least two weighings may be made within 24 hours of the termination of the test. Solvent is evaporating from the specimens during weighing, thus they should be removed from the solvent,

blotted, then placed on the balance as quickly as possible. The highest value read is to be recorded, as the weight will be decreasing radically during the weighing process if an analytical balance is used.

3.6 - Calculate the value of the ultimate potential swell (s_m), the rate of swell (k) and the intercept constant (C) as shown below. The percent swell (s) is related to time by equation (1).

(1) $s = s_m (1-Ce^{-kt})$

or, for convenience of plotting

(2) $\text{Ln} \left(\frac{s_m}{s_m - s}\right) = kt - \ln C$

3.6.1 Tabulate s and t (in hours).

3.6.2 Estimate the value of s_m.

3.6.3 Based upon the estimated value of s_m, calculate

$\text{Ln} \left(\frac{s_m}{s_m - s}\right)$ for each value of t, and plot

$\text{Ln} \left(\frac{s_m}{s_m - s}\right)$ vs t.

3.6.4 If the plot curves upward, the estimate of s_m is too low. Try a higher value and replot. If the plot curves downward, try a lower value and replot. Continue until a straight line is obtained.

3.6.5 Report the value of s_m which provided a straight line and call it the ultimate potential swell.

3.6.6 Determine the slope of the straight line obtained in 3.6.4. Report the slope, k, as the rate constant in days^{-1}.

3.6.7 Determine the value of Ln $\left(\frac{s_m}{s_m - s}\right)$ when the plot is extrapolated to t = 0. Call that -ln C. Calculate C, the intercept constant.

3.6.8 Report the values of s_m, k and C for the swell of the rubber specimens in toluene.

4.0 Determination of Swell in Asphalt

In this section of the test method, the asphalt submitted for testing is compared to a control asphalt with respect to its ability to swell rubber.

4.1 - The control asphalt is to be that produced from Wilmington crude by Edgington Oil Company, blended to a viscosity of 150-160 cs at 135°C (275°F).

4.2 - Determine the viscosities of the control asphalt and the submitted asphalt at 60°C (140°F) per ASTM 2171 and at 135°C (275°F) per ASTM 2170.

4.3 - Prepare containers for the swelling experiments thusly. Select six 3 oz. ointment cans (per test) and place within the cans small stands on which to place rubber specimens. The stands may be made by cutting out pieces of window screen and bending the corners to serve as legs, then placing the screens in the cans.

4.4 - Weigh two sets of triplicate rubber samples to the nearest 0.1 mg and place each onto a screen in a can.

4.5 - Heat a sample of asphalt to be tested, and the control asphalt, no higher than 163°C (325°F), then pour 60 grams of the unknown asphalt into each of one set of triplicate cans, and 60 grams of the control asphalt into each of the other set of triplicate

cans. These tests should be started on a Wednesday and concluded on a Thursday, eight days later.

4.6 - Place specimens in a convection oven at 135°C (275°F). The lids should be placed loosely on the cans.

4.7 - Weigh each swollen specimen after 1, 2, 5, 6, 7 and 8 days. The specimens are removed each day with tongs, blotted on a paper towel while still hot and then weighed to the nearest 0.1 mg. The specimen is then placed back into the can containing asphalt, and the assembly placed back into the oven. This process should not take over five minutes.

4.8 - Upon completion of the test, the maximum swell, s_m the swelling rate constant, k, and the intercept constant, C, are determined per section 3.6.

5.0 Calculations

5.1 - Divide the values of the ultimate swell (s_m) of the specimens in asphalt by that of the specimens in toluene for that lot of rubber specimens. This will correct for minor variations in cure. Report for unknown asphalt and control.

5.2 - Divide the s_m value for the unknown asphalt by that for the control asphalt, multiply by 100 and report.

5.3 - Divide the value of k for the unknown asphalt by that for the control asphalt, multiply by 100 and report.

APPENDIX II

Viscosity of Asphalt Rubber Mixes

1.0 Scope

1.1 This procedure may be used for determination of the absolute viscosity of asphalt rubber mixtures. The method is a modification of AASHTO-T-202-74, (ASTM D-2171-66), Absolute Viscosity of Asphalts.

2.0 Summary of Method

2.1 The time is measured for a fixed volume of liquid to be drawn up through a capillary tube by means of vacuum. Both the vacuum and temperature are carefully controlled. The absolute viscosity is calculated by a formula as given in Section7.0.

3.0 Apparatus

3.1 Viscometers, Asphalt Institute Vacuum Viscometer. Size 400.

3.2 Thermometer ASTM Kinematic Viscosity Thermometer No. 47F, having a range of 137.5-142.5^{o}F, as prescribed in ASTM-E-1.

3.3 Bath, constant temperature bath as described in Section 4.3 of AASHTO, T-202-74.

3.4 Vacuum System - Capable of maintaining a vacuum of 3-300 mm of mercury within ± 0.5 mm.

3.5 Timer or stopwatch graduated in division of 0.1 sec. and accurate to within 0.05% when tested over a 15 minute interval.

4.0 Sample Preparation

4.1 Heat the sample with occasional stirring to a temperature of 135°-150°C (275°-300°F).

4.2 It is essential that the mixture be of uniform consistency.

5.0 Procedure

5.1 Preheat the viscometer in a 135°C (275°F) oven for a minimum of 10 minutes.

5.2 Charge the viscometer to a level approximately one (1) cm. above the fill line. Note 1. - A satisfactory method of charging the viscometer with the asphalt-rubber mixture is as follows:

a) Use a rubber bulb to draw the sample into a 9.5 mm (3/8 inch) ID glass tube. The removable inner tube from a demountable 250 mm Liebig condenser used for the distillation of cutback asphalt products is satisfactory.

b) Insert the filled glass tube into the viscometer to the bottom of the fill bulb.

c) Use a 9.5 mm (3/8 inch) diameter hardwood dowel to force the sample out of the glass tube and into the viscometer.

d) Be sure the sample is forced around the bottom of the "U" and to approximately the level of the fill line in the fill bulb.

5.3 Immediately chill the viscometer in a water bath held at a temperature of 24°±3°C (75°±5°F). This prevents the migration of the rubber to the bottom of the viscometer.

5.4 Place the chilled viscometer in the 60°C (140°F) bath and condition for 40 ± 5 minutes.

5.5 Establish 10 cm Hg vacuum in the system.

5.6 Start the mixture flowing in the viscometer by opening the vacuum line to the viscometer.

5.7 Measure the time to within 0.1 second for the material to pass each succesive pair of timing marks in the tube.

5.8 Shut off the vacuum and disconnect from the viscometer.

6.0 Calculation

6.1 Since the viscometer constant for each viscometer is given for use at 30 cm., a revised constant for each bulb the following equation should be used $\frac{K}{H-h} = K_R$

where: K = Viscometer constant at 30 cm Hg.

H = Applied Vacuum (30 cm).

h = Average liquid head in each bulb (in cm of Hg).

K_R = Revised K.

6.3 H-h must then be determined for the actual vacuum being used.

6.4 The revised formula for deriving poises in then K_R (H-h) t

where: t = time in seconds to the nearest 0.1.

7.0 Example

7.1 A.I. tube Size 400, No. A-111, to derive K_R.

Bulb	Average K		H-h		K_R
B	544.0	÷	29.76	=	18.28
C	259.4	÷	29.61	=	8.76
D	168.1	÷	29.46	=	5.71
E	124.4	÷	29.31	=	4.24
F	97.8	÷	29.17	=	3.35

7.2 In use at a vacuum of 10 cm Hg for Bulb E the formula would be K_R x H-h x t = Poises. For a measured time of 72.3 seconds in Bulb E, the sample viscosity would be:

4.24 x 9.31 x 72.3 seconds = 2854 poises.

APPENDIX III

Elastic Rebound of Rubber-Asphalt Mixes

1.0 Scope

1.1 This procedure can be used to determine the relative elasticity of asphalt rubber mixes by measuring the percentage of rebound a sample makes after being stretched a given distance along one axis.

2.0 Summary of Method

2.1 A 2.54 mm (0.10 inch) film of the sample is cast between a pair of 2 cm x 3 cm glass microviscosity plates using 2.54 mm (0.10 inch) spacers. The plates are placed in the microviscometer and a 50 gram load is applied to the front beam of the instrument. After the sample has been stretched 500 microns, the weight is removed. The distance the sample rebounds from the stretching after 30 minutes is noted and calculated as a percentage of the original 500 micron deformation.

3.0 Apparatus

3.1 Microviscometer, sliding plate type, Hallikainen (Shell Development Design).

3.2 Glass microviscosity plates, 2 cm x 3 cm x 1 cm.

3.3 Spacers, brass or stainless steel, 2.54 mm (0.10 inch).

3.4 Water Bath, capable of maintaining $25^{\circ}C \pm 0.05^{\circ}C$ ($77^{\circ}F \pm 0.1^{\circ}F$).

3.5 Thermometer, ASTM 17F.

3.6 Weights, 50 grams and 500 grams.

3.7 Strip chart recorder- 10 mv, 4 inch/hour chart speed.

4.0 Sample Preparation

4.1 Heat the sample with occasional stirring to a temperature of 135°-$150^{o}C$ (275°-$300^{o}F$).

4.2 It is essential that the mixture be of uniform consistency.

5.0 Procedure

5.1 Warm the glass microviscosity plates on a hot plate at a low heat setting.

5.2 Lightly lubricate a suitable level surface with silicone grease and apply silicone grease to the edges of the metal spacers.

5.3 Place one glass microviscosity plate on the greased surface and position the spacers on the ends of the plate, leaving an exposed plate area of 2 cm x 2.5 cm.

5.4 Transfer a quantity of the sample onto the glass microviscosity plate, taking care to fully cover the exposed area and rising high enough to fully clear the top of the spacers.

5.5 Position the other glass microviscosity plate on top of the first, making sure the spacers are keeping the plates 2.54 mm (0.10 inch) apart. Be sure the top plate is centered on the bottom plate.

5.6 Place a 500 gram weight on top of the plates.

5.7 Allow to cool to room temperature undisturbed for a minimum of one hour.

5.8 Stabilize the temperature of the water bath at $25^{o}C \pm 0.05^{o}C$ ($77^{o}F \pm 0.1^{o}F$).

5.9 After one hour cooling, remove the weight and spacers from the microviscosity plates.

5.10 Carefully clean the excess sample from the sides of the plates with a heated spatula. Remove all traces of sample from the edges of the plates by wiping with benzene saturated paper towels.

5.11 Place a 50 gram weight on the front balance beam of the microviscometer and a corresponding counter weight on the rear beam.

5.12 Place the plates in the microviscometer. Allow 5 minutes for the plates to come to thermal equilibrium with the water bath.

5.13 Turn on strip chart recorder and observe pen movement. If pen is not moving, rotate microvsicosity plates 180° in plate holder.

5.14 Allow sufficient time for chart tracing to reach a constant value. This will assure that deformations caused by cleaning and handling the plates will have fully recovered.

5.15 Remove the 50 gram weight from the rear weight hanger and manually drive the microviscometer contact down until 100 chart division (500 microns) movement has been recorded.

Note: If the sample plate moves too fast for the microviscometer to follow, repeat the determination using a 20 gram weight and counterweight.

5.16 Reapply the 50 gram weight to the rear weight hanger.

5.17 Note start of run on chart.

5.18 Allow sample to rebound for a minimum of 30 minutes.

5.19 From the strip chart, determine the amount of rebound after 30 minutes since reapplication of weight. This data may be recorded as either chart divisions or microns rebound.

6.0 Calculations

6.1 Calculate the percent rebound from the recorded data as follows:

a) % rebound = number chart divisions recovered

or b) % rebound = $\frac{\text{microns recovered}}{5}$

6.2 Calculate the stress used in Pascals. Pa = grams x 19.61

50 gms = 980.5 Pa.

7.0 Report

7.1 Report the percent rebound for the sample tested.

7.2 Report the stress used in Pascals.

APPENDIX IV

Sampling Procedure for Rubber-Asphalt Systems

1.0 Scope

1.1 This procedure is intended for use in sampling asphalt rubber mixes from the spreader trucks. The method when used as outlined will stop the asphalt rubber reaction. The resultant sample should then be representative of the material characteristics when applied.

2.0 Summary of Method

2.1 A one (1) gallon sample of the hot mix is taken at the spray bar and immediately chilled to stop the reaction. The material is then forwarded to the central laboratory under specified conditions for further testing.

3.0 Apparatus and Supplies

3.1 One (1) gallon cans - Paint type cans are suitable.

3.2 A cold box - Insulated to maintain a low temperature.

3.3 Dry Ice.

4.0 Procedure

4.1 Secure approximately 0.75 gallon of the mix from the spray bar.

4.2 The sample should be taken approximately half-way through the discharge of the load.

4.3 Care should be taken that the sample is not taken from an inactive section of the spray bar.

4.4 Immediately after taking the sample, the lid should be firmly placed on the can.

4.5 A hole approximately 1/8 inch in diameter should be punched in the lid.

4.6 The can should immediately be placed in the previously prepared cold box. Dry ice should be in the box for a minimum of two (2) hours to prepare it for the sample.

5.0 Sample Transportation

5.1 The sample must be transported to the laboratory in the cold box.

5.2 At no time should the sample be allowed to rise in temperature. This is of utmost importance.

6.0 Required Information

6.1 The following information must accompany each sample:

6.2 a. Truck Number

b. Time of Sample

c. Temperature of asphalt at start of rubber addition.

d. Temperature of asphalt at finish of rubber addition.

e. Elapsed time for rubber addition.

f. Elapsed time from end of rubber addition until sample is taken.

g. Temperature of truck when sample is taken.

h. Type and size of rubber - Source and grade of asphalt.

i. Time of kerosene addition - if used.

A suggested Log Sheet is appended.

ASPHALT RUBBER SAMPLE

DATE _____ TIME _____ TRUCK NO. _____

ASPHALT, AR- _____ SOURCE _____

RUBBER, SIZE _____ SOURCE _____

OPERATION	TIME	TEMPERATURE
START RUBBER ADDITION	_____	_____ °F
FINISH RUBBER ADDITION	_____	_____ °F
KEROSENE ADDITION (% IF ANY)	_____	_____ °F
START OF APPLICATION	_____	_____ °F
SAMPLE TAKEN	_____	_____ °F

PLEASE RECORD ALL TIME TO THE NEAREST MINUTE. YOUR COOPERATION IS APPRECIATED.

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