NRC Publications Archive Archives des publications du CNRC

Effect of weathering on the increase in hardness of asphalts

Jones, P. M.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version
acceptée du manuscrit ou la version de l'éditeur.

Publisher's version / Version de l'éditeur:

I & EC Product Research and Development, 4, 1, pp. 57-60, 1965-06-01

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=c516a86f-fede-497e-9039-e52ac66bc86f>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=c516a86f-fede-497e-9039-e52ac66bc86f>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research
Council Canada

Conseil national de
recherches Canada

Canada

Ser
THL
N21r2
no. 253
c. 2

BLDG

18114
ANALYZED

NATIONAL RESEARCH COUNCIL
CANADA

CONSEIL NATIONAL DE RECHERCHES

EFFECT OF WEATHERING ON THE INCREASE IN HARDNESS
IN ASPHALTS

BY

P. M. JONES

REPRINTED FROM
I AND E C PRODUCT RESEARCH AND DEVELOPMENT, VOL. 4,
NO. 1, MARCH 1965, P. 57 - 60

26127

RESEARCH PAPER NO. 253
OF THE
DIVISION OF BUILDING RESEARCH

BUILDING RESEARCH
- LIBRARY -

APR 20 1966

NATIONAL RESEARCH COUNCIL

OTTAWA
JUNE 1965

PRICE 10 CENTS

NRC 8522

EFFET DE L'EXPOSITION AUX INTEMPERIES SUR LE
DURCISSEMENT DES ASPHALTES

SOMMAIRE

Un essai modifié Fraass pour déterminer le point de cassure est employé pour étudier le durcissement de l'asphalte causé par une usure accélérée. Quatre types d'asphalte pour couverture comportent différentes températures initiales du point de cassure, lesquelles peuvent être reliées au comportement de ces matériaux durant un essai d'usure accélérée. Le durcissement progressif qui accompagne l'usure est suivi d'une élévation de la température du point de cassure.

A reprint from

PRODUCT RESEARCH AND DEVELOPMENT
Vol. 4, March 1965, Pages 57-60
Copyright 1965 by the American Chemical
Society and reprinted by permission of
the copyright owner

EFFECT OF WEATHERING ON THE INCREASE IN HARDNESS OF ASPHALTS

P. M. JONES, *Division of Building Research, National Research Council, Ottawa, Ontario, Canada*

A modified Fraass brittle point test is used to study the hardening of asphalts that accompanies accelerated weathering. Four roofing asphalts exhibit variations in the initial brittle point temperature that may be related to the performance of the materials in an accelerated weathering test. The progressive hardening accompanying weathering is followed by an increase in the brittle point temperature.

THE DETERIORATION of asphalt results from chemical and physical changes, which are in turn dependent upon the source of the crude and the nature of exposure of the material. The process of asphalt oxidation is used advantageously in the blowing still when the asphalt is processed to a suitable consistency for further uses. However, the oxidative process continues during the service life of the asphalt product as a result of the atmospheric exposure, and degradation proceeds until the product fails to perform its intended purpose. The chemical changes resulting from exposure, which may include dehydrogenation, carbonization, polymerization, and evaporation (7), produce variation in the physical characteristics of the asphalts.

The increase in the hardness of an asphalt is probably the most important of the physical changes from a practical viewpoint. A reasonable supposition is that increase in hardness which is closely associated with a loss in ability to deform plastically is a primary factor in the breakdown of asphalts, and may also affect adhesion to mineral particles and self-healing properties. Loss of extensibility may make the asphalt unable to resist the variety of strains that are applied to it as a result of thermal and moisture changes, structural movements, and wind vibrations.

There have been several investigations of asphaltic hardening (7). The concept of stiffness is used by Van der Poel (12). This concept is an elastic modulus dependent upon time and temperature; rupture of the asphalt occurs when the stiffness exceeds a critical value in relation to some operative strain. The magnitude of the increase in stiffness and the conditions of time and temperature on the strain are the important criteria. Since long-term thermal loading is considered to be more important than impact or vibrational strain, it is relevant that stiffness is a realistic evaluation. Stiffness studies were made by Griffin and coworkers (2) with a sliding plate microviscometer as a way of measuring accelerated oxidation of thin films of asphalt when these films are heated in an oven. Martin (6) has used the sliding plate microviscometer to correlate hardening with weathering. The relationship between the failure time of a thin asphalt film in a weatherometer and the durability of asphalts has been studied by Wright and Campbell (13).

Lee and Dickinson (5) used the Fraass brittle point temperature to evaluate the nature of coal tars, and a modified form of this test has been used by the Division of Building Research, National Research Council of Canada, in low temperature studies of bitumens (4). This article examines the application

of this test to the measurement of the hardness of asphalt, and some results are given of the changes in hardness that accompany the degradation of roofing asphalts.

Brittleness and Its Measurement

Brittleness is the tendency to fracture with little or no plastic deformation and, like other measures of hardness, it depends upon the circumstances of testing. Three types of brittleness are distinguished by Pfeiffer (9):

Static brittleness, when the material breaks immediately after exceeding the elastic limit with no plastic deformation.

Impact brittleness, when a material shows plastic behavior under slow deformations, but is brittle under impact loading.

Dynamic brittleness, when a material is subjected to varying loads of prolonged duration, fracture may occur at a lower maximum load than with a constant load. If there is no plastic deformation, the material is said to be dynamically brittle.

The measured brittleness will depend not only upon the rate of deformation but also upon the temperature. This is utilized in the Fraass brittle point test as a way to express the degree of brittleness by means of the temperature at which breakage occurs under given conditions.

The Fraass test has been used in Europe for a number of years; it was originally designed by Fraass and is described in the Institute of Petroleum Specification I.P. 80/53 (3). In this test, a spring steel plaque (4.1 cm. by 2.0 cm.) is coated with a thin layer (0.5 mm.) of asphalt and placed in an apparatus in which it is flexed by turning a handle that operates a conical cam. The flexing operation is suspended in an inner vessel and cooling is accomplished by blowing air over ether or by adding solid carbon dioxide to acetone. The handle is turned to produce one flex of the plaque every minute. This

flex is such that the coated film is outward and the ends of the plaque have attained a distance of 3.64 cm. The temperature of the plaque is steadily lowered at a rate of 1° C. per minute until flexure of the plaque causes a crack to appear in the center of the asphalt film (Figure 1). The temperature at which this cracking is first observed is the brittle condition of the material.

The theory of the brittle fracture of asphalts in the Fraass test has been studied by Van der Poel (12) and by Rigden and Lee (11). Rigden and Lee calculated stress-strain relationships in the test from the elastic theory of a bent beam. Vander Poel used Fraass' breaking strength of asphalt and his stiffness concept, but both studies resulted in the conclusion that the brittle point temperature is an equiviscous temperature corresponding to a viscosity of 4×10^9 poises or, if expressed as stiffness, is 1.1×10^9 dynes per sq. cm. Thus, the test in fact gives the temperature at which the asphalt has a viscosity of 4×10^9 poises, and, as hardness increase can be considered as a change in viscosity, a measure of viscosity is also a measure of the hardness of asphalt.

Experimental

Performing the Fraass test is very difficult and repeatability is often very poor. Pickles (10) made several modifications that improve the operation of the test, including an electrical drive to produce the flexing deformation and transparent plaques of a polyester film to permit easy observation of the cracks by transmitted light. In the study now reported, an apparatus very similar to that described by Pickles is used. This apparatus, shown in Figure 2, has been described in detail (4).

In the Institute of Petroleum Specification I.P. 80/53, 0.40 ± 0.01 gram of asphalt is applied to the plaque, which has an area of 8.4 sq. cm., by wiping the surface with a ball of asphalt and then heating the plaque and asphalt until the asphalt flows to produce a film of uniform thickness. Pickles also used this procedure, which results in a film thickness of 0.05 cm. (0.0197 inch). The Division of Building Research procedure was to prepare five plaques at a time, as described in ASTM D 1669-59T. This is a method for the preparation of panels of coating grade asphalts for vertical exposure in accelerated weathering studies and was adapted to prepare plaques of a uniform coating of asphalt on the Mylar polyester film.

The previous report (4) investigated the effects of rate of cooling and asphalt thickness upon the brittle point temperature. Figure 3 summarizes the effect of the film thickness;

Figure 1. Brittle point apparatus in flexed position

Figure 2. Brittle point unit

Table I. Physical Characteristics of Asphalts

	Asphalt Number			
	1	2	3	4
	Source of Crude			
	Lloydminster, Alberta	Pembina, Alberta	Lloydminster, Alberta	Tiajuana, Venezuela
Softening point, ^a ° F.	147.5	145.0	173	173
Penetration ^b at 32° F., dmm.	14	...	18	12
Penetration at 77° F., dmm.	32	34	30	26
Penetration at 115° F., dmm.	112	...	65	57
Susceptibility ^c	3.06	...	1.57	1.73
Ductility ^d at 77° F., cm.	49.0	...	5.5	3.5
Flash point ^e C.O.C., ° F.	505	545	470	580
Dispersibility parameter ^f	0.656	0.906	0.624	0.752
Predicted durability, ^g days	61	117	54	82

^a ASTM D36-26. ^b ASTM D5-52. ^c Susceptibility $S = \text{Pen. at } 115^\circ \text{ F.} - \text{Pen. at } 32^\circ \text{ F.} / \text{Pen. at } 77^\circ \text{ F.}$ ^d ASTM D71-52. ^e ASTM D92-57. ^f Mertens' procedure (8). ^g Obtained from dispersibility parameter.

there is very little difference in the brittle point temperature for films of thicknesses 0.375 to 0.75 mm. (0.015 to 0.030 inch). As other studies on the weathering of asphalt films use a thickness of 0.625 mm. (0.025 inch), this thickness was used in this study. Figure 4 illustrates the influence of the rate of cooling and shows that a rate of 1° C. per minute results in a minimum value of the brittle point temperature and that any deviation from this rate of cooling results in an apparent increase in the brittle point temperature. Using these conditions of 1° C. per minute rate of cooling and a film thickness of 0.625 mm., a standard deviation of 0.7° C. was obtained for a series of 10 determinations. Thus for a 95% confidence level, two results on the same sample with a single operator should agree within 1.4° C.

Changes in Brittle Point Temperature with Accelerated Weathering

A standard procedure, used to study the performance of coating grade asphalts in accelerated weathering testing, involves the vertical exposure of asphalt films on aluminum panels and subjection of these films to photooxidation until degradation progresses to an arbitrary condition of failure. The failure condition is determined by a spark-gap pattern of the number of flaws in the panel, and the number of cycles to reach an arbitrary level of failure is the durability. No such procedure exists for roofing asphalts because the low softening points of these asphalts make a vertical exposure unsuitable. As asphalt degradation is accompanied by hardening, or an increase in brittleness, a test to measure the initial brittleness may indicate the potential service of an asphalt, and the progress in degradation may be followed by a measurement of the brittleness.

To investigate the use of the modified Fraass test in this study, asphalt-coated plaques were prepared from four roofing asphalts. Two were 140° F. softening point dead level roofing asphalts and the other two were 170° F. softening point roofing asphalts. A summary of their physical properties is given in Table I.

A durability prediction, also included in Table I, was obtained from information on the dispersibility of the least soluble asphaltene. The performance of coating-grade asphalts in the accelerated weathering tests depends upon the source of

Figure 3. Effect of film thickness upon brittle point temperature

Figure 4. Effect of cooling rate upon brittle point temperature

Figure 5. Change in brittle point temperature with weathering

the crude and may be as high as 75 cycles. The determination of this value is a very long process, and various methods have been proposed to predict this performance by rapid laboratory evaluations. One of these methods, developed by Mertens (8), is to measure the dispersibility of the least soluble asphaltene. This value was determined and is reported in Table I.

Figure 6. Relation between brittle point temperature and predicted durability

Predicted durability obtained by Mertens' procedure (8)

Mertens also obtained a correlation between this value and the durability of coating grade asphalts as measured in ASTM D 529-59T, and this correlation has been used to indicate the predicted durability of these asphalts.

The asphalt-coated plaques were placed in the horizontal position in a weatherometer operated in accordance with ASTM D 529-59T, and samples were removed every 10 cycles to determine the brittle point temperature. This cycle consists of 51 minutes of carbon-arc radiation, which produces a panel temperature of 160° F., followed by a 9-minute period of radiation with water sprayed on the panels at a temperature of 45° ± 5° F. This cycle repeated 22 times constitutes a single daily cycle. Some local flow and deformation occurred on some of the plaques, and this was removed by again placing the plaque in the heated press and pressing the film to a uniform thickness prior to testing. The average values of five determinations of the brittle point temperatures before and after various periods of exposure are shown in Table II; Figure 5 illustrates the change in brittle point temperature with accelerated weathering. The relationship between the initial brittle condition of the asphalts and the predicted durability is shown in Figure 6. The results of the weatherometer exposure represent single periods of exposure, with five plaques of each asphalt removed and tested for the brittle point temperature every 10 cycles.

Results

The physical properties in Table I indicate a close similarity between the materials of the same softening point. This is anticipated, however, as these materials are produced to meet specifications. The dispersibility parameters include a variation such that a difference would be expected in the performance of these materials upon weathering. This is substantiated by the initial brittle point temperature, which produces the nearly straight line shown in Figure 6 when these temperatures are plotted with the predicted durability. More materials would need to be examined before the brittle

point temperature could alone be a measure of durability. A lower brittle point is indicative of a more flexible material which in general will perform longer in any accelerated weathering test.

Figure 5 shows the rate at which the brittle point temperature changes with the length of exposure of the asphalt in an accelerated weathering test. A progressive increase in the brittle point temperature is observed with three of the four asphalts. The second asphalt—a Pembina material—has an initial increase in brittleness followed by a progressive decrease in this parameter. This particular asphalt exhibits unusual properties in other tests, but in the coating-grade consistency of this material, it is a very durable asphalt. The slow rate of change of brittleness would also indicate a durable material capable of withstanding severe exposure conditions.

Asphalts 1 and 3 are Lloydminster asphalts processed to different consistencies, but both show similar rates of change of brittleness. In contrast to these is asphalt 4, a Tiajuana asphalt which has a more rapid rate of change of brittleness.

Conclusion

The determination of the brittle point temperature provides a useful method to study changes in the hardness of asphalts exposed to accelerated weathering. The accepted method of studying durability of coating-grade asphalts is not applicable to roofing asphalts because of their low softening points, but the brittle point temperature can be used to measure the initial tendency of the asphalt for durability and also to follow the progressive hardening during exposure. The results from four asphalts indicate a variation in the initial brittle point temperature that may be related to the performance of the materials in accelerated weathering. A progressive increase in brittleness has been observed with three of the asphalts. These results indicate that studies should be continued to evaluate the use of this concept with other asphalts and under other conditions of aging.

Acknowledgment

The author is grateful for assistance given by J. G. Quenneville in performing the experiments, the results of which are now reported. This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division.

Literature Cited

- (1) Abraham, H., "Asphalt and Allied Substances," 6th ed., Vol. 5, pp. 298-304, Van Nostrand, New York, 1960.
- (2) Griffin, R. L., Miles, T. K., Penner, C. J., *Proc. Assoc. Asphalt Paving Technologists* **24**, 31-62 (1955).
- (3) Institute of Petroleum, Specification I.P. 80/53, "Standard Methods for Testing Petroleum and Its Products," 17th ed., p. 76, London, 1958.
- (4) Jones, P. M., *Proc. Can. Tech. Asphalt Assoc.* **VII**, 15-24 (1962).
- (5) Lee, A. R., Dickinson, E. J., D.S.I.R. Road Research Laboratory, Tech. Paper No. 31, 1954.
- (6) Martin, K. G., *J. Appl. Chem. (London)* **14**, 423-35 (1964).
- (7) Martin, K. G., *J. Inst. Petrol.* **47**, 321-8 (1961).
- (8) Mertens, E. W., *ASTM Bull.* No. 250, 40-4 (1960).
- (9) Pfeiffer, J. P., "The Properties of Asphaltic Bitumen," p. 177, Elsevier, New York, 1950.
- (10) Pickles, S., *J. Appl. Chem. (London)* **9**, 219-23 (1959).
- (11) Rigden, P. J., Lee, A. R., *Ibid.*, **3**, 62-70 (1953).
- (12) Van der Poel, C., *Ibid.*, **4**, 221-36 (1954).
- (13) Wright, J. R., Campbell, P. G., *Ibid.*, **12**, 256-66 (1962).

RECEIVED for review October 19, 1964

ACCEPTED January 18, 1965

Division of Petroleum Chemistry, 147th Meeting, ACS, Philadelphia, Pa., April 1964.

Table II. Changes in the Brittle Point Temperature with Weathering

Asphalt No.	No. of Weatherometer Cycles (51-9 Cycle)			
	0	10	20	30
	Brittle point temperature, ° C.			
1	-8.3	-1.5	-1.8	0
2	-12.3	-3.8	-5.0	-6.5
3	-4.8	+1.8	+4.5	+7.6
4	-7.2	-0.3	+5.1	+7.4