A GENERAL SYSTEM DESCRIBING THE VISCO-ELASTIC PROPERTIES OF BITUMENS AND ITS RELATION TO ROUTINE TEST DATA*

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After dynamic and static experiments on the mechanical behaviour of bitumens an attempt was made to incorporate all the essential factors into a simple system. This was found to be possible in the form of a nomograph, by means of which the deformation of bitumens can be calculated as a function of stress, time and temperature. Origin or method of manufacture proved to be of less importance than hardness and rheological type. For correlation with standard test-methods, the ring-and-ball temperature and the penetration index were found to be suitable parameters. The nomograph enables the average behaviour of a given grade to be calculated with an accuracy sufficient for engineering purposes.

Another feature of the nomograph is that it creates the possibility of giving an interpretation of other routine tests. By way of example both penetration and Fraass breaking test are discussed.

Introduction

The object of this paper is to provide the engineer with a comprehensive system enabling him to deduce quickly the mechanical properties of a given bitumen in the whole range of temperatures and times of loading that are of practical interest. To be successful, such a system should give the required property in a form that is familiar to him, and which he can use without further modification in his calculations.

The most simple rheological magnitude used in applied mechanics is Young's modulus, which, however, is defined only when the material is a purely elastic solid, i.e. when there is a linear relationship between stress and strain, and this should be independent of the time of loading. Without modification this modulus cannot be used for visco-elastic materials such as bitumens.

Provided we confine ourselves to such conditions of stress and deformation under which a linear relationship between the two exists, a simple extension of the concept of Young's modulus can be given that also applies to visco-elastic materials. The ratio can be defined as

$$S = \frac{\sigma}{\epsilon} = \frac{\text{tensile stress}}{\text{total strain}} \quad \text{(1)}$$

which will be denoted as stiffness (modulus). This stiffness modulus will, in general, depend on: (*a*) loading procedure, (*b*) time of loading or frequency, and (*c*) temperature.

Two types of loading experiments formed the basis for the work to be described in this paper, namely the constant-stress experiment—static creep test—and the dynamic test with an alternating stress of constant amplitude and frequency. It was shown in an earlier paper[1] that there is no fundamental difference between the two methods, and that also a practical system can be given to relate results from the creep test with those of the dynamic test method. For details the reader is referred to that paper; only the points important for this discussion will be briefly mentioned here.

In the static creep test, a load (σ) is applied at the time $t = 0$, and kept constant from that instant; the resulting deformation (ϵ) is then measured as a function of the time of loading. The ratio $S_s = \sigma/\epsilon$ is plotted as a function of time.

In the dynamic experiment a stress

$$\sigma = \hat{\sigma} \sin \omega t \quad \text{(2)}$$

is applied. The material then displays an alternating deformation of the same frequency:

$$\epsilon = \hat{\epsilon} \sin (\omega t - \varphi) \quad \text{(3)}$$

The test is carried out at various values of the angular frequency ω ($\omega = 2\pi \times$ frequency), and the ratio of the amplitudes of stress to strain, $S_d = \hat{\sigma}/\hat{\epsilon}$, is plotted as a function of $1/\omega$.

If we now plot S_s and S_d in a single diagram with logarithmic scales, using the same scales for the time of loading and for $1/\omega$ ($1/\omega$ has a time dimension), the curves are found to coincide for the greater part. There are ranges where there is some difference, but this never exceeds 40% of the value of S. Thus, for practical purposes, the difference between the two loading procedures largely disappears, and we will therefore not distinguish between them further.

The two methods of loading cover a large field of practical applications. When a different

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loading procedure is used, the results can always be calculated from the results of either method. For, since we postulated a linear behaviour, the superposition principle holds, and the deformation resulting from the stress actually applied can always be found by analysing the stress/time curve, replacing it by a number of successive loading steps of known type and adding the resultant deformations.

This procedure, when related to the dynamic stiffness, is identical with the well-known Fourier analysis.

However, one step or one term of the Fourier analysis is often sufficiently accurate. The stiffness modulus, as defined above, is then simply substituted for the ratio of maximum stress to strain. The time of loading then refers to the time scale of the experiment in question.

The question of linear behaviour will be referred to later. We may mention here that this condition is always fulfilled at low temperatures and short loading times, because here the linearity was found to occur up to the point where brittle-fracture occurs. At high temperatures and long loading times the material behaves almost entirely as a Newtonian fluid, so there our condition is again fulfilled. Only in the range of moderate temperatures and loading times can non-linear effects occur, and these become more marked with increase of deformation. In fact only for blown grades is the deviation from linear behaviour in a certain range serious enough for them to be taken into account for engineering applications, and even then only for large deformations. These deformations, however, are far greater than those normally met in practice, where generally the object is to avoid excessive deformations.

We may thus say that a fair picture of the rheological behaviour of a bitumen can be obtained if we know the stiffness as a function of temperature and time of loading or frequency.

When we are dealing with a purely elastic material in the classical sense, the stiffness, as is immediately clear from the definition, equals Young's modulus.

When the material is purely viscous, the following relation holds:

$$\frac{d\epsilon}{dt} = \frac{\sigma}{\lambda} \qquad (4)$$

where λ, the analogue of the viscosity coefficient η, is Trouton's coefficient of viscous traction.

The relation between λ and η for an incompressible fluid is given by:

$$\lambda = 3\eta \qquad (5)$$

If we consider the static experiment, integration of (4) gives, after substitution of (5):

$$\epsilon = \frac{\sigma}{3\eta} \cdot t \qquad (6)$$

And therefore, from (6) and (5):

$$S = 3\eta/t \qquad (7)$$

The stiffness is inversely proportional to the time of loading for a purely viscous material.

For the dynamic experiment, it is found by substituting (2) and (3) in (4):

$$\lambda\hat{\epsilon}\omega \cos(\omega t - \varphi) = \hat{\sigma} \sin \omega t \qquad (8)$$

This condition can only be met if:

$$\lambda\hat{\epsilon}\omega = \hat{\sigma} \qquad (9)$$

and

$$\varphi = \pi/2 \qquad (10)$$

From (9) it follows that:

$$S = 3\eta\omega \qquad (11)$$

If equations (7) and (11) are compared the dynamic stiffness is found to be equal to the static one if we substitute $1/\omega$ for the time of loading.

In the intermediate case, when the material is neither elastic nor viscous, the stiffness will decrease with time, but less than for a purely viscous material. In a (log S)/(log time) plot the slope of the curves representing the behaviour of a bitumen may consequently vary between horizontal and 45°, but will never be steeper.

Unless specially stated, stiffness is to be taken as the ratio of tensile stress to tensile strain, as indicated above. The analogue in terms of shear stress/shear strain may also be used, since this is the analogue of the shear modulus G. When both definitions are used side by side we will distinguish between them by using S_E and S_G respectively.

In general the material can be considered as incompressible, and then:

$$S_E = 3S_G \qquad (12)$$

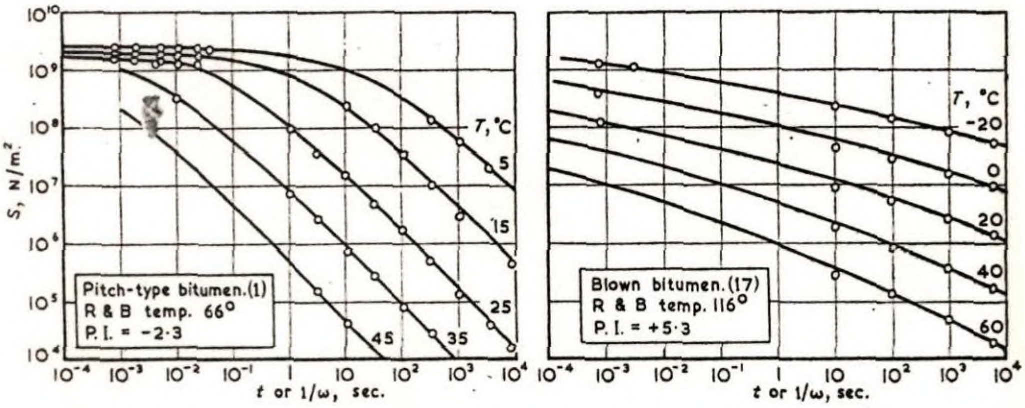
Experimental results

Measurements were carried out in various ways. For the constant-stress experiment, tensile and bending tests and rotation viscometers (Couette type) were used; for the dynamic method, flexural vibrations of free and clamped bars of the material were employed.

As indicated, results of static and dynamic measurements are plotted in the same graph, the time of loading for the dynamic experiment being replaced by the inverse of the angular frequency ω.

There will never be any doubt as to whether the plot refers to a static or a dynamic experiment, as dynamic tests can only be used for times smaller than 1 second and static tests only for longer times.

Typical results are shown in Figs. 1 and 2 for two bitumens, one having a very low penetration index, the other, a blown bitumen, a rather high penetration index. Results are given for various temperatures. Attention should be paid to the wide ranges of loading time and stiffness covered by these graphs. (In the system used here, the unit of force is the newton, N, the unit of mass is the kg. and units of length and time are metre and second respectively. These units differ from c.g.s. units only by whole powers of 10. Consequently the unit for the stiffness is: $1\text{N/m.}^2 = 10 \text{ dynes/cm.}^2 = 1{\cdot}02 \times 10^{-5} \text{ kg./cm.}^2 = 1{\cdot}45 \times 10^{-4}$ lb./sq. in., and for the viscosity: $1\text{N sec./m.}^2 = 10 \text{ dynes sec./cm.}^2 = 10$ poises.)



FIGS. 1 and 2. *Stiffness at various temperatures for a low P.I. and a high P.I. bitumen.*

It is seen from Fig. 1 that the bitumen of low penetration index behaves almost purely elastically at short times of loading, and shows a fairly sharp change at longer times, where the behaviour fairly soon becomes purely viscous (slope of 45°). The behaviour of the blown bitumen is different, the decrease in stiffness with increasing time of loading being far smaller. This is because retarded elastic effects are very marked for this bitumen.[1]

The curves in Figs. 1 and 2 are drawn so that they coincide when shifted in the direction of the log (time) axis; in this way good agreement with the experiments can be obtained. This is a most important conclusion, for it greatly facilitates the description of the rheological behaviour. Mathematically it can be expressed by saying that the dependence of the stiffness on time and temperature for each bitumen can be described by one variable, which is composed of log (time) plus some function of the temperature, or:

$$S = f\{-\log t/t_o + \chi(T)\} \qquad (13)$$

Here t_o is some constant with a time dimension and f and χ are empirical functions; t_o, f and χ will differ for the two bitumens.

Routine test methods

Such a representation would not be of much help if it were necessary to determine the constant t_o, f and χ for each bitumen separately. However, a fair correlation with data from routine test methods proved to be possible. These routine methods are briefly mentioned here; for further details the reader is referred to the literature.[2]

(a) Penetration

This is defined as the depth, measured in multiples of 0·1 mm., that a standardized needle penetrates into a bituminous surface under a constant load (100 g.) in a specified time (5 sec.). The method has been standardized by ASTM under No. D 5–25 and by IP under No. 49/46.

(b) Softening point, ring-and-ball

A ring of given dimensions, filled with bitumen, is loaded with a steel ball (3·5 g.). The whole is heated in a bath and the temperature at which the bitumen reaches a certain deformation is reported as the ring-and-ball (R & B) softening point. The method has been standardized by ASTM under No. D 36–26 and by IP under No. 58/52. In this paper the method referred to is the ASTM method, which differs from the IP method in that no stirring is carried out in the bath. In the method with stirring, the ring-and-ball softening point is found to be 1·6° lower.[3]

(c) The penetration index (P.I.)

This is not a test method, but an index figure, introduced by Pfeiffer & Van Doormaal[4] to indicate the temperature susceptibility of the penetration of a bitumen.

FIG. 3. *Nomograph for determination of penetration index*

If the logarithm of the penetration is plotted against the temperature (T), an almost straight line is obtained, and this suggests that the slope of this line might be used as a susceptibility index. This would require two penetration tests to be carried out at two temperatures for each bitumen. If, however, the straight line is extrapolated to the temperature of the ring-and-ball softening point, the corresponding penetration proves to be approximately 800. Therefore the P.I. can be calculated from one penetration and the ring-and-ball softening point, the slope of the penetration line being given by

$$\frac{\log 800 - \log \text{penetration}}{T_{R\&B} - T},$$

where T refers to the temperature in °c at which the penetration test is carried out.

The penetration index, as used by Pfeiffer & Van Doormaal, is not directly proportional to this slope, but the relation is given by the formula:

$$\frac{\log 800 - \log \text{penetration}}{T_{R\&B} - T} = \frac{20 - \text{P.I.}}{10 + \text{P.I.}} \cdot \frac{1}{50} \quad \ldots\ldots (14)$$

This relation, which may appear unusual, was chosen for historical reasons, one being that a Mexican bitumen with a penetration of 200 at 25° gives a P.I. of zero.

As is clear from equation (14), a bitumen with a penetration that is completely independent of the temperature has a P.I. of + 20, whereas, at the other extreme, a bitumen with an infinite temperature susceptibility should have a P.I. of −10.

These extremes are never found in practice; the P.I. of bitumens varies from $-2 \cdot 6$ to $+8$. The lower the P.I., the higher the temperature susceptibility.

The penetration index can be easily read from the nomograph given in Fig. 3. As can be seen from that nomograph and also from equation (14), the only data required to determine the P.I. are a penetration value and the difference between the temperature at which it is determined and the temperature of the ring-and-ball test. Consequently, the temperature at which the penetration test has to be carried out is left to the option of the investigator. This would not cause difficulties if the ring-and-ball temperature invariably corresponded to a penetration of exactly 800; the value of the penetration at ring-and-ball temperature may, however, vary from 600 to 1000.

We shall therefore give the P.I. as determined from the ring-and-ball temperature and a penetration at 25°. Only when we are dealing with hard bitumens (penetration <10 at 25°) will we use a penetration at 40° instead. In general, however, the P.I. determined at other temperatures shows no appreciable difference from that defined above.

A close relationship exists between the P.I. and the rheological type of asphaltic bitumen,[1,2] and this is the real importance of this index figure, as will be shown below.

Representation of results

Measurements were carried out on a great number of bitumens, routine test data of which are collected in Table I.

Table I

Bitumens used for the construction of the nomograph

Sample No.	P.I.	R & B temp., °c	Manufacturing method	Origin of base material
1	−2·3	66	distillation	East India
2	−2·6	54	distillation	East India
3	−2·6	46⁵	distillation	East India
4	−0·9	52	distillation	Middle East
5	−0·7	51	semi-blowing	Middle East
6	−0·6	51	distillation	South America
7	−0·4	64⁵	distillation	Middle East
8	−0·2	66⁵	distillation	South America
9	−0·2	61⁵	distillation	South America
10	+2·0	142	precipitation	Middle East
11	+2·1	89	blowing	South America
12	+3·3	84	blowing	Middle East
13	+4·2	98	blowing	South America
14	+4·3	86	blowing	South America
15	+4·9	110	blowing	South America
16	+5·3	119⁵	blowing	South America
17	+5·3	116	blowing	Middle East
18	+5·5	118⁵	blowing	South America
19	+6·3	137⁵	blowing	South America
20	+0·5	74	distillation	South America
27	−1·0	39	distillation	South America
28	−0·1	41	distillation	South America
29	+0·6	41⁵	distillation	Mexico
30	+0·6	39	distillation	—
31	−1·0	49	distillation	California
32	+0·2	56⁵	distillation	Mexico
33	+1·0	43	distillation	South America
34	−1·8	48⁵	semi-blowing	East India
35	−1·6	47⁵	semi-blowing	California
36	−1·4	51	thermal cracking	—
37	−1·1	38	distillation	South America
38	−1·1	84⁵	thermal cracking	California
39	+2·2	59	blowing	mixed base
40	+3·2	68	blowing	mixed base
41	−0·7	62⁵	mixing	mixed base
43	−0·5	65	mixing	mixed base
44	−0·3⁵	55	distillation	South America
45	−0·3	55	distillation	South America
46	+0·8	58	mixing	Mexico
47	+1·4	66	mixing	mixed base

The experimental results obtained with these bitumens can be represented in the same way as in Figs. 1 and 2, which requires a great number of graphs. Such a representation, however, is not sufficient for practical use. Interpolation for temperatures and loading times differing from those given cannot be performed rapidly and accurately. Besides, it is very difficult to estimate from such figures what would have been the result for bitumens that fall between two of the types measured, or what is the effect of slight differences in hardness and P.I.

It is therefore necessary to have the correlation between all the variables involved available in an easily accessible form. As is clear from the account given above, the most simple representation still requires four variables to determine the value of the stiffness, namely (i) hardness of the bitumen; (ii) rheological type of the bitumen; (iii) temperature; (iv) loading time or frequency.

From the previous section it is clear that if the logarithm of the penetration of a bitumen is plotted against the difference between the ring-and-ball temperature and the test temperature, lines for various bitumens with the same P.I. will coincide.

It therefore seems worth while to plot the stiffness against $T_{R\&B} - T_{test}$. This is done in Figs. 4 and 5 for a frequency of 200 c/s and a time of loading of 1000 sec. respectively.

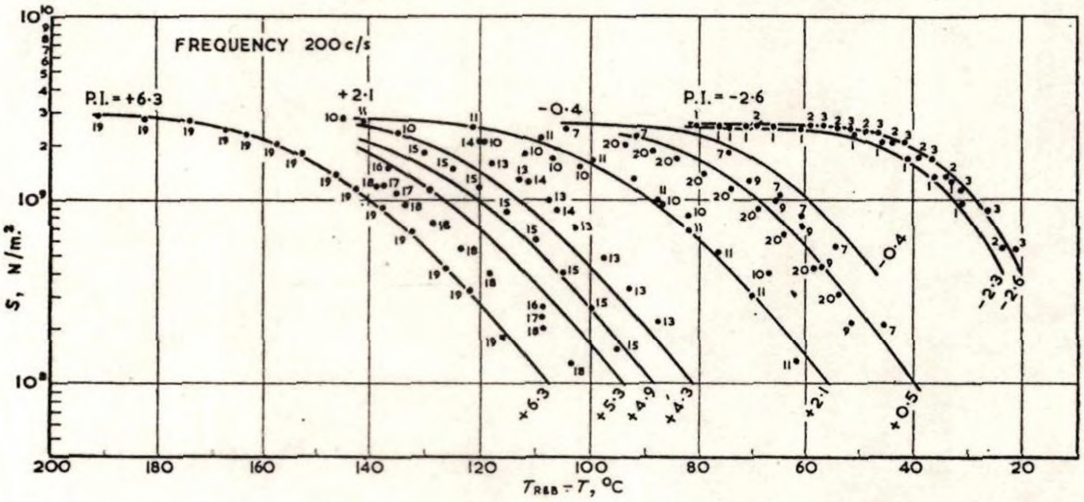


FIG. 4. *Stiffness from vibrating bar experiments as a function of temperature for various bitumens. Numbers refer to Table I*

It is then found that curves for bitumens with the same P.I., but with different values for the ring-and-ball point, coincide. Compare for instance, in Fig. 4, the results of bitumens 1, 2 and 3, which all have about the same P.I. (−2·3 to −2·6), but ring-and-ball temperatures of 66°, 54° and 46·5°, and Nos. 13 and 14 with P.I. +4·2 and +4·3 and ring-and-ball points of 98° and 86°. Experimental points for Nos. 10 and 11, P.I. +2·0 and +2·1 and ring-and-ball points of 142° and 89°, likewise show little difference, though the harder bitumen tends to be less susceptible to temperature. The results given in Fig. 5 for the much longer times of loading of 1000 sec. point in the same direction; see bitumens Nos. 6, 7 and 8.

If we accept this to be a general rule, it means that equation (13) can now be written more explicitly as:

$$S = f\{-\log t/t_0 + c.\psi(T_{R\&B} - T)\} \quad \ldots\ldots (15)$$

Here the temperature function has been replaced by a function of $T_{R\&B} - T$. The constants t_0 and c and the experimental functions f and ψ are still to be determined, but will depend solely on the rheological character of the bitumen. For the hardness of the bitumen mentioned under (i) is fully characterized by the $T_{R\&B}$ and also (iii) and (iv) are accounted for. A relation of type (15) has the advantage that it permits nomographic representation by means of a line-co-ordinate chart.

Such a chart consists of three parallel lines on which suitable scales for t, $(T_{R\&B} - T)$ and S are marked in such a way that a set of values for the variables obeying formula (15) lie on a straight line crossing the scale lines.

Nevertheless, such a representation would still make it necessary to provide different nomographs for each rheological type. Fortunately, however, it was found possible to use the same function ψ for all types of bitumen by choosing suitable values of the 'constant' c. This c was then proved to be a function of the P.I. (rheological type) only; the function f

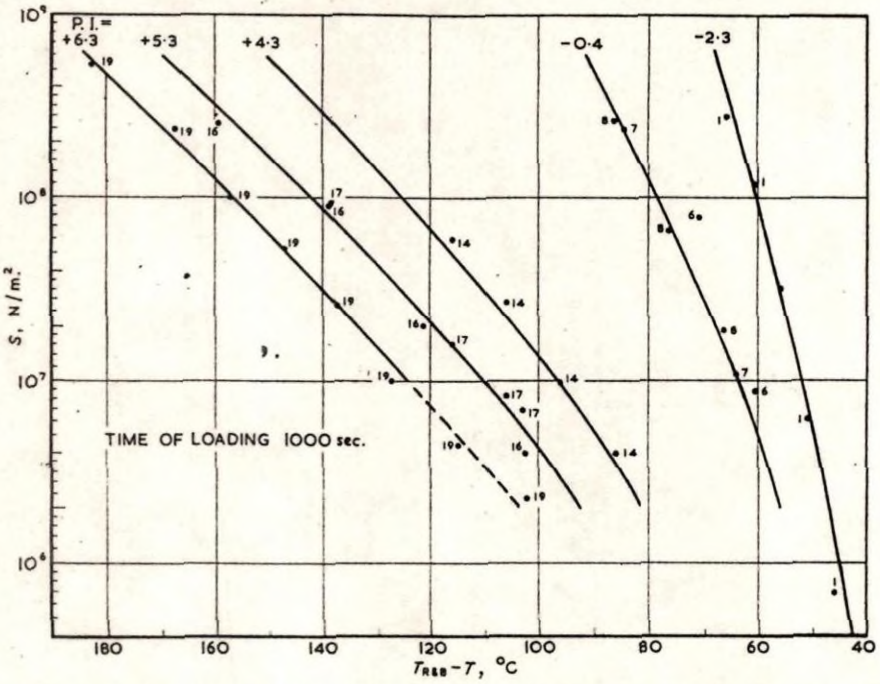


FIG. 5. *Stiffness from static bending tests as a function of temperature for various bitumens. Numbers refer to Table I*

also depends on the P.I. This means that the same scales for time and temperature difference with ring-and-ball temperature could be used for all bitumens; the scale for S, however, lies at different distances and is graduated in different ways according to the rheological type (penetration index) of the bitumen.

The nomograph of Fig. 6 was constructed on this basis, from which the S value can be read very easily. The method of using the nomograph is given on the Figure.

The agreement between nomograph readings and experimental results is evident from Figs. 4 and 5, the solid curves of which are obtained from the nomograph. In many instances the deviations are of the order of the accuracy of measurement, which includes not only the S determination but also the ring-and-ball test. The dynamic measurements are far more accurate than the static ones, their accuracy being of the order of 6%. The curve for P.I. + 4·3 in Fig. 4, however, shows greater deviations from the measurements in the high S region. In Fig. 5 there is excellent agreement between nomograph and experiment, including results for the +4·3 P.I. bitumen.

As the nomograph is based on a finite number of experiments it is possible to draw it in such a way that better agreement with the available experimental results is reached, including the dynamic measurements for 4·3 P.I. This would mean that the nomograph is less systematic and contains wavy curves. However, only smooth curves for constant S are drawn and wavy lines are avoided. Also the distance between the P.I. line and the temperature scale is a simple—in this instance linear—function of the P.I. In this way it was tried to obtain a nomograph with mean values, ruling out minor variations.

The extent to which the nomograph complies with experiments in the stiffness range between 1 and 10^7 N/m.² is shown in a different way in Figs. 7 and 8.

These results were obtained by measurements with rotating cylinder viscometers in a range of times of loading from 1 to 10,000 seconds at various temperatures. As we are dealing with an experiment in shear, S_G is measured. The material in this range of stiffness can be considered as incompressible and consequently S_E is three times S_G [see equation (12)].

The number of results available in this range are such that a representation similar to that in Figs. 4 and 5 cannot be easily given. The experimental values of S_E are therefore plotted against the stiffness, as read from the nomograph. For each temperature, where a measurement was carried out, only two points were plotted, namely for 10 and 1000 seconds.

It is seen that the points lie near a straight line, as they should. There is a clear spread, but the deviations are not a function of hardness or P.I. They seldom exceed a factor of 2.

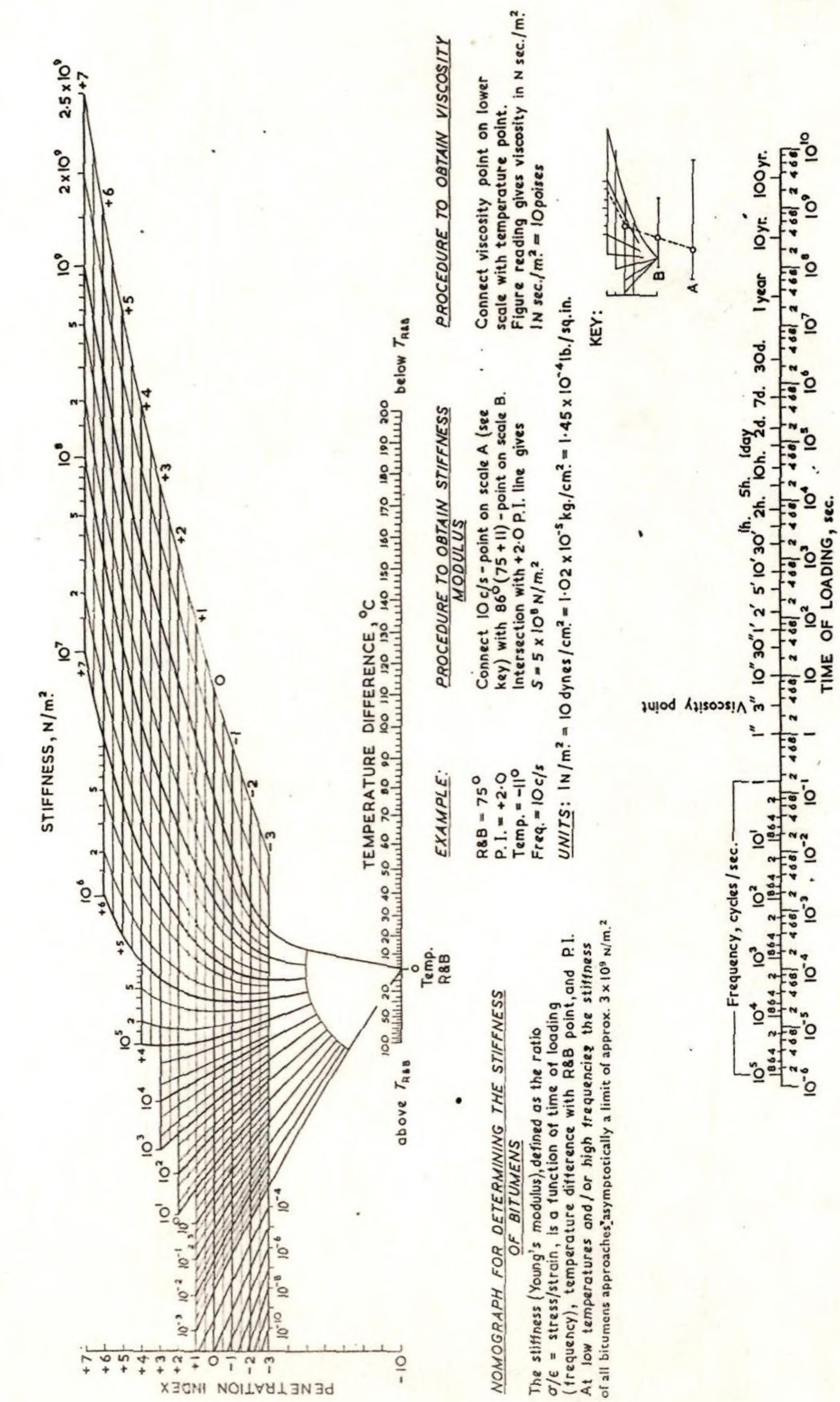


FIG. 6. *Nomograph for determining the stiffness of bitumens*

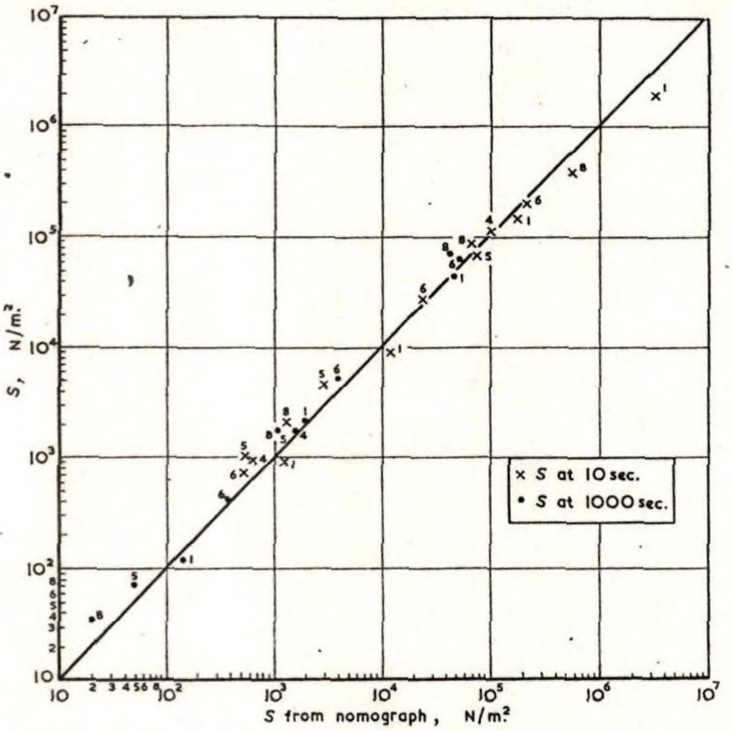


FIG. 7. *Stiffness as measured with rotating cylinder viscometer compared with nomograph reading for various bitumens. Numbers refer to Table I*

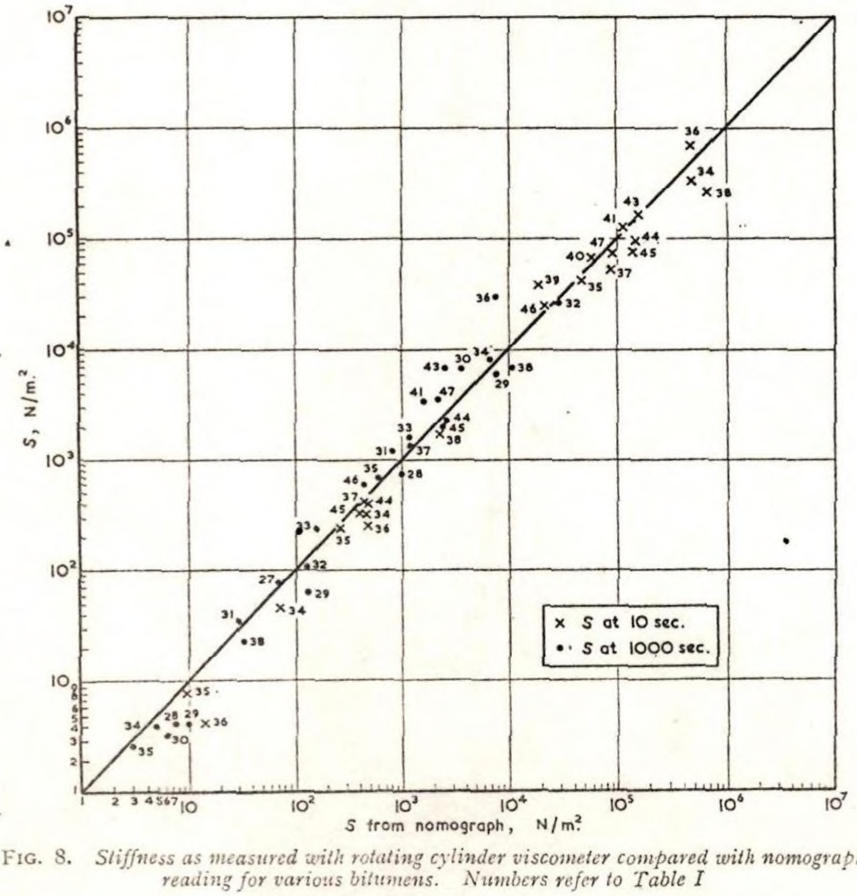


FIG. 8. *Stiffness as measured with rotating cylinder viscometer compared with nomograph reading for various bitumens. Numbers refer to Table I*

In judging these deviations it should be remembered that they are small compared with the tremendous variation in stiffness with variation in temperature, which amounts to many decades in the logarithm of the stiffness; a deviation of a factor of 2 is therefore unimportant. In fact it corresponds to a temperature difference of about 2°; this accuracy is greater than that with which the engineer can specify the temperature limits in a practical example.

Secondly, the accuracy with which the ring-and-ball temperature and the P.I. can be determined gives rise to deviations of the same order of magnitude. In this connexion it may be remarked that no special measures were taken to obtain extremely accurate ring-and-ball and P.I. values of the bitumens. Normal routine test data of the stocks from which samples were taken were used.

So far, correlation is given for temperatures below the ring-and-ball temperature. Nomographic representation also proved to be possible up to a P.I. of +1, at temperatures above the ring-and-ball softening point. At this temperature all bitumens with a P.I. below +1 show purely viscous behaviour and the experimental work can be carried out with capillary-tube viscometers. In normal routine testing these determinations are carried out at various temperatures. From these results the temperature was deduced at which the viscosity is 20 N sec./m.^{2} (200 poises). This temperature (or rather temperature difference with ring-and-ball) is plotted against the temperature read from the nomograph for that viscosity. (For procedure see the next section.) The result is shown in Fig. 9. It is seen that the correlation is satisfactory. Deviations amount to 5° maximum, which corresponds to a factor of 2 maximum in stiffness, as is readily deduced from the nomograph.

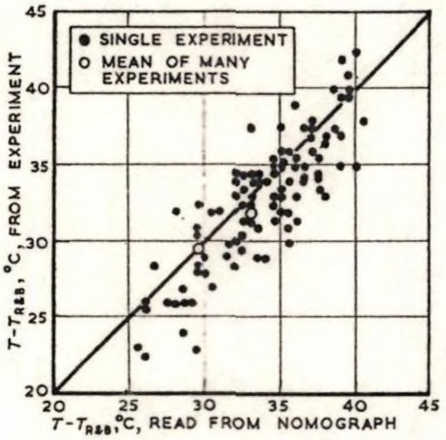


FIG. 9. *Temperature above ring-and-ball, where viscosity, as measured with capillary-tube viscometer, is 20 N sec./m.^{2} (200 poises), compared with nomograph reading. P.I. values of bitumens, −2.5 to + 2·0*

In conclusion, it can be said that the nomograph gives a good correlation in the temperature range from about 100° above to 200° below ring-and-ball temperature, with an accuracy of a factor of 2 in the stiffness corresponding to a few degrees in the temperature and often better. This covers the whole range of interest.

Extremes in the nomograph

As may be seen from Fig. 1, in certain ranges the constant-temperature curves are straight lines with a slope of 1 to 1, which means, as has already been mentioned, a purely Newtonian behaviour.

Such a behaviour is reflected in the nomograph in that the curves for constant S intersect a horizontal P.I. line at constant intervals. These intervals correspond with those on the time scale. This is best illustrated by an example. Let us take a −1·0 P.I. bitumen at a temperature of 10° above the ring-and-ball point.

For t = 1 sec. .... $S = 10^3$ N/m.^{2}
t = 10 sec. .... $S = 10^2$ N/m.^{2}
t = 100 sec. .... $S = 10$ N/m.^{2}

This confirms that the bitumen is purely viscous. In this stiffness range the relation (7) holds. In other words, when the loading time t is equal to 3 seconds, the viscosity η is *numerically* equal to the stiffness in the corresponding system of units. This provides a simple rule for determining the viscosity of a bitumen at a certain temperature from the nomograph: Connect the 3-second point with the temperature difference with ring-and-ball on the temperature scale. Intersection with the corresponding P.I. line permits direct reading of η in N sec./m.^{2}. To find the results in poises, this figure has to be multiplied by 10, because 1 N sec./m.^{2} = 10 dynes sec./cm.^{2} = 10 poises.

It should be stressed that this procedure is allowed only when the behaviour in the range considered is really viscous, i.e. only when the stiffness value lies in the left-hand lower part of the nomograph. Nor is it permissible to start at the 3×10^{-1} sec. point or 3×10^{-3} sec. point to obtain the result directly in poises or centipoises respectively, because the risk of the reading's falling in the non-viscous part of the nomograph is too great.

Another extreme in the nomograph follows from the fact that at low temperatures the stiffness of all bitumens approaches asymptotically to a limit of about 3×10^9 N/m.^{2}. This means that the S curve for this value interesects the P.I. lines at infinity. Since for these temperatures the stiffness also becomes independent of frequency, it follows that the curve for the limiting value of 3×10^9 N/m.^{2} coincides with the right-hand part of the temperature-scale line.

We can now also answer the question why all curves for constant S must intersect in the ring-and-ball temperature point. For a theoretical bitumen with a P.I. $= -10$, the P.I. line also coincides with the temperature scale. Consequently, such a bitumen shows, as it should, a stiffness of 3×10^9 N/m.^{2}, independent of the loading time, at all temperatures above that of ring-and-ball. At ring-and-ball temperature it melts and S falls abruptly to zero. This zero value is represented by the left-hand part of the temperature line and this is possible only when all S curves meet in the ring-and-ball point. The recognition of this fact was a great help in constructing the nomograph.

Validity of the nomograph

The nomograph is essentially not more than a convenient method for representing a great number of experimental results, and has the object of making these results easily accessible for practical use. The nomograph cannot therefore be said to show the behaviour of a particular bitumen, but only the average behaviour of a certain grade. If more data than are used here become available, changes in the nomograph may be required, but major changes seem unlikely. There is nothing theoretical behind it: all correlations have been empirically deduced. For instance, one may be inclined to draw the conclusion that the ring-and-ball temperature is an 'equiviscous' or 'equistiffness' temperature. As may be deduced from the nomograph, however, this is not true. The stiffness at ring-and-ball temperature is in general dependent on the penetration index. Only for one time of loading (0·4 sec) is the stiffness independent of penetration index (see also below).

The nomograph shows clearly that with two figures—ring-and-ball temperature for hardness and P.I. for rheological type—the whole complex rheological behaviour of a bitumen can be determined. It will therefore be clear that this nomograph cannot be used to predict the behaviour of very waxy bitumens, because it is known that, especially for soft bitumens, the ring-and-ball temperature is greatly influenced by the presence of paraffin wax. The bitumens used for the work described here all meet the specification D.I.N. 1995 (test method U 11), which permits a maximum wax content of 2%. They contained amounts of wax varying from 0·4 to 1·9%, which, apparently, does not lead to measurable differences in stiffness.

The nomograph gives the S values for 'small stresses'. The effect of shearing stress for a blown bitumen is illustrated in Fig. 10. Whether the non-linearity becomes evident depends not only on the shearing stress but also on the loading time.

The effect is rather marked in this instance, but it will be noted that the corresponding range of stiffness for this P.I. cannot be read from the nomograph. With increasing P.I., the range over which the stiffness is given is smaller. This is not for lack of data; apart from being stress-dependent, experimental results show large differences between bitumens from various origins and consequently the principle on which the nomograph was based (no influence of origin except that accounted for by P.I.) no longer holds here. In short, the upper left-hand portion of the nomograph is left blank, because of structural effects becoming prominent in this region. The accuracy of data deduced from the border region of this blank portion will consequently be less accurate than those from more 'inward' regions.

The penetration test

Though the systematic correlation work described so far was meant primarily as an instrument for engineering calculations, it may also be used to explain the significance of routine test methods that, up to now, have not been used directly. We will give the correlation with penetration and ring-and-ball test results as an example. It may be mentioned that this is a correlation *a posteriori*, and that the results given later were not obtained by introducing them beforehand in the nomograph.

From a rheological point of view the penetration test can be considered as a very imperfect type of stiffness determination. Still, the test is widely accepted and has considerable practical importance, and the question whether its results can be related to the stiffness defined above cannot be neglected.

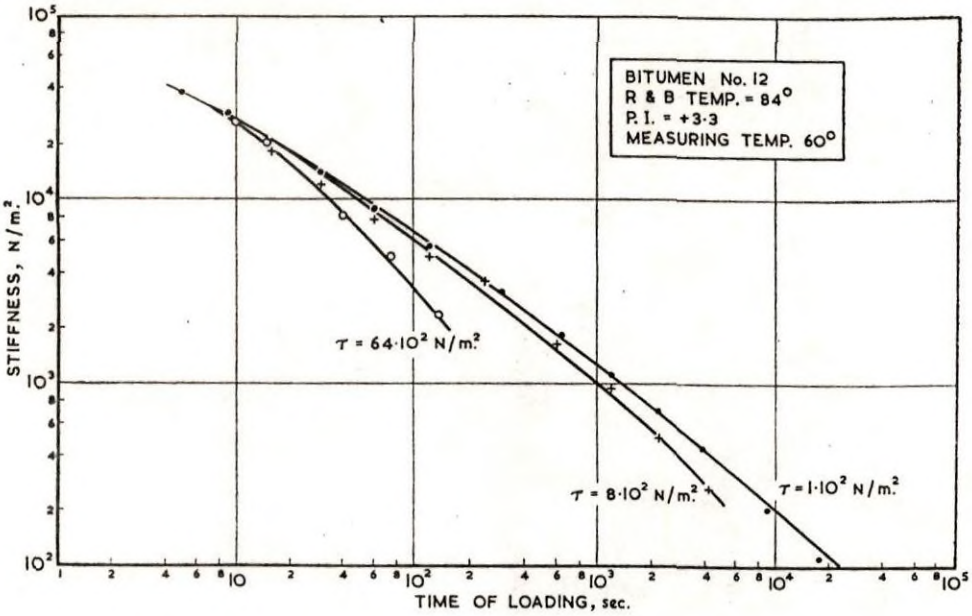


FIG. 10. *Stiffness of a blown bitumen as a function of time of loading for various shearing stress values*

From the definition of the penetration index [equation (14)], or from the nomograph of Fig. 3, it can be readily deduced at which $T_{R\&B}-T$ a given penetration for a certain P.I. is reached. In this way we can find how, for a constant penetration, the P.I. correlates with $T_{R\&B}-T$. From the stiffness nomograph we can then read how, for these P.I. values and temperature differences, the stiffness depends on time of loading. These stiffnesses can be plotted in a [log (stiffness)/log (time)] diagram and a line for each P.I. is then obtained (see Fig. 11). All these lines intersect in one point, which corresponds to a time of loading of 0·4 second and a certain stiffness.

We may thus conclude that this particular penetration corresponds to a certain stiffness at 0·4 second. If we repeat this procedure for another penetration value the lines are found to intersect in one point at the same time of 0·4 second, which, however, corresponds to a different stiffness (see Fig. 11 where this has been done for a penetration of 30 and 250).

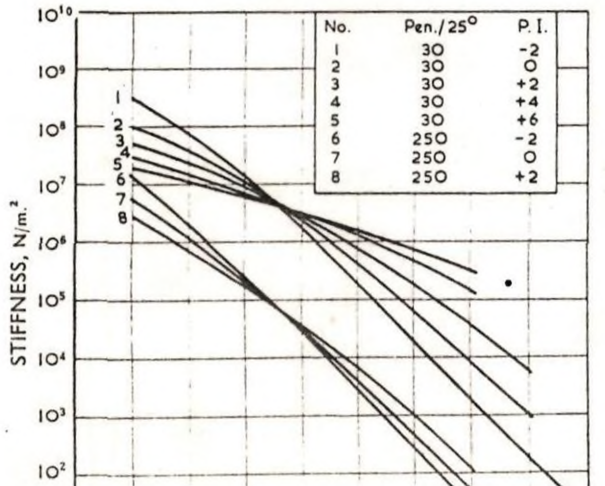


FIG. 11. *Stiffness of bitumens with penetrations of* 30 *and* 250 *and various P.I. values, as read from nomograph*

This cannot be accidental and we may conclude that a certain penetration corresponds to a certain stiffness at 0·4 sec. The correlation has been shown in Fig. 12, where both measured stiffnesses are correlated with measured penetrations (individual points) and where also the correlation as obtained from the two nomographs is given (solid line).

As mentioned before, bitumens at the ring-and-ball temperature all have the same penetration of roughly 800. According to Fig. 12 this corresponds to a stiffness of 10^4 N/m.² In fact, it is found that the line for a stiffness of 10^4 N/m.² in the stiffness nomograph is a straight line, which intersects the log (time) axis in the 0·4-sec. point, which means that the stiffness is independent of the P.I. at that time.

It may seem strange that a time of loading of 0·4 sec. should be used in the correlation of stiffness with penetration, since the loading time for the latter test amounts to 5 sec. It should be remembered, however, that the stress in that test is not constant, but far greater at the very beginning than at the end. Consequently, the effective time of loading may indeed be much smaller than 5 sec.

Saal & Koens[5] have tried to correlate penetration with viscosity. This is justified only when the behaviour of the bitumen is viscous for the whole effective period. Saal & Koens therefore only gave a correlation for low P.I. bitumens. If, moreover, only high penetration values are considered, good results are obtained, and then such a correlation is essentially the same as that given here. Low penetrations, however, correspond to a high stiffness (e.g. 10^8 N/m.^{2}) and, as can be read from Fig. 1 or from the nomograph, low P.I. bitumens can no longer be characterized in this instance by a viscosity coefficient. Consequently, the correlation given in this range by Saal & Koens can be used only for bitumens having the same P.I. as the bitumens used in their experiments.

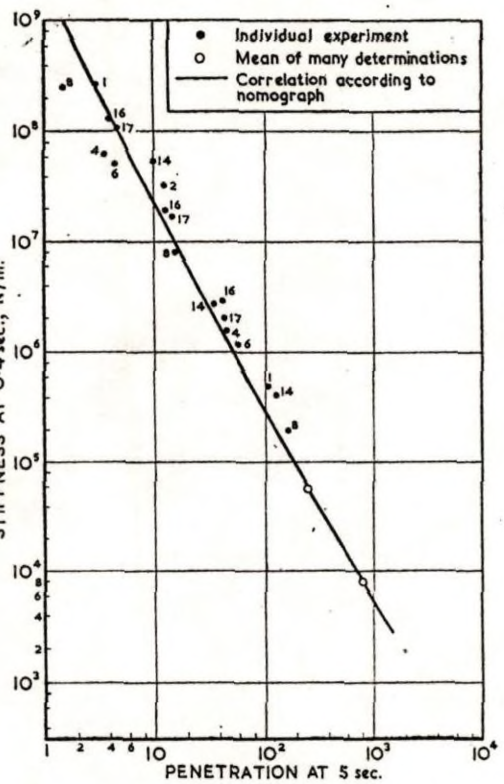


FIG. 12. *Relation between stiffness at 0·4 sec. and penetration at 5 sec. for bitumens with different P.I. values. Numbers refer to bitumens in Table I*

The Fraass breaking test

In this test, which was first described by Fraass, and which has also been standardized by IP under No. 80/53, a standard steel plaque coated with a thin layer of bitumen (0·05 cm.) is repeatedly bent to a given extent in a standard time (11 sec.) and unloaded again. The bitumen is in a bath, the temperature of which is lowered at a certain rate. The temperature at which cracks appear in the bitumen is reported as the Fraass brittle temperature.

A detailed analysis of the test cannot be given here, but a calculation based on the well-known elastic theory of a bent beam shows that the maximum strain in the bitumen layer reached under the conditions of test is 1·64% (see also Ref. 8). This was also confirmed by measuring the curvature of the steel plaque by means of an optical method, which yielded 1·60% for the maximum strain in the bitumen. To calculate the temperature of fracture not only the stiffness of the bitumen has to be known, but also its breaking strength.

A full description of breaking properties of bitumens falls outside the scope of this paper, but a few results obtained by the author, which are reproduced in Fig. 13, may give a general impression of breaking strength.

These results have been obtained by loading strips of bitumen with a constant tensile stress and observing the moment after which rupture occurs. To keep the stress constant at great elongations the well-known apparatus described by Andrade was used; this permits loading under constant stress by decreasing the active load at the same rate as the cross section of the specimen decreases.

The breaking strength is dependent both on temperature and on loading time. At sufficiently low temperatures, and for not too long loading times, bitumens show the same approximate maximum breaking strength, which is of the order of 3×10^6 N/m.^{2} (30×10^6 dynes/cm.^{2}), range about 2×10^6 to 5×10^6. Fraass temperatures and time of loading are of such an order that this maximum breaking strength applies.

These results are largely confirmed by results obtained by Lethersich,[6] Eriksson[7] and recently by Rigden & Lee.[8]

The last-mentioned authors point out that these high values for the breaking strength only obtain for the normal unilateral test method, where there is no lateral restraint. If there is lateral restraint, lower values are found, and their results suggest that it is the mean hydro-

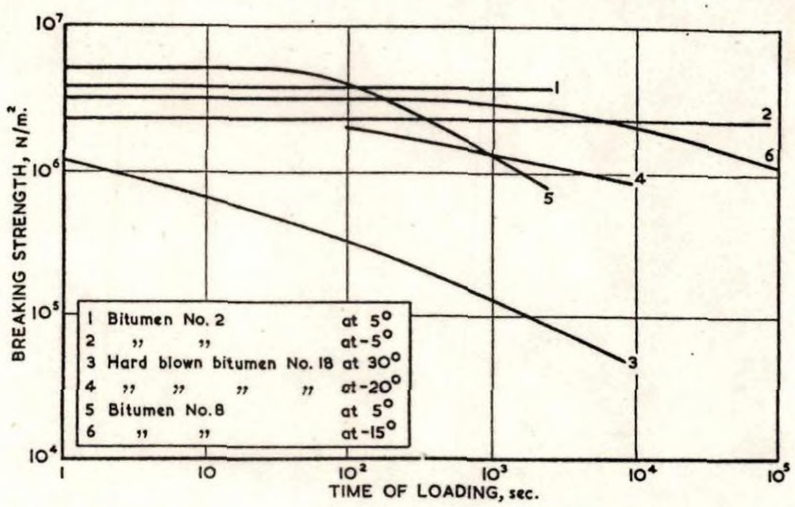


FIG. 13. *Breaking strength of asphaltic bitumens*

static tensile stress that determines whether rupture will occur or not. Accordingly, the corresponding hydrostatic tension is $1/3 \times 3 \times 10^6 = 10^6$ N/m.²

In the stress system at the top of the bitumen layer on the Fraass plaque the following general formulae hold for an incompressible material:

$$\left.\begin{aligned} \sigma_1 - p &= \frac{2}{3}E\epsilon_1 \\ \sigma_2 - p &= \frac{2}{3}E\epsilon_2 \\ \sigma_3 - p &= \frac{2}{3}E\epsilon_3 \end{aligned}\right\} \qquad (16)$$

$$\epsilon_1 + \epsilon_2 + \epsilon_3 = 0 \qquad (17)$$

where E is Young's modulus, p (the hydrostatic tension) $= \frac{1}{3}(\sigma_1 + \sigma_2 + \sigma_3)$, and σ and ϵ denote stress and strain respectively.

If the suffix 1 be the direction along the arc of the Fraass plaque, 2 the direction normal to the plaque and 3 the transverse direction, then $\sigma_2 = 0$ and $\epsilon_3 = 0$.

Substitution in (16) and (17) gives:

$$\sigma_1 = 2p \qquad (18)$$

and the first equation of (16) becomes:

$$p = \frac{2}{3}E\epsilon_1 \qquad (19)$$

Assuming that brittle fracture occurs at a hydrostatic tension p exceeding 10^6 N/m.², we find from (19) that to obtain fracture the stiffness should exceed:

$$S = \frac{3p}{2\epsilon_1} = \frac{3}{2} \times \frac{10^6}{0{\cdot}016} = 0{\cdot}94 \times 10^8 \text{ N/m.}^2$$

where S has been substituted for E.

Thus, as all bitumens have approximately the same breaking strength, the Fraass temperature should be an equistiffness temperature, corresponding to a stiffness of roughly 10^8 N/m.² at 11 sec.

From the nomograph it follows that only the P.I. and the difference with ring-and-ball temperature will decide whether this stiffness value is reached.

It therefore follows that all bitumens of the same P.I. should show the same difference between ring-and-ball and Fraass temperature. The correlation can be easily checked in the nomograph when connecting the 11-second point with the stiffness curve of 10^8 N/m.². Intersection with the temperature line gives $T_{R\&B} - T_{Fraass}$.

To what extent this correlation actually obtains can be seen from Fig. 14, where results are given for a great number of bitumens. In the P.I. range from -1 to $+2$ so many results were available that means and not individual results are given. These correspond with many results obtained on the same grade of bitumen.

From Fig. 14 it can be seen that the best correlation with the readings of the nomograph is obtained when an S value of $1 \cdot 1 \times 10^8$ N/m.^{2} instead of $0 \cdot 94 \times 10^8$ N/m.^{2} is taken as the critical value.

The correlation is obvious, though there is a large spread. This spread can in principle be due to the following three causes: (1) The nomograph does not give accurate values for all bitumens; there are small deviations. (2) The Fraass determination is too inaccurate. (3) The maximum breaking strength of bitumens is not equal but shows variations according to their origin.

A further investigation into these points is being carried out. It can already be mentioned that the nomograph has so far invariably been proved to be valid. This is not surprising, for the nomograph uses as basic data the ring-and-ball and the penetration tests, which are deformation tests, not breaking tests. The Fraass determination is not very accurate, which is also clear from Fig. 14, where mean values show less scatter than single ones. However, sometimes deviations of 10° occur, and in those instances the difference may be due to a lower or higher breaking strength than the average.

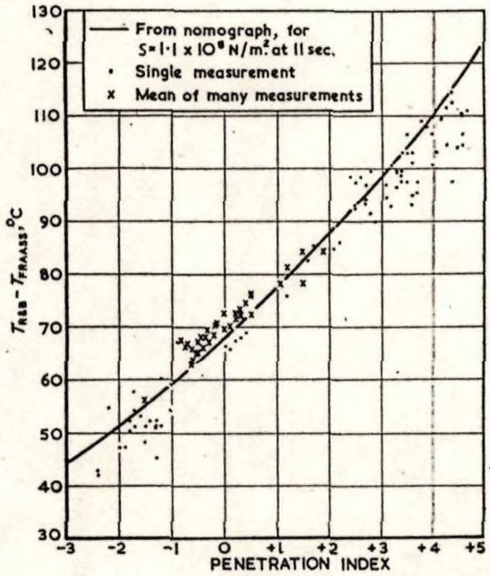


FIG. 14. *Correlation between penetration index and temperature difference between R & B and Fraass point*

For bitumens with a P.I. $> +4 \cdot 5$ there is a clear deviation. This is because these bitumens show a considerable evaporation loss when the thin layers on the Fraass plaque are being prepared; the bitumen therefore hardens and shows a higher Fraass temperature. Here the heating procedure used in the Fraass test needs revision.

Bitumens with P.I. $< -2 \cdot 0$ also show some deviations. Here the explanation is that they show a somewhat lower breaking strength.

The results given above show that breaking in the Fraass test is primarily a question of the stiffness of the bitumen, not of breaking strength. This conclusion is safe when we have to carry out calculations for engineering purposes.

On further investigation, we find that the breaking strength has some influence.

The results given here are in complete accordance with those found by Rigden & Lee[8] for tars. They state that the Fraass test is, to a first approximation, an equiviscous temperature test corresponding to a viscosity of 4×10^9 poises $= 4 \times 10^8$ N sec./m.^{2}.

Applying formula (7) and bearing in mind that the time of loading is 11 sec., this corresponds to a stiffness of

$$S = 3\eta/t = 3 \times 4 \times 10^8/11 = 1 \cdot 1 \times 10^8 \text{ N/m.}^2,$$

which is identical with the result found here.

As tars have a very low P.I. ($-2 \cdot 5$ to $-3 \cdot 0$) their behaviour is purely viscous up to high stiffness values, and correlation with viscosity is justified. For bitumens, however, such a correlation fails and stiffness should be used instead.

In conclusion, it may be said that if two independent test data for a bitumen or tar are specified, e.g. P.I. and ring-and-ball or penetration and ring-and-ball, the Fraass temperature cannot be specified independently.

Conclusions

1. The mechanical behaviour of bitumens can be described for almost the whole temperature range of practical interest by a stiffness modulus, defined as the ratio of stress to strain.

2. This stiffness modulus depends on four variables: (*a*) time of loading or frequency, (*b*) temperature, (*c*) hardness of the bitumen and (*d*) rheological type of the bitumen.

3. Hardness of the bitumen can be completely characterized by the ring-and-ball temperature, and rheological type by the penetration index.

4. A nomograph can be constructed from which the stiffness of any bitumen at any temperature and time of loading can be read, if the ring-and-ball temperature and the penetration index are given. The accuracy of this nomograph, which covers a temperature range of 300°, is amply sufficient for engineering purposes.

5. At low temperatures all bitumens behave elastically in the classical sense, and their Young's modulus (stiffness) is equal to 3×10^9 N/m.^{2} = 3×10^{10} dynes/cm.^{2}.

6. The penetration of a bitumen corresponds to its stiffness at 0·4 sec.

7. The Fraass test is essentially an equistiffness test and gives the temperature at which the stiffness is $1 \cdot 1 \times 10^8$ N/m.^{2} ($1 \cdot 1 \times 10^9$ dynes/cm.^{2}) at 11 seconds.

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DETERMINATION OF TIN–IRON ALLOY COATING IN ELECTRO-TINPLATE

By C. J. THWAITES and W. E. HOARE

In electrolytic tinplate the tin–iron alloy layer, formed during the flow-brightening operation, may range in thickness from approximately 1·5 to 8 μin. Refined methods of determination are thus necessary. Four procedures have been studied and compared. Gravimetric methods, involving determination of the free-tin (unalloyed) and alloy layers either separately, or simultaneously as the total coating, appear to be sufficiently accurate and trustworthy provided that a large enough sample-area is available. A 'coulometer' method, involving measurement of the quantity of electricity required to dissolve the coating anodically in dilute hydrochloric acid, was found to be most suitable for rapid routine determinations on relatively small specimens for which gravimetric or volumetric methods would be inappropriate.

It has been confirmed, by chemical and *X*-ray examinations, that the tin–iron alloy layer in flow-brightened electrolytic tinplate is the intermetallic compound $FeSn_2$.

The coating of tinplate, whether applied by hot-dipping or by electrodeposition and flow-brightening, comprises an overlay of substantially pure tin and a thin layer of tin–iron alloy intermediate between the tin overlay and the basis steel.[1] In the hot-dipped product the amount of alloy present is about 3 to 3·5 oz. per basis box and usually does not vary very significantly. [The basis box is a unit of area and is equal to 31,360 sq. in. of tinplate or 62,720 sq. in. of surface. In the U.K. it is customary to express coating weights in ounces per basis box (oz. b.b.); in the