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ABSTRACT

Recently, the California Air Resources Board (CARB) has proposed a new set of evaporative emissions and "Useful Life" standards, called LEVII EVAP regulations, which are more stringent than those of the enhanced EVAP emissions regulations. If the new regulations are enforced, it will become increasingly important for the carbon canister to reduce Diurnal Breathing Loss (DBL) and to prevent deterioration of the canister. Therefore, careful studies have been made on the techniques to meet these regulations by clarifying the working capacity deterioration mechanism and the phenomenon of DBL in a carbon canister.

It has been found that the deterioration of working capacity would occur if high boiling hydrocarbons, which are difficult to purge, fill up the micropores of the activated carbon, and Useful Life could be estimated more accurately according to the saturated adsorption mass of the activated carbon and the canister purge volume. As a result, it is presumed that a more adaptable, longer Useful Life can be realized by providing a sufficient purge.

It has been also found that the butane diffusion in a carbon canister during vehicle parking which is loaded to the canister during the DBL test, is the main cause of evaporative emissions from the canister. To prevent such diffusion, it is effective to divide the carbon bed into separated segments and insert some "labyrinth" between such carbon beds. Compared with the conventional canister, the improved canister was able to reduce DBL by half. Furthermore it became clear that DBL is reduced to approximately 1/3 when the gasoline fuel vapor is loaded to the canister instead of butane, which is the main cause of DBL. It was also concluded that the evaluation method should be reconsidered to account for real world conditions.

INTRODUCTION

CARB has proposed for 2004, which is when both the enhanced EVAP emissions regulations and On-Board Refueling Vapor Recovery (ORVR) regulations will once be settled, a new set of LEVII regulations including a more stringent set of evaporative emissions and Useful Life standards as compared to those of the enhanced EVAP emissions regulations. In these regulations CARB also has required the evaporative emissions to be restricted to 1/4th of the parameter stated in the 1995 regulations and the Useful Life to be extended from 10 to 15 years.

The sources of evaporative emissions generated in DBL test have already been investigated and it is clarified that a canister is one of the typical sources of the evaporative emissions. To meet the LEV II regulations, it has become more important for the canister to reduce DBL and to extend its useful life span.

The useful life span of the canister depends on that of the activated carbon which adsorbs the hydrocarbons(HC). Therefore, several studies have been made on the deterioration of adsorption performance of the carbon canister withdrawn from the vehicles after long usage and the change in adsorption performance during the adsorption/desorption cycle tests in the laboratory. However, little research analyzing the relation between characteristics of activated carbon and its deterioration phenomenon has been done, and a general method for estimating canister life span has not been developed.

Furthermore the effects on DBL by external factors such as temperature and the length of parking have been clarified, and this information has led to the formulation of the present Federal Test Procedure. Recent studies show the effects of the design factors of canister configuration and purge amount on DBL. However, detailed analysis on the adsorption states of activated carbon in the canister and on the mechanism of DBL have been few.

Therefore, the authors tried to clarify the mechanisms for canister life span and DBL. In addition, the authors demonstrated by a simple model, and tried to make clear a canister design that would comply with the LEVII regulations.

EXPERIMENTAL METHODS

The test equipment used in the experiment is shown in Figure 1. The equipment continuously measures the canister conditions, as recording the adsorption mass in the canister, the breakthrough concentration from the canister, fuel temperature, and fuel tank pressure, and then logs these data onto a computer file.

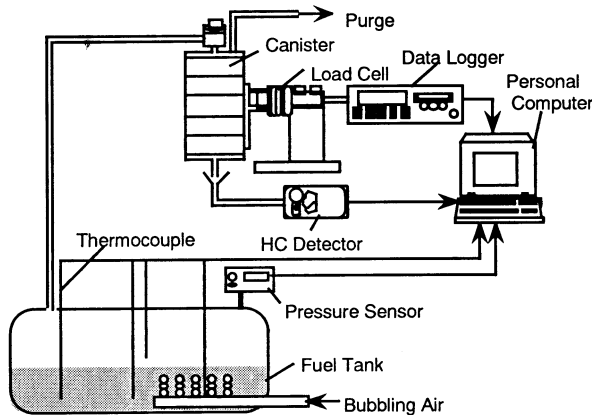


Figure 1. Test Equipment

DETERIORATION ANALYSIS – The adsorption/desorption cycles test procedure is shown in Figure 2. By using a 0.12 liter, small-sized canister enclosed with activated carbon, gasoline temperature was adjusted to 35°C and gasoline fuel vapor was generated by bubbling dry air through gasoline in the fuel tank. 1.0-1.2g/min HC were loaded by breakthrough at a room temperature of 25°C. Then the canister was purged with dry air at 10 liter per minute for 3.6 minutes(300 bed volume). This adsorption/desorption was carried out for 240 cycles. Reid Vapor Pressure_(RVP) of the gasoline used for this test was 62KPa, and it was exchanged with new gasoline every thirty cycles. The gasoline working capacity of the canister was prescribed by the amount of adsorption of each cycle. Residual HC components adsorbed in the activated carbon were extracted by using dichloromethane (CH₂Cl₂) as a solvent, and were then analyzed by gas chromatography.

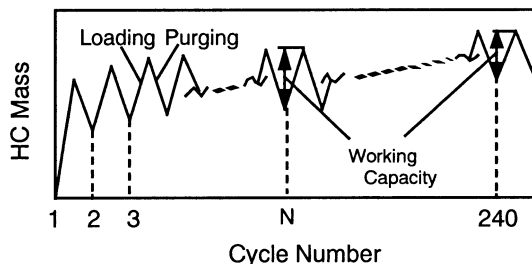


Figure 2. Test Pattern (Adsorption/Desorption Cycles)

DBL ANALYSIS – The diurnal test procedure is shown in Figure 3, and the conditions of each process are as follows.

1. Canister stabilization: The gasoline fuel vapor generated by bubbling dry air through gasoline was loaded by breakthrough to the 2.0 liter canister which enclosed activated carbon. Then the canister was purged with dry air at 20 liters per minute for 30 minutes(300 bed volume). This adsorption/desorption was carried out for 6 cycles at 25°C.
2. Canister loading and purging: Loading was conducted by 2 grams breakthrough using a 50/50 percent by volume mixture of n-butane and nitrogen at a flow rate equal to 40g butane/hour. Then the purging was conducted with dry air at 20 liter per minute for 15 minutes(150 bed volume).
3. Environmental conditions at parking: After soaking for 12 hours at 25°C, the canister went through two 24-hour EPA diurnal temperature cycles.

The canister was divided into 5 layers, as shown in Figure 4, and the activated carbon in each layer was removed. After measuring the adsorption mass of the activated carbon removed from each layer, the components adsorbed in the activated carbon were analyzed by gas chromatography.

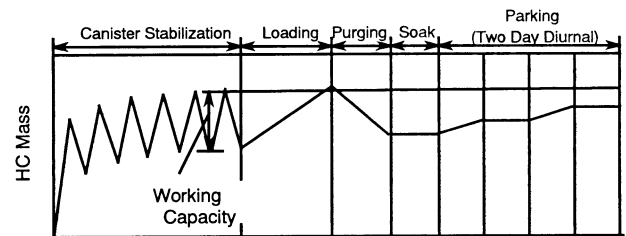


Figure 3. Diurnal Test Procedure

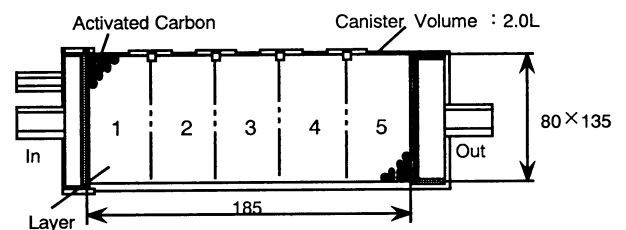


Figure 4. Canister Configuration Used in Diurnal Test

CANISTER PERFORMANCE DETERIORATION MECHANISM

After long usage, canister performance may occasionally show reduced working capacity which could sometimes result in aggravated DBL as well. This is called "deterioration". In this experiment, the canister was repeatedly loaded and purged. The results of compositional analysis of the fuel and its vapor applied in

Figure 6 shows the transitions of the adsorption mass. In the first cycle of adsorption/desorption, approximately 1/3 of the adsorption mass that was unable to desorb remained after purging. The residual HC continued to climb after every adsorption/desorption cycle, but after the 10th cycle, this trend leveled out considerably. The adsorption mass at such time was also found to be stable. After such stable conditions continued for a while, the adsorption mass began to reduce. This is called a "deterioration phase". This entire transition span from the beginning of a stable state to a definite deteriorating state is counted as one span of the "Useful Life".

Figure 7 shows the transitions of mass and components of the residual HC after purging in the canister. The residual HC in the initial aging phase was mostly dominated by C4, C5, C6. Likewise, in the stabilized phase, all such components were replaced with high boiling hydrocarbons of C7 and over for a long time. In the deterioration phase, C4, C5 were not apparent in the residuals, but hydrocarbons of C7 and over continued to increase.

Figure 8 shows the transitions of pore conditions of the activated carbon. In the initial aging phase, micropores over 13 angstroms decreased whereas those of approximately 9 angstroms to 11 angstroms increased. In the stabilized phase, the pores of 9 angstroms to 11 angstroms continued to decrease. The decrease in micropores of larger size was small. In the deterioration phase, micropores of the size equivalent to hydrocarbon molecules in the gasoline fuel vapor began to decrease.

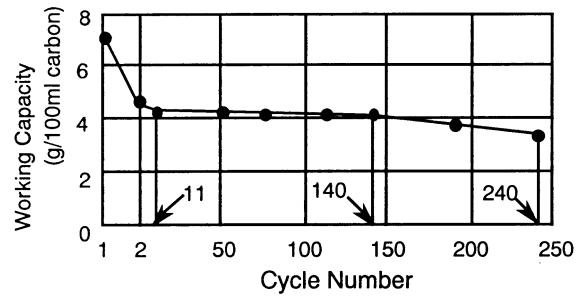


Figure 6. Transition of Working Capacity during Adsorption/Desorption Cycles

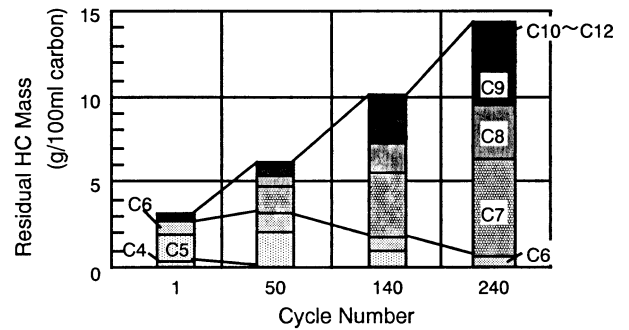


Figure 7. Transition of Mass and Components of Residual HC in Canister

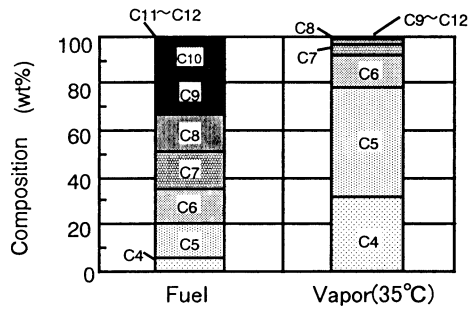


Figure 5. HC Components of Fuel and Vapor Applied in Adsorption Cycle

Thus, based on the above-mentioned results, it can be concluded that deterioration is caused when high boiling hydrocarbons of C7 and over begin to accumulate in, and fill up those pores effective for adsorption, subsequently causing the working capacity to drop. (See Fig.9)

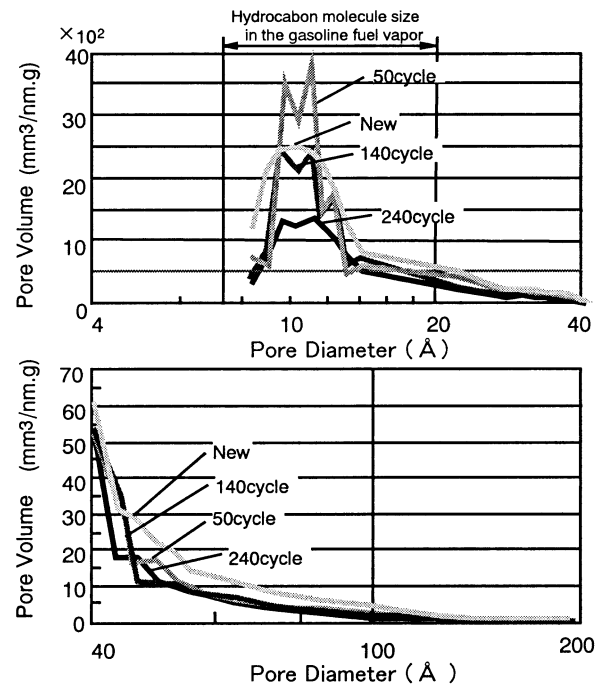


Figure 8. Transition of Pore Conditions in Activated Carbon

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