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Current EPA and CARB regulations allow a maximum of 2.0 g/test for Hot Soak + Diurnal evaporative emissions. The State of California has adopted LEV II regulations that will decrease the evaporative emissions standard to 0.5 g/test starting in the 2004 model year. These regulations also include a Zero Emission Vehicle or ZEV program. The ZEV program allows car manufacturers to substitute vehicles that meet the SULEV tail pipe emission standards and have zero fuel evaporative emissions for electric vehicles. The increased stringency of these regulations has necessitated significant decreases in hydrocarbon emissions from evaporative emission canisters. For example, canister vent emissions may be at levels of 100-300 mg/test for a vehicle that meets the current regulations. However, canister emission targets should be 50 mg/test and less for LEV II and 10 mg/test and less for zero evaporative emission vehicles. Emissions at this level are not due to a lack of adsorptive capacity in the canister, but rather are due to diffusion of hydrocarbon species. These emissions are often referred to as bleed emissions.

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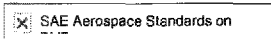
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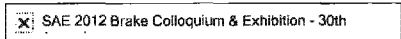
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2001-01-0733

Impact and Control of Canister Bleed Emissions

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ABSTRACT

Current EPA and CARB regulations allow a maximum of 2.0 g/test for Hot Soak + Diurnal evaporative emissions. The State of California has adopted LEV II regulations that will decrease the evaporative emissions standard to 0.5 g/test starting in the 2004 model year. These regulations also include a Zero Emission Vehicle or ZEV program. The ZEV program allows car manufacturers to substitute vehicles that meet the SULEV tail pipe emission standards *and* have zero fuel evaporative emissions for electric vehicles. The increased stringency of these regulations has necessitated significant decreases in hydrocarbon emissions from evaporative emission canisters. For example, canister vent emissions may be at levels of 100-300 mg/test for a vehicle that meets the current regulations. However, canister emission targets should be 50 mg/test and less for LEV II and 10 mg/test and less for zero evaporative emission vehicles. Emissions at this level are not due to a lack of adsorptive capacity in the canister, but rather are due to diffusion of hydrocarbon species. These emissions are often referred to as bleed emissions.

A technique was developed to study the level of bleed emissions specifically from canister vent ports. Canister design and purge volume were shown to have a significant impact on bleed emissions. Further, the incorporation of a small auxiliary chamber in series with the primary canister was shown to decrease bleed emissions significantly.

INTRODUCTION

Activated carbon has been used since the early 1970's to capture gasoline vapors from vehicle fuel vapor systems. The activated carbon is housed in canisters and is required to adsorb gasoline vapors at high efficiency and release them during the purge regeneration cycle. The canisters are used as part of a system to control evaporative emissions.

This paper is concerned with hydrocarbon emissions from evaporative emission canister atmosphere ports specifically during diurnal testing. Diurnal emissions occur while a vehicle is parked and the fuel tank is

heated due to daily temperature changes. Both the California Air Resources Board (CARB) and the Environmental Protection Agency (EPA) have established test standards that measure and control hot soak and diurnal emissions during real-time, two- or three-day procedures. These procedures, adopted for 1995 (CARB) and 1996 (EPA) model year vehicles, have identical standards of 2.0 g/test maximum emissions for the two and three-day tests in addition to the SHED measured emissions from a 1 hour Hot Soak test. The procedures differ somewhat in their temperature profile and test fuel volatility.

Recently, CARB adopted LEV II regulations that will decrease the evaporative emissions standard for all cars and light trucks to as low as 0.5 g/test starting with the 2004 model year. Additionally, the LEV II program calls for 10% of the 2003 model year fleet to be Zero Emissions Vehicles (ZEV or battery electric vehicles). The law allows the car manufacturer to substitute vehicles with very low tailpipe emissions (SULEV) and zero fuel evaporative emissions to satisfy some of the ZEV requirement. The increased stringency of these regulations has necessitated significant decreases in hydrocarbon emissions from evaporative emissions canisters. For example, under the current standard, emissions from carbon canisters could be as high as 0.1 - 0.3 g/test for an in-compliance vehicle. However, canister emissions targets for "near-zero" evaporative emissions vehicles (0.5 g/test standard) should be 50 mg/test and less. Target canister emissions levels for "zero-evap" vehicles (0.0 g/test) are in the 3-10 mg/test range. Emissions at this level are not due to a lack of adsorptive capacity in the canister, but are due to diffusion. These emissions are often referred to as bleed emissions.

Bleed emissions are those emissions from the canister that occur prior to breakthrough. Breakthrough is defined by ASTM D 2652 as "the first appearance in the effluent of an adsorbate of interest under specified conditions." In the automotive carbon application, breakthrough is usually considered to be that point when 2.0 g of hydrocarbon have been emitted from the canister or when the total hydrocarbon concentration in the effluent reaches 5000 ppm.

Canister bleed emissions during diurnal testing are rarely due to carbon bed inefficiencies but are rather due to diffusion. That is, the bleed emissions most likely consist of hydrocarbons that were already adsorbed in the canister prior to the start of the diurnal. Repeated loading/purging of carbon canisters produce a hydrocarbon concentration gradient within the carbon bed (1,2). The adsorbed hydrocarbon concentration will tend to be higher near the fuel tank port of the canister (vapor inlet) and gradually decreases as the vapor flow path approaches and exits the canister atmosphere port (purge inlet). There will exist some concentration of hydrocarbon at the atmosphere port, even after extended

purging. The amount of hydrocarbon remaining after purge is referred to as hydrocarbon heel.

During extended soak periods, the hydrocarbon vapors will tend to diffuse from areas of higher concentration to areas of lower concentration. Thus, the concentration of hydrocarbons in the section of the carbon bed near the atmosphere port will increase with time. During diurnal loading, a mixture of air and gasoline vapor enters the canister through the tank port. Virtually all of the gasoline vapor is adsorbed by the carbon within a specific region of the bed known as the mass transfer or adsorption zone. The adsorption zone will move in the direction of vapor flow with time. On the downstream side of the adsorption zone, a small volume of clean air will move through the remainder of the bed, potentially causing bleed emissions.

Diffusion can be described by Fick's Law, one form of which is:

$$\text{Amount of Diffusion} = dn/dt = - A * D * dC/dx ,$$

Where, n = moles of a species

t = time

A = cross sectional area

D = diffusion coefficient of a species
(temperature dependent)

C = concentration

x = diffusion path length

Although an exhaustive examination of this law is not within the scope of this paper, inspection of it with respect to evaporative emissions canisters yields several characteristics that affect bleed emissions.

The first characteristic that affects bleed emissions is time. Bleed emissions are important in evaporative emissions testing because of the potential for long soak times prior to and during the real-time diurnal. Although important, most of the time elements in the procedure are fixed and cannot be changed.

Another characteristic that affects bleed emissions is the concentration gradient. This can be viewed in two ways. First, the concentration gradient from one portion of the canister to another affects the diffusion rate. This is controlled primarily by the amount of purge used. Second, the hydrocarbon concentration gradient between the hydrocarbons adsorbed in the carbon pores and the hydrocarbons in the gas phase affects the diffusion rate between the phases. Although this is also controlled by the amount of purge used, the pore size distribution of the carbon used will influence the equilibrium. Thus, a well-purged canister filled with a high-capacity, low-heel carbon is desired to reduce bleed emissions.

Two characteristics that can be considered together are the diffusion path length and the cross-sectional area.

Both are elements of canister design. Decreasing the cross-sectional area can be accomplished by simply narrowing the canister bed profile or effectively by placing a plate with restricted open area across the carbon bed. Both of these options will increase the pressure drop, a critical canister parameter particularly important for Onboard Refueling Vapor Recovery and should be considered carefully. Therefore, a canister with an optimized length-to-diameter ratio is desired to reduce bleed emissions.

Two final characteristics that affect bleed emissions are temperature and hydrocarbon species. The diffusion coefficient is temperature-dependent and is unique for a given species. Since the temperatures of the test conditions are fixed, there is little reason to consider their effect. However, the effect of the hydrocarbon species is an important consideration. For like species, the diffusion coefficient will decrease with increasing molecular weight. For example, n-butane will have a higher diffusion coefficient than will n-pentane. Prior to the diurnal test, the canister is preconditioned by loading to either breakthrough or 1.5 times breakthrough with 50% n-butane. Butane is the lightest major component of gasoline vapor (3) and has a diffusion coefficient greater than that of the other major components of gasoline vapor. That is, butane will have a higher diffusion rate compared to "gasoline vapor." Thus, it is quite important to purge as much of the butane loaded during preconditioning as possible.

In this paper, we will examine the effects of soak time, purge volume, canister geometry, and carbon type on bleed emissions.

EXPERIMENTAL METHODS

Bleed emissions were evaluated using three different test procedures. Each test featured the following common elements: an initial canister pre-conditioning, vapor load, purge followed by a time-controlled soak, and emissions measurement during a final canister vapor load simulating a diurnal loading event

GASOLINE VAPOR AND BUTANE CYCLING - Gasoline vapor cycling was performed using automated cycle test equipment that precisely controlled and monitored all testing conditions. Gasoline vapors were generated by bubbling air at a rate of 200 ml/min through 2 liters of 9.0 RVP-certified test gasoline heated to 36°C. Under these conditions, the vapor generation rate was approximately 40 g/hr and the hydrocarbon concentration was approximately 50% by volume. The vapors were sent to the canister until a breakthrough concentration of 5000 ppm was detected using a flame ionization detector (FID). If breakthrough was not detected after 100 minutes of vapor loading, the liquid gasoline was replaced with a fresh 2-liter aliquot. After breakthrough was detected, the canister was purged for a specified

volume, typically 300 bed volumes, using dry air at a rate of 15 liters per minute. The soak time between load and purge events was no more than 5 minutes. The ambient temperature of the equipment, including the canister storage compartment, was maintained at 25°C during all stages of the testing.

Butane vapor cycling was also performed using automated cycle test equipment. Butane, diluted with laboratory air to a concentration of 50% by volume, was delivered to the canister at a rate of 40 g/hr. The breakthrough concentration used was 5000 ppm. After breakthrough was detected, the canister was purged with dry air, typically for 300 bed volumes, at a rate of 15 l/min. The soak time between load and purge events was no more than 5 minutes. The ambient temperature of the equipment, including the butane gas cylinder, was maintained at 25°C during all stages of the testing.

BWC BLEED TEST - The BWC Bleed Test involved measuring emissions from the atmosphere port of the canister using a flame ionization detector while loading the canister with butane. The goal in performing the BWC bleed test was to evaluate carbon bleed performance under controlled conditions.

A 1.0-liter test canister was used for all BWC bleed testing. The properties of the test canister are described elsewhere in the experimental methods. The temperature of the entire system including canister and butane fuel source was controlled at 25°C. Canister preconditioning included three butane adsorb/purge cycles with loading to 5000-ppm breakthrough and 300 bed volumes of purge according to the procedures described above. Following the three conditioning cycles, the canister was soaked for a specified length of time. After the soak, the canister was again loaded with 50% butane vapors to breakthrough and the canister emissions were measured and recorded during the course of the loading using a flame ionization detector.

DIURNAL TESTS - Two separate test procedures were developed for measuring bleed emissions under diurnal temperature conditions. Both of these tests involved measuring emissions directly from the canister vent rather than from the entire vehicle as in a SHED test, or from an entire fuel system, as with a mini-SHED.

The first test, referred to as the compressed diurnal test, was developed for measuring canister bleed emissions during a one-day diurnal using the 11-hour temperature ramp segment of the CARB temperature profile. A 1.0-liter test canister was used in combination with a 60-liter fuel tank and 9.0 R.V.P. fuel in order to load the carbon bed to a near-breakthrough condition within an 11-hour test period. The compressed test introduced the CARB temperature profile as a variable without the time requirements of the two- and three-day diurnal test. However, the results are useful only on a relative basis,

because the canister and tank size combinations were not realistic and the test time was shortened. Also, the vapor generation rates were much higher using 9.0 RVP fuel as compared to using 7.0 RVP fuel.

Pre-conditioning for the compressed diurnal test consisted of six gasoline vapor load / purge cycles with 300 bed volumes of purge and a loading rate of 40 g/hr as described previously. Within 2 hours of the final gasoline vapor purge, the canister was loaded with 50% butane vapors in air at a rate of 40 g/hr until a breakthrough of 5000 ppm was measured by a flame ionization detector. The canister was soaked for 60 minutes before the final purge. The final purge was performed at a rate of 15 liters per minute with dry air for 300 bed volumes. Following the purge, the canister was soaked at 20° C for 24 hours before starting the diurnal test.

A second diurnal test procedure, referred to as the simulated real-time diurnal test, subjected a fuel tank and canister to the entire two-day or three-day CARB diurnal temperature profile. A 60-liter fuel tank was used in combination with commercial automotive canisters, typically with a nominal size of about 2 liters. The fuel used for the simulated real-time diurnal test was a 7.0 RVP Phase II fuel as specified in the CARB test procedures. This test was designed to simulate the diurnal portion of the CARB vehicle emissions test procedure in order to generate quantitative canister emissions data.

Pre-conditioning for the simulated real-time diurnal test included multiple gasoline vapor load / purge cycles as described above. The loading rate for the gasoline cycles was 40 g/hr, and the most typical purge was 400 bed volumes. Following the gasoline cycles, the canister was loaded with 50% butane vapor to 5000 ppm breakthrough in preparation for a two-day diurnal test and was loaded to 1.5 times the nominal butane working capacity in preparation for a three day diurnal test. After the butane load, the canister was allowed to soak for 60 minutes before purging for a specified volume. Typical purge volumes were 400 bed volumes in preparation for the three-day diurnal test and 150 bed volumes for the two-day diurnal test. Following the purge, the canister was soaked at 20 °C for 24 hours before starting the diurnal test.

After the 24-hour soak, for both the compressed and real time diurnal tests, the canister was attached to a commercial 60-liter, steel fuel tank containing 24 liters of certified test fuel, previously equilibrated to 18.3 °C overnight. A 9.0 RVP fuel was used for the compressed diurnal test and a 7.0 RVP fuel was used for the real-time diurnal test. A Tedlar bag was attached to the atmosphere port of the canister as shown in Figure 1 to collect the hydrocarbon emissions. During the 11-hour

temperature ramp from 18.3° C to 40.6° C, the canister weight and emissions were measured several times. During the portion of the diurnal when the temperature decreased, the Tedlar bag was removed in order to allow the system to back purge.

The removed Tedlar bag was filled to a known volume with nitrogen. The hydrocarbon concentration was determined by evacuation of the bag contents into an FID. Once the concentration and volume were determined, the mass of hydrocarbon was calculated and recorded.

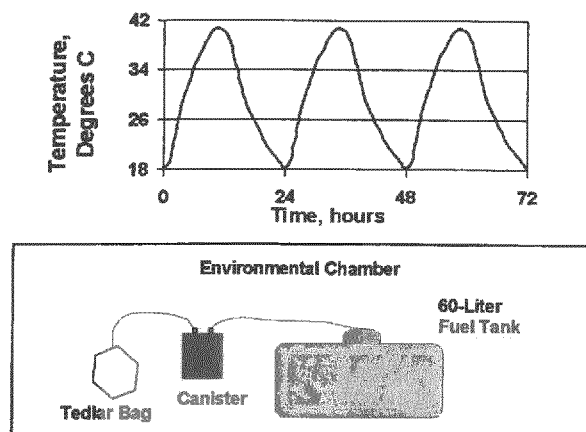


Figure 1. CARB temperature profile and simulated diurnal test setup.

IN-USE CANISTERS - In some cases, in-use evaporative emission canisters were used to measure diurnal bleed emissions. Automotive Testing Laboratories Inc. was contracted for procurement of the canisters. The canisters were obtained from in-use vehicles, with odometer readings ranging from 16,000 km to 53,000 km. The nominal size of the canisters tested was about 2.0 liters. The canisters were filled with wood-based carbon from Westvaco. The carbon had a nominal specified new ASTM butane working capacity (BWC) of 15 g/dl.

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