



400 Commonwealth Drive ■ Warrendale, PA 15096-0001 U.S.A.

**RECOMMENDED METHODS FOR
DETERMINING PHYSICAL
PROPERTIES OF POLYMERIC
MATERIALS EXPOSED TO
GASOLINE/METHANOL FUEL
MIXTURES**

An SAE Cooperative Research Report

October 1993

CRP-8



No part of this publication may be reproduced in any form, in an electronic retrieval system or otherwise, without the prior written permission of the publisher.

ISBN - 1-56091-460-2

CRP-8

Copyright© 1993 Society of Automotive Engineers, Inc.

Full document details: SAE CRP-008

**RECOMMENDED METHODS FOR DETERMINING
PHYSICAL PROPERTIES OF POLYMERIC
MATERIALS EXPOSED TO GASOLINE/METHANOL
FUEL MIXTURES**

TABLE OF CONTENTS

Introduction 1

I. Determining Worst Case Fuel 2

II. Conditioning Test Specimens in Worst Case Fuel(s) Prior to Testing 5

III. Individual Tests for Properties of Polymers Exposed to
Methanol-Gasoline Fuel Mixtures 6

Appendix A i

Appendix B vi



RECOMMENDED METHODS FOR DETERMINING PHYSICAL PROPERTIES OF POLYMERIC MATERIALS EXPOSED TO GASOLINE/METHANOL FUEL MIXTURES

In 1989, an Oxygenated Fuels Task Force comprised of Chrysler, Ford, and General Motors automotive engineering executives, operating in accordance with the 1984 Cooperative Research Act, was formed to address the many issues related to the use of oxygenated fuels in automotive applications. Project Group 2, one of four committees formed by the Task Force to address those issues, was charged with reviewing and developing materials test methods and evaluating materials for use in methanol-gasoline fuel blends. To this end, Project Group 2 (see Appendix B) developed and published "Gasoline/Methanol Mixtures for Materials Testing" and "Recommended Methods for Conducting Corrosion Tests in Gasoline/Methanol Fuel Mixtures".

INTRODUCTION

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 methanol content poses new problems. This document seeks to address those concerns by detailing changes to standard tests that make them suitable for that purpose.

TEST PROTOCOL

A problem arises in testing materials for use in vehicles which can run on fuels with methanol concentrations varying from 0% to 85%. 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 I) 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 into 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 and also swelling of the sample periphery may 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 conclusion 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. And finally, the third part details the test methods for evaluating polymeric materials for use in methanol fuels.

I. DETERMINING WORST CASE FUEL

A. Equilibrium Weight Increase

To compare the extent of polymer swelling by the five test fuels, given in Table I, 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.

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. 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 ± 2°C and 50 ± 5% relative humidity for a minimum of 40 hrs according to ASTM D618 Procedure A. For rubber, mark twenty-five ASTM D471 volume change test specimens with a punch, for identification.

Conditioning the samples

Weigh the specimens individually, in grams, to 4 decimal places. Place 6 plastic specimens (only 5 for elastomers) into each of 5 glass vessels furnished with a reflux apparatus, as specified in ASTM D543, 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 samples are weighed. Samples should be separated using stainless steel wire and glass beads according to ASTM D471. Fill each vessel with a different methanol blend test fuel such that all specimens are completely submerged. Fuel formulations are provided in Table I. Allow at least 1 cm of fuel above the plastic samples to compensate for any evaporation. For elastomers, allow at least 3cm fuel above the samples to compensate for swelling as well as evaporation. Heat the test fuel uniformly in the vessel to 55° ± 2°C, using a water or sand bath. 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 plasticizers, 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, but for a minimum of 500 hours. Observe safety precautions applicable to the handling of flammable and toxic mixtures (refer to OSHA and local laboratory standards).

Weighing the samples during conditioning.

Except for special situations, applicable to the second part below (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 four 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, five of the 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.

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

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.

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°C to constant weight. Weigh them 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.).

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

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 aging 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.

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