# Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method) ${ }^{1}$ 

This standard is issued under the fixed designation D 5191; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

## 1. Scope*

1.1 This test method covers the use of automated vapor pressure instruments to determine the total vapor pressure exerted in vacuum by air-containing, volatile, liquid petroleum products. This test method is suitable for testing samples with boiling points above $0^{\circ} \mathrm{C}\left(32^{\circ} \mathrm{F}\right)$ that exert a vapor pressure between 7 and $130 \mathrm{kPa}(1.0$ and 18.6 psi$)$ at $37.8^{\circ} \mathrm{C}\left(100^{\circ} \mathrm{F}\right)$ at a vapor-to-liquid ratio of $4: 1$. Measurements are made on liquid sample sizes in the range from 1 to 10 mL . No account is made for dissolved water in the sample.

Note 1-Samples can also be tested at other vapor-to-liquid ratios, temperatures, and pressures, but the precision and bias statements need not apply.
1.1.1 Some gasoline-oxygenate blends may show a haze when cooled to 0 to $1^{\circ} \mathrm{C}$. If a haze is observed in 8.5 , it shall be indicated in the reporting of results. The precision and bias statements for hazy samples have not been determined (see Note 10).
1.2 This test method is suitable for calculation of the dry vapor pressure equivalent (DVPE) of gasoline and gasolineoxygenate blends by means of a correlation equation (see 13.2). The calculated DVPE very closely approximates the dry vapor pressure that would be obtained on the same material when tested by Test Method D 4953.
1.3 The values stated in SI units are regarded as standard. The inch-pound units given in parentheses are provided for information only.
1.4 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific warning statements, see 7.2 through 7.7.

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## 2. Referenced Documents

2.1 ASTM Standards: ${ }^{2}$

D 2892 Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D 4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)
D 5190 Test Method for Vapor Pressure of Petroleum Products (Automatic Method)

## 3. Terminology

3.1 Definitions of Terms Specific to This Standard:
3.1.1 absolute pressure - the pressure of the air-free sample. It is calculated from the total pressure of the sample by subtracting out the partial pressure of the dissolved air.
3.1.2 dry vapor pressure equivalent ( $D V P E$ ) -a value calculated by a correlation equation (see 13.2) from the total pressure.
3.1.2.1 Discussion-The DVPE is expected to be equivalent to the value obtained on the sample by Test Method D 4953, Procedure A.
3.1.3 total pressure-the observed pressure measured in the experiment that is the sum of the partial pressure of the sample and the partial pressure of the dissolved air.

## 4. Summary of Test Method

4.1 A known volume of chilled, air-saturated sample is introduced into an evacuated, thermostatically controlled test chamber, the internal volume of which is five times that of the total test specimen introduced into the chamber. After injection into the test chamber, the test specimen is allowed to reach thermal equilibrium at the test temperature, $37.8^{\circ} \mathrm{C}\left(100^{\circ} \mathrm{F}\right)$. The resulting rise in pressure in the chamber is measured using a pressure transducer sensor and indicator. Only total pressure

[^1]measurements (sum of the partial pressure of the sample and the partial pressure of the dissolved air) are used in this test method, although some instruments can measure the absolute pressure of the sample as well.
4.2 The measured total vapor pressure is converted to a dry vapor pressure equivalent (DVPE) by use of a correlation equation (see 13.2).

## 5. Significance and Use

5.1 Vapor pressure is a very important physical property of volatile liquids.
5.2 The vapor pressure of gasoline and gasoline-oxygenate blends is regulated by various government agencies.
5.3 Specifications for volatile petroleum products generally include vapor pressure limits to ensure products of suitable volatility performance.
5.4 This test method is more precise than Test Method D 4953, uses a small sample size ( 1 to 10 mL ), and requires about 7 min to complete the test.

## 6. Apparatus

6.1 Vapor Pressure Apparatus-The type of apparatus suitable for use in this test method employs a small volume test chamber incorporating a transducer for pressure measurements and associated equipment for thermostatically controlling the chamber temperature and for evacuating the test chamber prior to sample introduction.
6.1.1 The test chamber shall be designed to contain between 5 and 50 mL of liquid and vapor and be capable of maintaining a vapor-to-liquid ratio between 3.95 to 1.00 and 4.05 to 1.00 .

Note 2-The test chamber employed by the instruments used in generating the precision and bias statements were constructed of stainless steel or aluminum.

Note 3-Test chambers exceeding a 15 mL capacity can be used, but the precision and bias statements (see Section 15) are not known to apply.
6.1.2 The pressure transducer shall have a minimum operational range from 0 to $177 \mathrm{kPa}(0$ to 25.7 psi$)$ with a minimum resolution of $0.1 \mathrm{kPa}(0.01 \mathrm{psi})$ and a minimum accuracy of $\pm 0.8 \mathrm{kPa}( \pm 0.12 \mathrm{psi})$. The pressure measurement system shall include associated electronics and readout devices to display the resulting pressure reading.
6.1.3 A thermostatically controlled heater shall be used to maintain the test chamber at $37.8 \pm 0.1^{\circ} \mathrm{C}\left(100 \pm 0.2^{\circ} \mathrm{F}\right)$ for the duration of the vapor pressure measurement.
6.1.4 A platinum resistance thermometer shall be used for measuring the temperature of the test chamber. The minimum temperature range of the measuring device shall be from ambient to $75^{\circ} \mathrm{C}\left(167^{\circ} \mathrm{F}\right)$ with a resolution of $0.1^{\circ} \mathrm{C}\left(0.2^{\circ} \mathrm{F}\right)$ and an accuracy of $0.1^{\circ} \mathrm{C}\left(0.2^{\circ} \mathrm{F}\right)$.
6.1.5 The vapor pressure apparatus shall have provisions for introduction of the test specimen into an evacuated test chamber and for the cleaning or purging of the chamber following the test.
6.2 Vacuum Pump, capable of reducing the pressure in the test chamber to less than $0.01 \mathrm{kPa}(0.001 \mathrm{psi})$ absolute.
6.3 Syringe, (optional, depending on sample introduction mechanism employed with each instrument) gas-tight, 1 to 20 mL capacity with a $\pm 1 \%$ or better accuracy and a $\pm 1 \%$ or
better precision. The capacity of the syringe should not exceed two times the volume of the test specimen being dispensed.
6.4 Iced Water Bath or Air Bath, for chilling the samples and syringe to temperatures between 0 to $1^{\circ} \mathrm{C}\left(32\right.$ to $\left.34^{\circ} \mathrm{F}\right)$.
6.5 Pressure Measuring Device, capable of measuring local station pressure with an accuracy of $0.20 \mathrm{kPa}(0.03 \mathrm{psi})$, or better, at the same elevation relative to sea level as the apparatus in the laboratory.
6.5.1 When a mercury manometer is not used as the pressure measuring device, the calibration of the pressure measuring device employed shall be periodically checked (with traceability to a nationally recognized standard) to ensure that the device remains within the required accuracy specified in 6.5.
6.6 McLeod Vacuum Gage, to cover at least the range from 0 to $0.67 \mathrm{kPa}(0$ to 5 mm Hg$)$. Calibration of the McLeod gage is checked in accordance with Annex A6 of Test Method D 2892.

## 7. Reagents and Materials

7.1 Purity of Reagents—Use chemicals of at least $99 \%$ purity for quality control checks (see Section 11). Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available. ${ }^{3}$ Lower purities can be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

Note 4-The chemicals in this section are suggested for use in quality control procedures (see 11.2) and are not used for instrument calibration.
7.2 Cyclohexane, (Warning-Cyclohexane is flammable and a health hazard).
7.3 Cyclopentane, (Warning-Cyclopentane is flammable and a health hazard).
7.4 2,2-Dimethylbutane, (Warning-2,2-dimethylbutane is flammable and a health hazard).
7.5 2,3-Dimethylbutane, (Warning-2,3-dimethylbutane is flammable and a health hazard).
7.6 2-Methylpentane, (Warning-2-methylpentane is flammable and a health hazard).
7.7 Toluene, (Warning-Toluene is flammable and a health hazard).

## 8. Sampling

8.1 General Requirements:
8.1.1 The extreme sensitivity of vapor pressure measurements to losses through evaporation and the resulting changes in composition is such as to require the utmost precaution and the most meticulous care in the drawing and handling of samples.

[^2]8.1.2 Obtain a sample and test specimen in accordance with Practice D 4057, except do not use the "Sampling by Water Displacement" section for fuels containing oxygenates. Use a 1 L (1 qt) sized container filled between 70 and 80 with sample.

Note 5-The present precision statement was derived using samples in $1 \mathrm{~L}(1 \mathrm{qt})$ containers. However, samples in containers of other sizes, as prescribed in Practice D 4057, can be used with the same ullage requirement if it is recognized that the precision can be affected.
8.1.3 In the case of referee testing, the $1 \mathrm{~L}(1 \mathrm{qt})$ sample container is mandatory.
8.1.4 Perform the vapor pressure determination on the first test specimen withdrawn from a sample container. Do not use the remaining sample in the container for a second vapor pressure determination. If a second determination is necessary, obtain a new sample.
8.1.5 Protect samples from excessive temperatures prior to testing. This can be accomplished by storage in an appropriate ice bath or refrigerator.
8.1.6 Do not test samples stored in leaky containers. Discard and obtain a new sample if leaks are detected.
8.2 Sampling Handling Temperature-Cool the sample container and contents in an ice bath or refrigerator to the 0 to $1^{\circ} \mathrm{C}$ ( 32 to $34^{\circ} \mathrm{F}$ ) range prior to opening the sample container. Allow sufficient time to reach this temperature. Verify the sample temperature by direct measurement of the temperature of a similar liquid in a similar container placed in the cooling bath or refrigerator at the same time as the sample.
8.3 Verification of Sample Container Filling-With the sample at a temperature of 0 to $1^{\circ} \mathrm{C}$, take the container from the cooling bath or refrigerator, and wipe dry with absorbent material. If the container is not transparent, unseal it and using a suitable gage, confirm that the sample volume equals 70 to $80 \%$ of the container capacity (see Note 6). If the sample is contained in a transparent glass container, verify that the container is 70 to $80 \%$ full by suitable means (see Note 6).
8.3.1 Discard the sample if the container is filled to less than $70 \%$, by volume, of the container capacity.
8.3.2 If the container is more than $80 \%$ by volume full, pour out enough sample to bring the container contents within the 70 to $80 \%$ by volume range. Do not return any sample to the container once it has been withdrawn.
8.3.3 Reseal the container if necessary, and return the sample container to the cooling bath or refrigerator.

Note 6-For non-transparent containers, one way to confirm that the sample volume equals 70 to $80 \%$ of the container capacity is to use a dipstick that has been pre-marked to indicate the 70 and $80 \%$ container capacities. The dipstick should be of such material that it shows wetting after being immersed and withdrawn from the sample. To confirm the sample volume, insert the dipstick into the sample container so that it touches the bottom of the container at a perpendicular angle, before removing the dipstick. For transparent containers, using a marked ruler or by comparing the sample container to a like container which has the 70 and $80 \%$ levels clearly marked, has been found suitable.
8.4 Air Saturation of the Sample in the Sample Container:
8.4.1 Transparent Containers Only—Since 8.3 does not require that the sample container be opened to verify the sample capacity, it is necessary to unseal the cap momentarily before resealing it, so that samples in transparent containers are treated the same as samples in non-transparent containers.
8.4.2 With the sample again at a temperature of 0 to $1^{\circ} \mathrm{C}$, take the container from the cooling bath or refrigerator, wipe it dry with an absorbent material, remove the cap momentarily, taking care that no water enters, reseal and shake vigorously. Return it to the cooling bath or refrigerator for a minimum of 2 min .
8.4.3 Repeat 8.4.2 twice more. Return the sample to the cooling bath or refrigerator until the beginning of the procedure.
8.5 Verification of Single Phase Samples-After drawing a test specimen and injecting it into the instrument for analysis, check the remaining sample for phase separation. If the sample is contained in a transparent container, this observation can be made prior to sample transfer. If the sample is contained in a non-transparent container, mix the sample thoroughly and immediately pour a portion of the remaining sample into a clear glass container and observe for evidence of phase separation. A hazy appearance is to be carefully distinguished from separation into two distinct phases. The hazy appearance shall not be considered grounds for rejection of the fuel. If a second phase is observed, discard the test and the sample. Hazy samples may be analyzed (see Section 14).

## 9. Preparation of Apparatus

9.1 Prepare the instrument for operation in accordance with the manufacturer's instructions.
9.2 Clean and dry the test chamber as required to avoid contamination of the test specimen. Prior to sample introduction, visually determine from the instrument display that the test chamber pressure is stable and does not exceed 0.1 kPa ( 0.01 psi ). When the pressure is not stable or exceeds this value, check that the chamber is clean of volatile materials remaining in the chamber from a previous sample or check the calibration of the transducer.
9.3 If a syringe is used for introduction of the sample specimen, chill it to between 0 and $4.5^{\circ} \mathrm{C}\left(32\right.$ and $\left.40^{\circ} \mathrm{F}\right)$ in a refrigerator or ice bath before drawing in the sample. Avoid water contamination of the syringe reservoir by sealing the outlet of the syringe during the cooling process.

## 10. Calibration

10.1 Pressure Transducer:
10.1.1 Perform a calibration check of the transducer at least once every six months, or sooner, as indicated from the quality control checks (see Section 11). The calibration of the transducer is checked using two reference points, zero pressure $(<0.1 \mathrm{kPa})$ and the ambient barometric pressure.
10.1.2 Connect a McLeod gage to the vacuum source in line with the test chamber. Apply vacuum to the test chamber. When the McLeod gage registers a pressure less than 0.1 kPa $(0.8 \mathrm{~mm} \mathrm{Hg})$, adjust the transducer control to zero or to the actual reading on the McLeod gage as dictated by the instrument design and manufacturer's instructions.

Note 7—Refer to Annex A6 of Test Method D 2892 for further details concerning the calibration of pressure sensors and McLeod gages.
10.1.3 Open the test chamber of the apparatus to atmosphere and observe the corresponding pressure value of the transducer. Ensure that the apparatus is set to display the total pressure and
not a calculated or corrected value. Compare this pressure value against the value obtained from the pressure measuring device, as the pressure reference standard. The pressure measuring device shall measure the local station pressure at the same elevation as the apparatus in the laboratory, at the time of pressure comparison. (Warning-Many aneroid barometers, such as those used at weather stations and airports, are pre-corrected to give sea level readings; these must not be used for calibration of the apparatus.)
10.1.3.1 For mercury barometers used as the pressure measuring device, the barometric pressure reading shall be corrected for the change in the density of the mercury column between $0^{\circ} \mathrm{C}$ and the operating temperature and converted to the same units of pressure as the vapor pressure apparatus display. After making the density correction, the conversion for the height of a mercury column at $0^{\circ} \mathrm{C}$ to kPa or psia is made as follows: $1 \mathrm{in} .(25 \mathrm{~mm}) \mathrm{Hg}$ at $0^{\circ} \mathrm{C}=3.3865 \mathrm{kPa}$ or $=0.49116$ psia.
10.1.4 Repeat 10.1.2 and 10.1.3 until the zero and barometric pressures read correctly without further adjustments.
10.2 Thermometer-Check the calibration of the platinum resistance thermometer used to monitor the temperature of the test chamber at least every six months against a National Institute of Standards and Technology (NIST) traceable thermometer.

## 11. Quality Control Checks

11.1 Use a verification fluid with known volatility as an independent check against the instrument calibration each day the instrument is in use. For pure compounds (see 7.1), multiple test specimens may be taken from the same container over time, provided the pure compound test specimen is air saturated according to the procedure given in 8.4 , and the spent test specimens are not re-used, in whole or in part. Record the dry vapor pressure equivalent value, and compare this to the statistical value of the control sample from your laboratory. If the difference exceeds your control limits, check the calibration of the instrument.
11.2 Some possible materials and their corresponding vapor pressures, as found in ASTM DS 4B, ${ }^{4}$ include: cyclopentane 68.3 kPa ( 9.91 psi ); 2,2-dimethylbutane 68.0 kPa ( 9.86 psi ); 2,3-dimethylbutane 51.1 kPa ( 7.41 psi ); 2-methylpentane 46.7 $\mathrm{kPa}(6.77 \mathrm{psi})$; and toluene $7.1 \mathrm{kPa}(1.03 \mathrm{psi}){ }^{5}$

Note 8-It is recommended that at least one type of control sample used in 11.1 be representative of the fuel(s) regularly tested by the laboratory. The total vapor pressure measurement process (including operator technique) can be checked periodically by performing this test method on previously prepared samples from one batch of product, as per procedure described in 8.1.2. Samples should be stored in an environment suitable for long term storage without sample degradation. Analysis of

[^3]result(s) from these quality control samples can be carried out using control chart techniques. ${ }^{6}$

## 12. Procedure

12.1 Remove the sample from the cooling bath or refrigerator, dry the exterior of the container with absorbent material, uncap, and insert a chilled transfer tube or syringe (see 9.3). Draw a bubble-free aliquot of sample into a gas tight syringe or transfer tube, and deliver this test specimen to the test chamber as rapidly as possible. The total time between opening the chilled sample container and inserting/securing the syringe into the sealed test chamber shall not exceed 1 min .
12.2 Follow the manufacturer's instructions for injection of the test specimen into the test chamber, and for operation of the instrument to obtain a total vapor pressure result for the test specimen.
12.3 Set the instrument to read the result in terms of total vapor pressure. If the instrument is capable of calculating a dry vapor pressure equivalent value, make sure that only the parameters in 13.2 are used.

## 13. Calculation

13.1 Record the total vapor pressure reading from the instrument to the nearest $0.1 \mathrm{kPa}(0.01 \mathrm{psi})$. For instruments that do not automatically record a stable pressure value, manually record the pressure indicator reading every minute to the nearest 0.1 kPa . When three successive readings agree to within 0.1 kPa , record the result to the nearest $0.1 \mathrm{kPa}(0.01$ psi).
13.2 Calculate the DVPE using Eq 1. Ensure that the instrument reading used in this equation corresponds to the total pressure and has not been corrected by an automatically programmed correction factor:

$$
\begin{equation*}
D V P E, \mathrm{kPa}(\mathrm{psi})=(0.965 X)-A \tag{1}
\end{equation*}
$$

where:
$X=$ measured total vapor pressure in $\mathrm{kPa}(\mathrm{psi})$, and
$A=3.78 \mathrm{kPa}$ (or 0.548 psi ).
Note 9-The correlation equation was derived from the results of the 1988 cooperative program ${ }^{7}$ and confirmed in the 1991 interlaboratory study. ${ }^{8}$
13.3 The calculation described by Eq 1 can be accomplished automatically by the instrument, if so equipped, and in such cases the user shall not apply any further corrections.

## 14. Report

14.1 Report the dry vapor pressure equivalent to the nearest $0.1 \mathrm{kPa}(0.01 \mathrm{psi})$ without reference to temperature.
14.2 If the sample was observed to be hazy in 8.5 , report the test result as in 14.1, followed by the letter H.

[^4]Note 10-The precision and bias statements have not been determined for hazy samples since these types of samples have not been evaluated as part of a interlaboratory study.

Note 11—The inclusion of the letter H in 14.2 is intended to alert the data recipient that the sample analyzed was hazy. In the event that a laboratory has a computer system that is incapable of reporting alphanumeric results in accordance with the requirements in 14.2, it is permissible for the laboratory to report the result obtained as in 14.1 , along with a statement or annotation that clearly conveys to the data recipient that the analyzed sample was hazy.

## 15. Precision and Bias ${ }^{8}$

15.1 Precision-The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows:

Note 12-The following precision data were developed in a 1991 interlaboratory cooperative test program. Participants analyzed sample sets comprised of blind duplicates of 14 types of hydrocarbons and hydrocarbon-oxygenate blends. The oxygenate content (MTBE, ethanol, and methanol) ranged from 0 to 15 by volume nominal and the vapor pressure ranged from 14 to 100 kPa ( 2 to 15 psi ) nominal. A total of 60 laboratories participated. Some participants performed more than one test method, using separate sample sets for each. Twenty-six sample sets were tested by Test Method D 5190 and 27 by this test method. In addition, six sets were tested by modified Test Method D 5190, and 13 were modified by this test method.
15.1.1 Repeatability-The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct
operation of the test method, exceed the value calculated as per Eq 2 only in one case in twenty:

$$
\begin{equation*}
\text { repeatability }=0.00807(\mathrm{DVPE}+B) \tag{2}
\end{equation*}
$$

where:

$$
B=124 \mathrm{kPa}(18.0 \mathrm{psi}) .
$$

15.1.2 Reproducibility-The difference between two single and independent test results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the value calculated as per the following equation only in 1 case in 20:

$$
\begin{equation*}
\text { reproducibility }=0.0161(\mathrm{DVPE}+B) \tag{3}
\end{equation*}
$$

where:

## $B=124 \mathrm{kPa}(18.0 \mathrm{psi})$.

15.2 Bias-Since there is no accepted reference material suitable for determining the bias for the procedures in this test method, bias cannot be determined.
15.3 Relative Bias-A statistically significant relative bias was observed in the 1991 interlaboratory cooperative test program between the total pressure obtained using this test method and the dry vapor pressure obtained using Test Method D 4953, procedure A. This bias is corrected by the use of Eq 1 (see 13.2), which calculates a DVPE value from the observed total pressure.

## 16. Keywords

16.1 dry vapor pressure; gasoline; hydrocarbon-oxygenate blends; mini method; petroleum products; vapor pressure

## SUMMARY OF CHANGES

Subcommittee D02.08 has identified the location of selected changes to this standard since the last issue (D 5191-02) that may impact the use of this standard.
(1) Updated 10.1.1.

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[^0]:    ${ }^{1}$ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.08 on Volatility.

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[^1]:    ${ }^{2}$ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service @astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

[^2]:    ${ }^{3}$ Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see Annual Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulary, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[^3]:    ${ }^{4}$ DS 4B, "Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds," ASTM International, W. Conshohocken, PA, 1991. (Order \#DS4B.)
    ${ }^{5}$ The vapor pressure values cited were obtained from Phillips Petroleum Company, Bartlesville, OK or ASTM DS 4B, "Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds."

[^4]:    ${ }^{6}$ MNL 7, Manual on Presentation of Data Control Chart Analysis, 6th Edition, Section 3: Control Charts for Individuals, ASTM International, W. Conshohocken, PA.
    ${ }^{7}$ Supporting data (the results of this program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1260.
    ${ }^{8}$ Supporting data (the results of this test program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1286.

