

Submitted for recognition as an American National Standard

**Methods for Determining Physical Properties of Polymeric Materials Exposed
to Gasoline/oxygenate Fuel Mixtures**

Foreword—This SAE Recommended Practice is a product of the SAE Cooperative Research Program, Project Group 2. The SAE Cooperative Research Project Group 2 was formed by the Oxygenated Fuels Task Force, which is composed of OEM automotive engineering executives. Their task is to identify and prioritize potential areas for precompetitive cooperative research programs to operate under the administration of SAE. The specific scope of Project Group 2 was to develop and exchange information relative to materials and test methods for use with blends of methanol and gasoline. The program was operated in accordance with 1984 Cooperative Research Act. This revision includes information relative to test methods for determining physical properties of polymeric materials exposed to gasoline/oxygenate fuel mixtures.

1. Scope—This SAE Recommended Practice applies to determining worst-case fuel, conditioning test specimens in worst-case fuel(s) prior to testing, individual tests for properties of polymers exposed to methanol-gasoline fuel mixtures. The determination of equilibrium, as well as typical calculations are also covered.

1.1 Purpose—Polymers are used in applications which require exposure to a variety of fluid environments. Tests to determine the effects of such exposure on material properties are well established. However, the determination of the effects on polymers exposed to fuels of variable alcohol and ether content poses new problems. This document seeks to address those concerns by detailing changes to standard tests that make them suitable for that purpose.

2. References

2.1 Applicable Publications—The following publications form a part of the specification to the extent specified herein. Unless otherwise indicated, the latest revision of SAE publications shall apply.

2.1.1 SAE PUBLICATION—Available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096-0001.

SAE J1681 SEP93—Gasoline/Methanol Mixtures for Materials Testing.

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2.1.2 ASTM PUBLICATIONS—Available from ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

- ASTM D 412—Test Method for Rubber Properties in Tension (ISO 37)
- ASTM D 413—Test Method for Rubber Property—Adhesion to Flexible Substrates, (Peel Test for Fabric Adhesion) (ISO 36)
- ASTM D 429—Test Methods for Rubber Property—Adhesion to Rigid Substrates, (Metal adhesion, using Method A, Button) (ISO 813 or ISO 814)
- ASTM D 471—Test Method for Rubber Property—Effect of Liquids (ISO 1817)
- ASTM D 543—Test Method for Resistance of Plastics to Chemical Reagents (No ISO Found)
- ASTM D 618—Practice for Conditioning Plastics and Electrical Insulating Materials for Testing, Procedure A. (ISO 291)
- ASTM D 624—Test Method for Tear Strength of Conventional Vulcanized Rubber and Thermoplastic Elastomers (ISO 34 Part 1)
- ASTM D 638—Test Method for Tensile Properties of Plastics (ISO 527 Parts 1 and 2)
- ASTM D 790—Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials (ISO 178)
- ASTM D 991—Test Method for Rubber Property—Volume Resistivity of Electrically Conductive and Anti-Static Products(No ISO Found)
- ASTM D 1053—Test Method for Rubber Property Stiffening at Low Temperatures; Flexible Polymers and Coated Fabrics (ISO 1432)
- ASTM D 1329—Test Method for Evaluating Rubber Property—Retraction at Low Temperature (TR Test) (ISO 2921)
- ASTM D 2240—Test Method for Rubber Property—Durometer Hardness (ISO 868)

3. Requirements

3.1 **General**—A problem arises in testing materials for use in vehicles which can run on fuels with methanol concentrations varying from 0 to 85% by volume. There is no single methanol-containing test fuel composition that can be used to evaluate the relative performance of different polymers. Because polymers differ in their molecular structure, the most damaging concentration of methanol for one material may not be the most damaging for another. This problem has necessitated the designation of a series of test fluids that can be used to compare the properties of one polymer in its "worst-case" fuel with those of another polymer in a different "worst-case" fuel. Nevertheless, it is desirable to reduce the total number of tests as much as possible. Therefore, a single test, using weight gain at equilibrium, has been chosen to determine which fuel composition (from Table 1) exerts the greatest effect on each polymer. Once a polymer's "worst-case" fuel has been determined, its properties will be measured after exposure to that fuel.

Since the rate of diffusion in plastics (glassy polymers) can be very slow, the time required for some plastics to reach equilibrium may be quite lengthy. In the simplest cases of diffusion with polymeric materials, the behavior may be described by Fick's Law. For Fickian diffusion, the time required to attain equilibrium sorption for a polymer slab or sheet exposed to a penetrant is proportional to the square of the sample thickness. Thus, the time does not increase linearly, but exponentially, as the thickness increases. However, for plastics exposed to organic liquids, the diffusion coefficient typically is not constant, may be because of non-uniformity, boundary conditions, physical effects (burrs, nicks, folds etc.), and swelling of the sample periphery may also occur. This leads to non-Fickian or anomalous diffusion and the effect of sample thickness on the equilibrium time is not as straightforward as for the ideal Fickian case; but, in either case, as the sample thickness increases, so does the time required to achieve sorption equilibrium. Therefore, to shorten conditioning times, sample thickness should be as small as possible and still be consistent with the requirements of the test for a particular physical property.

This same guidance also applies to elastomers.

This document consists of procedures which are designed to evaluate the performance of polymeric materials when they are exposed to variable methanol content fuels. The first part of this document addresses the determination of the worst-case fuel. The second part contains the procedure for conditioning actual test specimens in fuel, prior to measuring their physical properties. Finally, the third part details the test methods for evaluating polymeric materials for use in methanol fuels.

The methodology presented is general enough that it can be extended to determine the physical properties of polymers and elastomers in gasoline mixtures with most other oxygenate additives such as ethanol, MTBE, ETBE, TAME, EAME, etc., by simply substituting these other additives for methanol in the recipes for the test fuels appearing in Table 1. Also, in Table 1, the addition of formic acid for plastics would have to be replaced by acetic acid with reagent grade ethanol. Formic acid can still be used with MTBE and other oxygenates made from methanol and acetic acid can be used with ETBE and other oxygenates made from ethanol. Because these additives are not used above 10 or 15% by volume, the range of test fuels to evaluate should be limited to the maximum regulated percent of the specific additive.

4. Determining Worst-Case Fuel

4.1 **Equilibrium Weight Increase**—To compare the extent of polymer swelling by the five test fuels given in Table 1, the polymer must be allowed to reach equilibrium with each fuel. Thus, the samples will be immersed in the test fuels until they attain a constant weight, as set forth in Appendix A.

TABLE 1—TEST FUEL RECIPES FOR POLYMERS TESTING⁽¹⁾

Test Fuel Component	CM0 (mL)	CM15 (mL)	CM30 (mL)	CM50 (mL)	CM85 (mL)
For Elastomers ⁽²⁾⁽³⁾ :					
Toluene	500	425	350	250	75
Iso-Octane	500	425	350	250	75
Methanol (Reagent Grade)	0.0	150	300	500	850
Distilled Water	0.0	0.0	0.30	0.50	0.85

1. From SAE J1681 SEP93, "Gasoline/Oxygenate Mixtures for Materials Testing"

2. For Plastics:

Add to each liter of test fuel:

0.005 g NaCl (0.003 g Cl⁻) = 3 ppm chloride ion

0.050 mL formic acid=60 ppm formic acid

3. For Auto-Oxidized Test Fuel

Add to each liter:

50 mMol of t-Butyl Hydroperoxide - 6.8 mL of 70% t-Butyl hydroperoxide per liter of fuel

0.01 mg/L Cu as cuprous sulfate final concentration in fuel

Peroxide added to a peroxide number of 180 per ISO 4639-3

4.1.1 **SAMPLE PREPARATION**—To reduce the amount of time required to complete the test, plastic samples used for this procedure will be thin films produced under a nitrogen blanket by hot-plate forming or other similar method. Note should be taken that the effect of fuel on very thin hot-plate formed films can vary significantly from the effect of fuel mixture on injection molded, or extruded specimens. Samples will have a minimum surface area of 12 cm² and will be made as thin as possible. Thicker specimens can be used but they will require much longer equilibration times. After thirty test specimens have been marked for identification with an engraver or punch, precondition them at 23 °C ± 2 °C and 50% ± 5% relative humidity for a minimum of 40 hours according to ASTM D 618, Procedure A. For rubber, mark twenty-five ASTM D 471 volume change test specimens with a punch, for identification.

4.1.2 CONDITIONING THE SAMPLES—Weigh the specimens individually, in grams, to 4 decimal places. Place 6 plastic specimens (only 5 for elastomers) into each of 6 glass vessels furnished with a reflux apparatus, as specified in ASTM D 543, and equipped with a calcium sulfate drying tube. The sixth, specially marked plastic sample, is to be used to evaluate long-term chemical effects on the plastic and should not be removed from the hot fuel when the other 5 samples are weighed. Samples should be separated using stainless steel wire and glass beads according to ASTM D 471. Fill each vessel with a different methanol blend test fuel such that all specimens are completely submerged. Fuel formulations are provided in Table 1, or SAE J1681. Allow at least 1 cm of fuel above the plastic samples to compensate for any evaporation. For elastomers, allow at least 3 cm fuel above the samples to compensate for swelling as well as evaporation. Using a water or sand bath, heat the test fuel uniformly in the vessel to $55\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. Do not use heating mantles or hot plates. For elastomers, replace the test solution daily for the first three days and weekly thereafter. For plastics containing plasticizer, replace the solution twice each week for the duration of the exposure. For other plastics, replace the fuel mixtures weekly. Continue sample exposure until constant weight is attained, or for a minimum of 500 hours. Observe safety precautions applicable to the handling of flammable and toxic mixtures (refer to OSHA and local laboratory procedures and standards).

4.1.3 WEIGHING THE SAMPLES DURING CONDITIONING—Except for special situations, applicable to the second part as follows (conditioning in the worst-case fuel), weigh each sample at one week intervals to determine if absorption of the fuel has stabilized. Remove the samples to be weighed from the vessel containing the hot fuel and place them in a container of the same fuel at room temperature. Let the samples stand in the fuel for a period of 0.5 to 1 hour. Weigh a weighing bottle, in grams, to 4 decimal places. Remove one sample from the cool fuel, blot it, drop it into the weighing bottle and seal it within 10 seconds to prevent any further weight loss due to evaporation. Weigh the bottle containing the sample and record the weight of the sample (obtained by difference from the tared bottle). Repeat this procedure for the other five samples (and for each fuel blend). If there is no change in **Apparent Percent Weight Increase** for each sample in a particular fuel (as defined in Appendix A) for three consecutive weighings, the five samples are to be removed for drying. The exposure of the sixth plastic sample in each set is to continue until the worst-case fuel has been determined, at which time exposure will be continued only for the sample in that fuel. (See Equation 1.)

$$\text{Apparent Percent Weight Increase} = \frac{[(\text{Wt of bottle} + \text{sample}) - \text{wt of bottle} - \text{Original wt}]}{\text{Original weight}} \times 100 \quad (\text{Eq. 1})$$

Once it has been determined that equilibrium has been reached, the weights for each sample for the last three weighing periods will be averaged. This value will be termed the **Equilibrium Swollen Weight** for that sample.

NOTE—The time necessary for the samples to reach equilibrium may vary from one test fuel to another. Therefore, exposure to a test fuel should continue until the statistical treatment of successive **Apparent Percent Weight Increase** determinations indicate that equilibrium has been attained in that fuel. It might be expected that samples in the worst-case fuel will reach equilibrium more rapidly than in any other. However, this assumes that there is only one mechanism involved in the absorption process, which might not be the case.

4.1.4 DRYING THE SAMPLES—After recording the Equilibrium Swollen Weights, air dry the samples in a hood for 24 hours, and then dry them in a vacuum oven at $100\text{ }^{\circ}\text{C}$ to a constant weight. Weigh the samples every 48 hours to determine the "interim dry weight" until there is no change in the **Percent Weight Lost** of any sample group for three consecutive weighing periods (using the statistical principles in Appendix A.). (See Equation 2.)

$$\text{Percent Weight Lost} = \frac{(\text{Equilibrium Swollen Weight} - \text{"interim dry weight"})}{\text{Equilibrium Swollen Weight}} \times 100 \quad (\text{Eq. 2})$$

Once it has been determined that an equilibrium dried state has been reached, the weights for each sample for the last three weighing periods will be averaged. This value will be termed the **Dried Weight** for that sample.

The fuel in which conditioning produces the greatest percentage difference between the **Equilibrium Swollen Weight** and the **Dried Weight**, is the **worst-case fuel** and will be used to condition samples for all subsequent property determinations. (See Equation 3.)

$$\text{Equilibrium Percent Weight Change} = \frac{(\text{Equilibrium Swollen Weight} - \text{Dried Weight})}{\text{Dried Weight}} \times 100 \quad (\text{Eq. 3})$$

NOTE—If CM0 is the worst-case fuel, physical property measurements should also be made after conditioning samples in CM15 for comparison.

4.2 Evaluation of Chemical Attack—For Thermoplastic materials only.

It is possible that some polymers may react chemically with methanol fuels without showing significant signs of physical change, such as weight gain. To verify that the polymer chain is not degraded by methanol, it is necessary to determine the Peak Molecular Weight of the polymers before and after fuel aging. This will be done by running a gel permeation chromatographic analysis (GPC), as given in the third part of this document, on both an original and an all-aged sample from each of the test fuels. However, permitting GPC analysis as the only method for determining degradation of the polymer chain is not practical for all polymers such as nylons and polyesters. Other methods such as solution viscosity measurements, in the case of polyamides and polyesters, are acceptable.

One dried sample from each fuel will be evaluated for chemical attack. If the peak molecular weight of the fuel-aged sample differs from that of the unaged sample, chemical attack has occurred. Record the percent change of the peak molecular weight of the aged sample from the unaged sample for each methanol fuel blend. Compare the results from the various fuels. If the fuel blend which gives the highest percent change in peak molecular weight is not the same (the percent change in peak molecular weight differs by more than 2 percentage points) as the fuel which produced the highest Equilibrium Percent Weight Change, then all evaluations of plastic properties will be determined after exposure of the appropriate test specimens to both fuels. See Table 2 for an example.

TABLE 2—EXAMPLE⁽¹⁾

Fuel	Weight Change	Peak Molecular Weight Change	Comment
CM0	+2.0%	-0.2%	
CM15	+7.2%	-8.6%	Worst-case for PMW change
CM30	+8.4%	-4.4%	Worst-case for Wt change
CM50	+4.1%	-1.2%	
CM85	+1.8%	-0.7%	

1. Since there is a different fuel which give the "worst result" in each test, and the changes in peak molecular weight differ by more than 2 percentage points, then two sets of physical properties must be determined; one after conditioning in CM15 and one after conditioning in CM30.

The exposure of the sixth thin film specimen in the worst-case fuel(s) should be continued for as long as the thicker samples are still being conditioned for either tensile or flex testing, according to the second part of this document. Upon completion of the conditioning period, another GPC analysis should be run on this sample to determine if there are any long-term effects.

5. Conditioning Test Specimens In Worst-Case Fuel(s) Prior To Testing

5.1 For Plastics—To minimize the time needed to saturate the sample in determining the worst-case fuel, the plastic specimens being aged were thin films. Unfortunately, physical property tests require samples which are significantly thicker.

5.1.1 **PROTOCOL**—Because of the experimental difficulty in handling unusual and large shapes, a set of surrogate samples having at least the same thickness as the physical property test specimens should be used to determine the exposure time required for the specimens to reach equilibrium. In the case of an unusual shape, a section taken from the thickest part of the physical property test specimen should be used. The only other requirement for a surrogate sample is that it be small enough to be placed into a weighing bottle. To save time, the actual physical property test specimens can be preconditioned at the same time as the surrogate samples. When the physical property test specimens for two or more tests have the same thickness, only one set of surrogate samples needs to be used to indicate the proper conditioning time.

5.1.2 **PROCEDURE**—Five samples of each surrogate for the desired tests and 5 test specimens for each physical property determination will be preconditioned at $23\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ and $50\% \pm 5\%$ relative humidity for a minimum of 40 h according to ASTM D 618, Procedure A. Mark the surrogate samples and weigh them, in grams, to 4 decimal places. Expose all the samples to the worst case fuel(s) in the same type of apparatus previously used, but the vessels must be large enough to contain the plastic test specimens without bending or straining them. (Note—If CM0 is a worst-case fuel, also test in CM15 for comparison.) Keep the temperature at $55\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$, and replace the fuel weekly. To determine the minimum exposure time before the first weighing, multiply the time required to determine the worst-case fuel for equilibrating the thin samples by the ratio of the thickness of the surrogate sample to that of the thin samples. (See Equation 4.)

Minimum Exposure Time Before Weighing Surrogate: (Eq. 4)

$$= \text{Equilibrium Time for Thin Samples} \times \frac{\text{Thickness of Surrogate}}{\text{Thickness of Thin Sample}}$$

Weighings may then begin on a bi-weekly schedule and the Apparent Percent Weight Increase compared to the value obtained from the thin samples. When equilibrium has been reached, as described as follows, property measurements on the aged test specimens can proceed after the vessel containing the test specimens has been allowed to cool for 24 hours.

5.1.3 **DETERMINATION OF EXPOSURE TIME**—The criterion for equilibrium will be the attainment of the same Apparent Percent Weight Increase in the surrogate samples as was found for the thin samples used to determine the worst-case fuel. When this state appears to have been reached (as determined by the procedures in the Appendix A), one additional exposure period and weighing must be carried out. The length of the additional exposure period should be at least one-tenth of the exposure time that the samples have already undergone. If the subsequent measurements of Apparent Percent Weight Increase agree statistically with the values of both the earlier measurement on this sample set and that from the thin samples, then equilibrium has been reached and exposure may be terminated and testing started. On the other hand, if the value does not agree with those two data sets then exposure must be continued. In this case, the procedure for detecting the attainment of equilibrium in the determination of the worst-case fuel must now be used, except that the time between weighings should be at least two weeks and the data from the latest three time periods must be statistically the same.

Problems will arise for semicrystalline materials to reach the same Apparent Percent Weight Increase, because thicker samples usually have higher crystallinity than thinner samples. Because only the amorphous regions absorb fuels, thicker samples have a lower weight increase than thinner samples used for the initial tests.

Another case may arise in comparing the data for the surrogates with that of the thin samples. The Apparent Percent Weight Increase may not reach the value previously obtained for the thin samples, and may not appear to change further (i.e., has leveled off). Again, in this instance, the same statistical treatment should be used as for the original attainment of equilibrium in the thin films. Compare the data from the last three weighings and terminate the exposure when there is no statistically significant difference, i.e., the F value is less than 3.89 (see Appendix A).

5.2 For Elastomers—Specimens for individual tests are to be aged in the same type of apparatus at $55\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$, and on the same fuel replacement and weighing schedule as previously used to determine the worst-case test fuel. For samples prepared from standard ASTM tensile slabs, there will be no need to follow the attainment of equilibrium, since the necessary time will be known from the worst-case fuel determination. For samples of other configurations, exposure should be continued until the samples reach the same Apparent Percent Weight Increase (based upon original weight) as that found at equilibrium in the samples used to determine the worst-case fuel. The same statistical methods as those used earlier to determine the equilibrium point should be used to compare the Apparent Percent Weight Increases of these types of samples.

6. Individual Tests For Properties Of Polymers Exposed To Methanol-Gasoline Fuel Mixtures—This section describes some commonly used tests which may be effective in determining property changes after exposure to methanol fuels. These tests are based on ASTM tests methods with some modifications for handling saturated specimens. There are tests for other physical properties which may be used, although many require the procedures to be carried out in a dry-out condition.

A NOTE ABOUT SAFETY—Although the preconditioning of the test specimens can be carried out in a fume hood, the determination of the properties of the swollen polymers requires equipment that is not normally fitted with ventilation. Care must be taken to follow proper OSHA procedures for limiting exposure to both toluene and methanol, each of which at this time have permissible exposure limits of 200 ppm.

6.1 For Plastics

6.1.1 CHANGES IN WEIGHT, DIMENSIONS, AND APPEARANCE USING ASTM D 543—The samples must be disc-shaped with a diameter of 50.8 mm (2 in) and a thickness of 1.6 mm (0.065 in). Omit section 5 of ASTM D 543 because the aging solutions are called out in Table 1 of this document. The time and temperature of exposure are also specified in this document. For changes in dimensions, samples must be taken from the fuel and measured within 30 seconds, while wet. Changes in weight must be determined using a closed weighing bottle. The samples are to be blotted and placed in a tared weighing bottle within 10 seconds, to minimize any weight loss due to evaporation.

6.1.2 TENSILE STRENGTH AND ELONGATION, USING ASTM D 638—Samples must conform to Type I specimens. Omit 7.1 from ASTM D 638, "conditioning" of the samples, since testing must be completed within 5 minutes of removal from the cooled fuel to minimize the effects of dryout. Determination of strength is to be based upon the original thickness before fuel exposure. To reduce aging time, the thickness should be $1.6\text{ mm} \pm 0.02\text{ mm}$ ($0.065\text{ in} \pm 0.01\text{ in}$). The tensile and elongation results from the aged and unaged samples must be reported along with the test speed using the rate determined from 9.2 of ASTM D 638.

6.1.3 FLEX MODULUS AND FLEX STRENGTH, USING ASTM D 790—Flexural properties will be tested using the 3-point loading procedure, Method I, Procedure A. The sample thickness must be 1.6 mm (0.0625 in) per 6.2.1. Omit 8.1 of ASTM D 790, "conditioning of the samples", since testing must be completed within 5 minutes of removal from the cooled fuel to minimize the effects of dryout. The crosshead speed must be calculated per 9.1.3 of ASTM D 790. Flex Modulus test results must be reported as 1% secant modulus. Flex strength must be calculated using equation 3 of ASTM D 790, 1.5. Run the procedure in ASTM D 790, 11.6 only if 11.55 does not produce a break in the material. Test results from both aged and unaged samples must be reported.

6.1.4 CHEMICAL ATTACK—The thin samples to be analyzed for evidence of chemical attack should be exposed to the worst-case fuel for at least the same length of time as that necessary for the thicker flex or tensile test specimens to reach equilibrium. Gel permeation chromatography (GPC) procedures will vary for each thermoplastic being tested. Where GPC is not applicable, other methods specified in 4.2 can be used. Test results should be reported as a ratio of the Peak Molecular Weight of the material preconditioned in methanol fuel to the Peak Molecular Weight of the unconditioned material. The time of the preconditioning period in the methanol fuel must also be included in the report.

6.1.5 PERMEABILITY—The complexity of the processes that are involved is deemed to be so great that there is no current test that can be readily adapted for our purposes. Due to the difference between the compositions of real-world methanol/gasoline fuels and the test fluids based on ASTM fuel C chosen for standards, it is impossible to gauge the relative permeability resistance of differing materials with any degree of certainty. SAE J1737, Permeation Test Procedure, is currently under development to address this need.

6.2 For Elastomers

6.2.1 TENSILE STRENGTH, MODULUS, ELONGATION, USING ASTM D 412 TENSILE TEST—Samples must be cooled to room temperature for at least 0.5 hour in fuel of the same composition as the aging medium. Testing must be accomplished within 3 minutes of removal from the fuel. Total elapsed time between the end of aging and completion of testing should not exceed 1.5 hours.

6.2.2 TEAR STRENGTH, USING ASTM D 624 TEAR TEST—Samples must be cooled to room temperature for 0.5 to 1 hour in fuel of the same composition as the aging medium. Testing must be accomplished within 3 minutes of removal from the fuel.

6.2.3 HARDNESS, USING ASTM D 2240 SHORE TEST—Samples must be cooled to room temperature for 0.5 to 1 hour in fuel of the same composition as the aging medium. Testing must be accomplished within 1 minute of removal from the fuel.

6.2.4 FABRIC ADHESION, USING ASTM D 413 PEEL TEST—Samples must be cooled to room temperature for 0.5 to 1 hour in fuel of the same composition as the aging medium. Testing must be accomplished within 3 minutes of removal from the fuel.

6.2.5 CONDUCTIVITY, USING ASTM D 991 VOLUME RESISTIVITY TEST—Due to the volatility of the fuels, if the conductivity of elastomers exposed to methanol fuels is to be determined, the sample conditioning procedures in Section 7 of ASTM D 991, must be eliminated. Instead, samples must be cooled for 0.5 to 1 hour in fuel of the same composition as the aging medium, patted dry, and tested immediately.

6.2.6 METAL ADHESION, USING ASTM D 429, METHOD A, BUTTON—Due to the volatility of the fuels, if the adhesion of elastomers exposed to methanol fuels is to be determined, samples must be cooled for 0.5 to 1 hour in fuel of the same composition as the aging medium and tested within 3 minutes of removal from the cool fuel.

6.2.7 LOW-TEMPERATURE FLEXIBILITY USING ASTM D 1329, TEMPERATURE RETRACTION—In many cases, low-temperature flexibility of elastomers exposed to swelling fluids is of little practical concern since the imbibed fluid usually provides sufficient plasticization, even when all of the original plasticizer has been extracted. In flexible fuel vehicles however, because of the possibility of a part being exposed to fuels that would swell it to different extents, a different protocol should be used to evaluate the low-temperature flexibility of an elastomer. Exposure to the fuel composition which produces the highest swelling will result in the most rapid replacement of plasticizer. If the elastomer is then exposed to a fuel to which it is more resistant, the swell is lowered, the plasticization by the fuel is decreased, and the low-temperature flexibility is reduced. To determine the effect of exposure to fuels of various methanol compositions, it is suggested that sequential fuel exposure is necessary.

- a. Expose the pre-cut elastomer samples to the worst-case test fuel at 55 °C. Replace with fresh fuel every 24 hours for the first 3 days and then every 3 days thereafter, until equilibrium has been established. The process need not be monitored since the time required for equilibrium in the test fuel was established during the determination of the worst-case fuel.
- b. Subject the samples to the same procedure with the lowest swell fuel.
- c. Conduct the desired low-temperature test on the wet samples using the lowest swell fuel as the cooling medium.

The results reported should identify the high-swelling fuel used to extract plasticizer as well as the low-swelling fuel used as the cooling medium in the test.

- 6.2.8 ASTM D 1053—Another commonly used test for low-temperature flexibility. However, as written, the dependence of the reported response on the geometry of the sample makes it unsuitable for swollen samples. Besides the conditioning procedure, the modifications to the test deal with the treatment of the individual data points. Samples are to be exposed sequentially to the worst-case fuel followed by the lowest swelling fuel, as specified previously. After conducting the test and recording the data, construct a twist versus temperature curve according to ASTM D 1053, 13.1. Report, as the result of the test, the temperature at which the extension of the baseline meets the downward extension of the rising straight portion of the curve. Also include the identity of the two test fuels used to precondition the samples.
- 6.2.9 CHEMICAL AGING—The complexity of the processes that are involved is deemed to be so great that there is no current test that can be adapted for our purposes.
- 6.2.10 FUEL CONTAMINATION—Materials leached out of elastomers by worst-case fuels can have adverse effects on other components in the fuel system or engine, when the leached out materials are transported with the fuel during vehicle operation. The level of contamination caused by leaching will be determined using the spent test fuels used to condition test specimens from Section 5. Measure the conductivity of the conditioning test fuel using ASTM D 2276 and/or ASTM D 381.

PREPARED BY THE SAE FUEL LINES AND FITTINGS COMMITTEE

APPENDIX A

DETERMINATION OF EQUILIBRIUM

Preface—In determining the effects of various fluids on the properties of polymers, one is always confronted by the difficulty in deciding when to halt the exposure. Ideally, measurements of properties should be taken only after equilibrium has been established. This requires the ability to determine that one set of data is statistically the same as another set. The general principles which can be used to determine that condition are as follows.

A.1 Equilibrium As Determined By Constant Weight

A.1.1 Equilibrium Fuel Exposure—Each period, weigh n samples, being careful to remove excess surface liquid and use a covered weighing bottle. For each period, determine the average of the **Apparent Percent Weight Increase** (%W), and the variance (VAR). (See Equation A1.)

$$\text{Apparent Percent Weight Increase} = \% W = \frac{\text{Swollen weight} - \text{Original weight}}{\text{Original weight}} \times 100 \quad (\text{Eq. A1})$$

$$\text{avg} = \frac{\sum \%W}{n} \quad \text{and} \quad \text{VARIANCE} = \frac{\sum (\%W - \text{avg})^2}{n - 1}$$

Compare the data from two or more periods (p) to see if they are the same, i.e., there has been no change and equilibrium has been established. This is done by determining the F value, which is the ratio of the variance of the averages [VAR(avg)] to the average of all the variances [AVG(var)], multiplied by the number of samples in a set. (See Equations A2 and A3.)

$$\text{Var}(\text{avg}) = \frac{\sum (\text{avg} - \text{AVG})^2}{(p - 1)} \quad (\text{Eq. A2})$$

where:

$$\text{AVG} = \frac{\sum \text{avg}}{p} \quad \text{and}$$

p = the number of periods

$$\text{AVG}(\text{var}) = \frac{\sum \text{VARIANCE}}{p} = \frac{\sum \text{Var}_1 + \text{Var}_2 + \text{Var}_i}{p} \quad (\text{Eq. A3})$$

Then calculate the F value: (See Equation A4.)

$$F = \frac{n \text{Var}(\text{avg})}{\text{AVG}(\text{var})} \quad (\text{Eq. A4})$$

If the ratio is less than that indicated in Table A1 for the number of samples and the number of periods being compared, there is no significant difference among the periods. One must be aware, however, that under this criterion the less precise the operator, and/or, the less controlled the exposure conditions, (i.e., the greater the variance), then the less is the ability to distinguish significant differences, and equilibrium will appear to have been reached. Therefore, comparisons can be made only if the coefficient of variation for a period is less than 0.015. The coefficient of variation is equal to the standard deviation for a period, divided by the average for the period. (See Equation A5.)

$$\text{STD DEVIATION} = \sqrt{\text{VARIANCE}} \quad \text{Coefficient of Variance} = \frac{\sqrt{\text{VARIANCE}}}{\text{avg}} \quad (\text{Eq. A5})$$

TABLE A1—F VALUE

No. Of Data Sets Or Periods	Number Of Samples (n) 3	Number Of Samples (n) 4	Number Of Samples (n) 5	Number Of Samples (n) 6
2	7.71	5.99	5.32	4.96
3	5.14	4.26	3.89	3.68
4	4.07	3.49	3.24	3.10
5	3.48	3.06	2.87	2.76

A.1.2 Equilibrium Drying to Constant Weight—Exactly the same principles are involved in determining when the samples are completely dry as when they are at equilibrium with the fuel. The only difference is the time period between weighings. This can be reduced to two days instead of one week. The same calculations and F value are to be used.

A.2 Equilibrium As Determined By Comparison Of Two Data Sets—To determine if the **Apparent Percent Weight Increase** in samples from two sources are the same (e.g., the thin samples used to determine worst-case fuel and the thicker surrogate samples used to determine the attainment of equilibrium for the physical property test specimens), divide the variance of the averages for each data set by the average of the variances for both sets and multiply by the number of samples. In other words, compare their F values. (See Equation A6.)

$$F = \frac{n\text{VAR}(\text{avg})}{\text{AVG}(\text{var})} \quad (\text{Eq. A6})$$

As shown in Table A1, for the 2 data sets, the value of F for 5 samples should be less than 5.32. If it is, then the difference in the data from the two sources is statistically insignificant and the two sample sets are at the same state of swelling. After the required additional exposure period, include that new data in the comparison, making three data sets. Now, if the F value is equal to or less than 3.89, the test specimens may be considered to be at equilibrium and the physical property determinations may be carried out.

A.3 Typical Calculations

A.3.1 Determination of Equilibrium by Constant Weight—The criterion used to determine when to stop a procedure, such as; exposure to a fluid or vacuum drying, is: the ratio of the variance of the averages for the last three periods, to the average of all the variances, times the number of samples in a set must be less than the appropriate F value. (See Table A2 - Example and Equation A7.)

TABLE A2—EXAMPLE—TYPICAL DATA

Sample Number	% Weight Increase After Period Number 1	% Weight Increase After Period Number 2	% Weight Increase After Period Number 3	% Weight Increase After Period Number 4	% Weight Increase After Period Number 5	% Weight Increase After Period Number i - 2	% Weight Increase After Period Number i - 1	% Weight Increase After Period Number i
1	%W							
2	%W							
3	%W							
4	%W							
5	%W							
AVERAGE	avg ₁	avg ₂	avg ₃	avg ₄	avg ₅	avg _{i-2}	avg _{i-1}	avg _i
VARIANCE	var ₁	var ₂	var ₃	var ₄	var ₅	var _{i-2}	var _{i-1}	var _i

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$$\text{Apparent Percent Weight Increase} = \% W = \frac{\text{Swollen weight} - \text{Original weight}}{\text{Original weight}} \times 100 \quad (\text{Eq. A7})$$

Calculate all the averages and variances for each weekly weighing (or each 2 days, for vacuum oven drying). (See Equation A8.)

$$\text{avg}_i = \frac{\sum \%W_i}{n}, \quad \text{and} \quad \text{var}_i = \frac{\sum (\%W_i - \text{avg}_i)^2}{n - 1} \quad (\text{Eq. A8})$$

To compare the last three periods, calculate their overall average value. (See Equation A9.)

$$\text{AVG} = \frac{\text{avg}_i + \text{avg}_{i-1} + \text{avg}_{i-2}}{3} \quad (\text{Eq. A9})$$

Calculate the variance of the individual values of the averages. (See Equation A10.)

$$\text{Var}(\text{avg}) = \frac{(\text{avg}_i - \text{AVG})^2 + (\text{avg}_{i-1} - \text{AVG})^2 + (\text{avg}_{i-2} - \text{AVG})^2}{2} \quad (\text{Eq. A10})$$

Calculate the average of all the variances. (See Equation A11.)

$$\text{AVG}(\text{var}) = \frac{\sum \text{Var}_i + \text{Var}_2 + \dots + \text{Var}_i}{p} \quad (\text{Eq. A11})$$

where:

p is the number of periods.

NOTE—The data from the last four, five, six, or more periods may be used for determining the Avg (var), as long as the coefficient of variation for each period meets the appropriate criterion.

To calculate the F value, divide the Var(avg) by the AVG(var), and multiply by the number of samples, n, in a data set. (See Equation A12.)

$$\frac{\text{VAR}(\text{avg}) n}{\text{AVG}(\text{var})} \leq F \quad (\text{Eq. A12})$$

If the result is less than the appropriate F value in Table A1 which, in our case of 5 (five) samples, 3.89 is less than 5.32, then equilibrium has been established.

A.3.2 Equilibrium as Determined by Comparison of Two Data Sets—To decide when to stop conditioning physical property test specimens, compare the **Apparent Percent Weight Increase** of the surrogate samples with that of the thin samples used to determine the worst-case fuel. (See Table A3.)

TABLE A3—TYPICAL DATA

Sample Number	Apparent % Weight Increase Thin Sample	Apparent % Weight Increase Surrogate Sample Week 1-2	Apparent % Weight Increase Surrogate Sample Week 1-1	Apparent % Weight Increase Surrogate Sample Week 1
1				
2				
3				
4				
5				
AVERAGE	Avg _t			Avg _s
VARIANCE	Var _t			Var _s