Attachment 3

Test Protocol and Results for the Determination of Permeation Rates from High Density Polyethylene Containers & Barrier Surface Treatment Feasibility Study

Introduction

Air Resources Board staff tested several High Density Polyethylene (HDPE) and metal portable fuel containers (containers) to determine average permeation rates and to assess the effectiveness of several barrier surface treatments. Barrier treatments included sulfonation and two levels of fluorination. Containers were subjected to a variable temperature profile and permeation rates determined gravimetrically. Both CERT fuel and gasoline containing 5% ethanol were used during the test. In all, over 50 portable fuel containers were tested over a period of several months. Containers selected for testing were purchased at retail outlets located throughout California, except for one particular type (Vemco, 1.25 gallon) that at present is only available through mail order. The test containers ranged in size from 1.25 gallons to 6.6 gallons and all initial tests were performed in duplicate.

Test Protocol

All containers selected for testing were preconditioned with fuel for a period of four weeks, minimum. During the preconditioning cycle containers were stored at ambient temperature and pressure in flammable storage cabinets. After a minimum of four weeks preconditioning, the containers were emptied, blown dry with compressed zero air, and immediately refilled with CERT fuel (see Attachment 1). CERT fuel was selected to minimize variation of the permeation results due to variations in fuel properties.

Each container was then sealed using a combination of metal filled epoxy with an overcoat of a special non-permeable two-part epoxy resin (SealPak CS3204 A1/2 Sealant). Where possible, plastic caps and plugs were removed from the containers and replaced with metal plugs and caps. All secondary vents were tapped and plugged with 1/8" brass fittings and coated with sealant.

After allowing sufficient time for the curing of all sealant, the containers were tested for leaks. Containers were heated and when positive pressure was observed (container swelling) a hydrocarbon analyzer was used to 'snoop' the seals. Suspect containers were immersed in a water bath while under positive pressure to determine leak points. All leak points were repaired prior to any gravimetric analysis. During the diurnal tests, all suspect containers were checked with the hydrocarbon analyzer and if necessary, repaired using the same methods.

Weight loss was used as the basis for determining relative permeation rates. Sealed containers were weighed using a high capacity balance (Sartorius Masterpro, 16k-gram capacity, sensitivity ± 0.1 gram) just prior to the start of each diurnal cycle. After each container was individually weighed and the weight recorded, they were placed in a

Sealed Housing for Evaporative Determination (SHED) and exposed to a 1-day / 24-hour/ 1440-minute variable temperature profile (see Attachment 2). Containers were then post weighed after the 24-hour diurnal cycle and the weight loss calculated.

Cumulative weight loss by the containers as a function of time was plotted for all initial 24-hour test cycles. Data were considered acceptable when weight loss became linear with respect to time. All test data include the following information: calculated wetted surface area, average wall thickness, weight lost per test (± 0.1 gram), and initial volume of test fuel. Container identification labels are described in Attachment 3.

In order to determine the durability of the barrier surface treated containers, secondary tests were conducted approximately one month after the initial tests. Staff was concerned that the barrier surface might be susceptible to degradation as the containers continually swelled and paneled during testing. At the conclusion of the initial tests, several containers were randomly selected and stored intact with their original CERT fuel. Prior to the start of the secondary tests the containers were emptied, blown dry with compressed zero air, and immediately refilled with fresh CERT fuel. Adhering to the previously mentioned test protocol, approximately two weeks of diurnal data were collected and compared with initial test data. (**Note:** due to scheduling conflicts one 48 hour and two 72-hour runs were used during this phase of testing with the 1-day variable temperature profile automatically reinitiated every 24-hours).

Staff also had significant interest in any differences an alcohol based oxygenated fuel might exhibit, with respect to average permeation rates, verses an ether based oxygenated fuel. As such, staff obtained a sample of CERT fuel without Methyl Tertiary Butyl Ether (MTBE) and instead blended a similar amount of fuel grade ethanol (see Attachment 4). A sample of the fuel was submitted for analysis and the results show a percent mass of ethanol of 5.27 (see Attachment 5). This fuel was then used in both treated and untreated containers adhering to the previously mentioned test protocol.

Results

The average permeation rate from untreated containers was determined to be 1.57 grams/gallon/day. This rate is based on data averaged from tests of 13 individual containers and represents a total of 188 individual 24-hour diurnal cycles. Container sizes for all tests ranged from 1.25 gallons to 6.6 gallons.

The average permeation rate from initial tests of containers fluorinated at level 5 was determined to be 0.53 grams/gallon/day. This rate increased during secondary tests to 0.69 grams/gallon/day for an overall average rate of 0.61 grams/gallon/day. This final rate is based on data averaged from tests of 12 containers and represents a total of 266 individual 24-hour diurnal cycles.

The average permeation rate from initial tests of containers fluorinated at level 3 was determined to be 0.42 grams/gallon/day. This rate increased during secondary tests to 0.93 grams/gallon/day for an overall average rate of 0.68 grams/gallon/day. This final rate is based on data averaged from tests of 14 containers and represents a total of 262 individual 24-hour diurnal cycles.

The average permeation rate from initial tests of sulfonated containers was determined to be 1.39 grams/gallon/day. This rate is based on data averaged from tests of 11 containers and represents 160 individual 24-hour diurnal cycles. No secondary tests were performed on the sulfonated containers.

The average permeation rate from metal containers was determined to be 0.06 grams/gallon/day. This rate is based on data averaged from 3 containers and represents a total of 48 individual 24-hour diurnal cycles.

The average permeation rate from untreated containers filled with the ethanol based oxygenated fuel was determined to be 2.28 grams/gallon/day. This rate is based on data averaged from tests of 8 containers and represents a total of 100 individual 24-hour diurnal cycles.

The following table best illustrates the permeation test results. Please note that the average untreated container permeation rate is used as a baseline for determining the efficiency of the barrier surface treated and metal containers.

Table 1

Initial Tests		Secondary Tests		Overall	
Container Type	Average Rate (g/gal/day)	Container Type	Average Rate (g/gal/day)	Combined Average (g/gal/day)	Control Efficiency (%)
Untreated	1.57	Untreated	N/A	1.57	0
Fluorinated Level 5*	0.53	Fluorinated Level 5	0.69	0.61	61.2
Fluorinated Level 3	0.42	Fluorinated Level 3	0.93	0.68	57.0
Sulfonated**	1.39	Sulfonated	N/A	1.39	11.4
Metal	0.06	Metal	0.06	0.06	96.2
Ethanol Oxygenate	N/A	Ethanol Oxygenate	2.28	2.28	N/A

* Wedco & Blitz containers may be treated incorrectly, follow up tests scheduled for June ’99.
** All Containers may be treated incorrectly, follow up tests scheduled for June ’99.

It should be noted that not all data points recorded in the attached data sheets were used in determining the various average permeation rates. Several data points were not included in the overall calculations for reasons identified in the field data sheets. These include but are not limited to: balance errors, excessive weight loss due to incompletely cured sealant(s), and mechanical difficulties with the SHED.

Conclusions

The average permeation rate for untreated containers is 1.57 grams/gallon/day based on exposure to a standard variable temperature profile (see Attachment 2). This permeation rate correlates closely with previous tests performed by several of the resin manufacturers.

Staff has serious doubts about the suitability of fluorination as a viable barrier surface treatment. While fluorinated containers initially provide a substantial reduction in permeation rates as compared to the untreated containers, it seems that continued swelling and paneling of the container walls degrades the integrity of the barrier surface treatment. As the data in Table 1 shows, the increase in permeation rates from the initial tests with respect to the secondary tests one month later is greater than 23 % for the level 5 treated containers and greater than 54% for the level 3 treated containers. These data suggest that fluorinated barriers may not provide sufficient longevity to be considered a permanent solution. Changing container geometry to mitigate it's ability to swell and panel may alleviate this particular problem.

Some issues concerning the treatment of the level 5 verses the level 3 containers are obvious when reviewing the data (Wedco & Blitz containers, level 5 verses level 3). It was anticipated that the level 5 treated containers would have a much lower permeation rate than the level 3 containers. However, for several containers this was not the case. Research into this anomaly has determined that the suspect containers may not have been properly treated (the possibility exists that a mechanical error in the treatment equipment may be at fault). The company that performed the barrier surface treatments has agreed to treat another set of the containers in question and staff will perform further testing after the containers have undergone sufficient preconditioning.

Again, looking at the data in Table 1, the sulfonated containers had an average permeation rate almost identical to the untreated containers. Previously documented tests using sulfonated containers suggests that perhaps an error occurred during treatment. Staff contacted the company that treated these containers and learned that due to a communications error, the wrong type of sulfite gas was used during the treatment process. The company has agreed to treat another set of containers and staff will perform further testing after these containers have undergone sufficient preconditioning. Therefore, the test results of the sulfonated containers are deemed inconclusive at this time.

Based on both the initial and follow up tests, metal containers do not permeate as compared to HDPE containers.

Alcohol based oxygenated fuel increases permeation rates of the untreated containers by more than 60%. This could be significant if a change in fuel formulation is required due to the elimination of MTBE.

In conclusion, permeation from HDPE containers contributes significantly to the overall hydrocarbon emissions associated with the use of these products. While permeation emissions from one container may seem insignificant, in the aggregate they contribute significantly to California's Air Quality problems. Additionally, further testing is required to determine the efficacy of existing barrier surface treatment technologies.