EPA/AA/CTAB/87-01

Technical Report

Durability of Low Cost Catalysts For Methanol-Fueled Vehicles

By

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NOTICE

U. S. Environmental Protection Agency
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Office of Mobile Sources
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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ANN ARBOR, MICHIGAN 48105

OFFICE OF
AIR AND RADIATION

December 14, 1987

MEMORANDUM

SUBJECT: Exemption From Peer and Administrative Review

FROM: Karl H. Hellman, Chief KH
Control Technology and Applications Branch

TO: Charles L. Gray, Jr., Director
Emission Control Technology Division

The attached report entitled "Durability of Low Cost Catalysts for Methanol-Fueled Vehicles," (EPA-AA-CTAB-87-01) describes catalysts tested at MVEL for efficiency at zero miles and then aged 12,000-14,000 miles in Los Angeles, California as part of a California Energy Commission sponsored program in cooperation with Ford, Toyota, and EPA. This report compares FTP and HWY test results at the 12,000-14,000 mile point with the zero-mileage results.

Since this report is concerned only with the presentation of data and its analysis and does not involve matters of policy or regulations, your concurrence is requested to waive administrative review according to the policy outlined in your directive of April 22, 1982.

Approved: ______________________________ Date: ____________
Charles L. Gray, Jr., Dir., ECTD

Attachment

Background

The objective of the project was to evaluate the efficiency durability of low cost catalysts operated on methanol-fueled vehicles in fleet service. The catalysts were first tested at EPA for efficiency at zero miles.[1]* The catalysts were then operated on cars in Los Angeles, California. After 12,000-14,000 miles were accumulated on the catalysts, they were removed from the cars and shipped back to EPA for further testing. This report compares the tests at the 12,000-14,000 mile point with the zero-mileage results. The California Energy Commission, Engelhard Specialty Chemical Division, Johnson Matthey Catalytic Systems Division, Ford and Toyota cooperated with EPA in this effort.

Description of Catalysts

Two catalyst types were tested in this program. Both catalyst types were monoliths with substrates of 400 cells per inch and a 6-mil wall thickness. Both were composed of two separate biscuits in a single container. Each biscuit has an oval cross section measuring 3.15 by 4.75 inches. The front biscuit is 2.98 inches long and the rear biscuit 4.3 inches long for a total substrate volume of 92.8 cubic inches.

Both catalyst types had loadings of 20 grams of noble metal per cubic foot. One catalyst type contained only palladium (Pd); the other contained platinum (Pt) and palladium in a ratio of 3:2. Using standard CTAB notation, these are denoted Pd(20) and 3Pt:2Pd(20), respectively.

A total of eight catalysts (four of each type) were prepared for this project. Three of the four units of each type were shipped to California in January 1984 without any testing at EPA. One catalyst of each type was zero-mileage tested at EPA before being shipped to California in April 1984.**

Table 1 gives a listing of the catalysts that were installed on the fleet vehicles for mileage accumulation: the catalyst type, formula, catalyst serial number, vehicle identification number (VIN), fleet vehicles, license plate, and odometer reading when the catalyst was removed from the car.

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* Numbers in brackets denote references listed at the end of the report.

** The two catalysts zero-mileage tested at EPA had serial numbers NPN 7-16 (PD(20)) and 9K-8579, EPA 2648 (3Pt:2Pd(20)). The catalysts were installed on the aging vehicles in January 1984 by Bill Stroppe & Son, Long Beach, CA, but the initial odometer readings were not recorded.

Table 1

Sample Numbers of Catalysts Aged on Fleet Vehicles

Sample Number	Catalyst Type	Catalyst Formula	Catalyst Serial No.	Vehicle Ident. No.	License Plate No.	Odometer Reading
1	OX	Pd(20)	NPN 6-15	1FABP137 XDW237350	0868571	13306.3
2	TWC*	Pd(20)	NPN 8-17	1FABP137 XDW237378	0868573	12732.0
3	TWC*	3Pt:2Pd (20)	9K-8583 EPA2650	1FABP137 6DW237359	0868572	14249.2
4	OX	3Pt:2Pd (20)	9K-8580 EPA2649	1FABP137 3DW237349	0868570	12493.8
5	OX	3Pt:2Pd (20)	9K-8584 EPA2651	1FABP137 9DW237405	0868575	11809.4
6	OX	Pd(20)	NPN 3-12	1FABP137 9DW237386	0868574	13247.9

* No thermactor belt.

For each catalyst used as an oxidizing catalysts, the downstream air tube was flush mounted with the exhaust pipe to put air (from the air pump) into the exhaust at least six inches upstream of the catalyst. For each catalyst used as a three-way catalyst, the belt to the air pump was removed, and the downstream air tube was capped.

EPA Test Vehicle

The catalysts were tested at EPA on a 1982 Toyota Cressida described in Table 2. This vehicle was modified by Toyota to operate on methanol fuel. Additional modifications were made to the Cressida's exhaust system to facilitate installation of the catalysts and to allow for the installation of thermocouples before and after the catalyst. Fuel injectors were changed by Toyota in March 1984, April 1984, May 1984, June 1984, July 1984, August 1986, and August 1987.

Zero Mileage Test Procedure

The initial plan called for testing of the catalysts over the following sequence:

1975 Federal Test Procedure (FTP)
Highway Test Procedure (HWY)
10 mph steady state
20 mph steady state
30 mph steady state

After baselining the test car without a catalyst, the sequence was performed three times for each catalyst at each of two exhaust oxygen levels. The higher of the two exhaust oxygen levels was measured at the catalyst inlet using a Sun oxygen analyzer and was obtained at 30 mph steady state. The two oxygen levels were stoichiometry (or near 0 percent) and about 6 percent. The air pump was installed (March 1984) in order to provide the 6 percent oxygen level. By testing at different exhaust oxygen levels we could, therefore, evaluate each catalyst as a three-way catalyst and also as an oxidation catalyst.

As the project proceeded, steady-state test points were deleted in order to speed up the testing. HC, CO, NOx, MPG, methane, and aldehydes were initially measured over each test in the sequence. Measurement for aldehydes was deleted for some of the steady-state tests. The apparatus used to measure HC, CO, NOx, and aldehyde emissions is described in references 2 and 3.

The test fuel used in this program was pure methanol. Five batches of methanol were consumed in this phase of the project; one was analyzed, and described in reference 2. The gasoline used in the cold-start system of the Toyota is Indolene clear (unleaded) and meets the EPA specifications for that fuel (40 CFR 86.307-82).

Table 2

Emission Test Vehicle Description

1982 Toyota Cressida (methanol-fueled)
Vehicle Identification Number: MX62-083780

Engine:	
Type	4-stroke Otto cycle, in-line 6
Bore x Stroke	83.0 x 85.0 mm
Displacement	2759 cc (168 CID)
Compression Ratio	10.0:1
Fuel Metering	Two separate fuel injection systems. (The main fuel injection system uses pure methanol; a separate cold-start fuel injection system uses pure gasoline.
Drive Train:	
Transmission Type	4-speed automatic with overdrive
Axle Ratio	3.73
Chassis:	
Type	4-door sedan
Tires	Dunlop 185/70SR14 steel belted radials
Curb Weight	2,855 pounds
Test weight (ETW)	3,000 pounds
Actual Dynamometer Horsepower	10.3

Zero Mileage Test Results

Tables 3 and 4 present average zero-mile FTP emissions and efficiencies. (More detailed data on these tests is presented in reference 2.) Due to the substantial shift in engine-out emissions following the replacement of the fuel injectors, the data in these tables is limited to those tests after the change in injectors. Tables 5 and 6 present zero-mileage highway emissions and efficiencies* for the two catalysts.

Table 7 contains zero-mile efficiencies for each bag of the FTP.

Mileage Accumulation Vehicles

Mileage accumulation was performed on six model year 1983 methanol-fueled Escorts (Tables 8 and 9). These cars were part of a fleet based at the Los Angeles airport and driven by State of California employees. Initial maintenance on the vehicles was performed under contract by Thrifty Rent-A-Car. After January 1, 1986, the maintenance was performed by Dollar Rent-A-Car.

Mileage accumulation on the Escorts was very uneven. Some selected cars were signed out almost continuously, while some were utilized only on those occasions when a great number of cars were needed. The level of maintenance of these cars apparently dropped off appreciably before January 1986. Appendix A gives a summary of the maintenance performed on each of the Escorts used in this project.

A Ford Motor Company engineer examined 17 of the fleet Escorts in June 1985 and observed a number of maintenance problems with these vehicles. Commonly observed problems were:

1. Carburetors had been adjusted to very rich idle mixtures; and

2. Ignition timing which should have been maintained at 14° BTDC had been retarded to approximately 8°.

Thus, the cars were operated by a number of drivers, on a number of unknown routes, under a number of different driving conditions, often under conditions of maintenance different from those recommended by the manufacturer.

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* Catalyst efficiency is defined as the percent difference between the emissions measured with and without a catalyst.

Table 3

Summary of Average Zero-Mile FTP Emissions at Different Oxygen Levels

Catalyst	HC (g/mi) Oxygen		Ald. (mg/mi) Oxygen		CO (g/mi) Oxygen		NOx (g/mi) Oxygen	
	0%	6+%	0%	6+%	0%	6%	0%	6%
None	.99	--	283.6	--	8.85	--	2.08	--
3Pt:2Pd(20)	.24	.27	37.3	264.6	2.80	0.34	0.51	1.35
Pd(20)	.29	.28	41.0	236.5	1.97	0.72	0.32	1.32

Table 4

Zero-Mile FTP Catalyst Efficiency (percent) at Different Oxygen Levels

Catalyst	HC (g/mi) Oxygen		Ald. (mg/mi) Oxygen		CO (g/mi) Oxygen		NOx (g/mi) Oxygen	
	0%	6+%	0%	6+%	0%	6%	0%	6%
3Pt:2Pd(20)	76	73	87	7	68	96	75	35
Pd(20)	71	72	86	17	78	92	85	36

Table 5

Summary of Average Zero-Mile HWY Emissions at Different Oxygen Levels

Catalyst	HC (g/mi) Oxygen		Ald. (mg/mi) Oxygen		CO (g/mi) Oxygen		NOx (g/mi) Oxygen	
	0%	6+%	0%	6+%	0%	6%	0%	6%
None	.42	--	167.2	--	6.33	--	1.88	--
3Pt:2Pd(20)	.01	.01	5.4	40.4	0.74	0.00	0.26	1.06
Pd(20)	.01	.01	7.3	31.9	0.74	0.02	0.06	1.06

Table 6

Zero-Mile Catalyst Efficiency (percent) Over HWY at Different Oxygen Levels*

Catalyst	HC (g/mi) Oxygen		Ald. (mg/mi) Oxygen		CO (g/mi) Oxygen		NOx (g/mi) Oxygen	
	0%	6+%	0%	6+%	0%	6%	0%	6%
3Pt:2Pd(20)	98	97	97	76	88	99+	86	44
Pd(20)	98	97	96	81	88	99+	97	43

Table 7

Zero-Mile Catalyst Efficiency (percent) Over FTP By Bag at Different Oxygen Levels*

	HC Effic. Run As:		Ald. Effic. Run As:		CO Effic. Run As:		NOx Effic. Run As:	
	TWC	OX	TWC	OX	TWC	OX	TWC	OX
3Pt:2Pd(20):								
Bag 1	49	48	67	8	54	87	65	19
Bag 2	97	94	96	5	73	100	82	50
Bag 3	88	78	90	8	74	98	77	31
Pd(20):								
Bag 1	38	44	65	1	54	77	72	18
Bag 2	97	97	96	39	90	99	92	53
Bag 3	84	81	85	-24	78	93	87	34

* "TWC" denotes a three-way catalyst (0 percent oxygen level), and "OX" denotes an oxidizing catalyst (6+ percent oxygen level).

Table 8

Mileage Accumulation Vehicle Description

1983 Methanol-Fueled Ford Escorts

Engine:	
Type	4-stroke Otto cycle, in-line 4
Bore x Stroke	80.0 x 79.5 mm
Displacement	1.6 liters (98 CID)
Compression Ratio	11.8:1
Fuel Metering	2-barrel carburetor
Drive Train:	
Transmission Type	3-speed automatic transaxle
Chassis:	
Type	4-door station wagon or 4-door sedan
Vehicle Identification Numbers	1FABP1373DW237349 1FABP137XDW237350 1FABP1376DW237359 1FABP137XDW237378 1FABP1379DW237386 1FABP1379DW237405

Table 9

Modifications Made to the Model Year 1983
Gasoline-Fueled Escorts to Convert Them to Methanol-Fueled

Fuel System

Fuel Tank:

Same design as gasoline-fueled Escort, but it is made of stainless steel for corrosion protection.

Fuel Tank Sending Unit:

Same design as standard unit, but it is nickel plated to prevent corrosion and has nickel plated brass float.

Fuel Tank Straps:

Same design as standard model, but the straps are coated with nylon to prevent dissimilar metal corrosion of the stainless steel methanol fuel tank.

Fuel Lines:

Same routing as standard Escort, but the lines are fabricated from stainless steel to prevent corrosion.

Fuel Pump:

Same design as standard unit, but all metallic parts have been made corrosion resistant through nickel plating, and all plastic and rubber parts are made from a material which will withstand methanol.

Carburetor:

The carburetor is stock, modified and recalibrated to meet the higher fuel-flow requirements of the methanol engine. All parts have been nickel plated or manufactured from a material which is compatible with fuel methanol. For example, idle adjusting needles and throttle shafts are made of stainless steel. The float unit is an acetal hollow design and replaces the standard unit.

Carburetor Spacer:

A rectangular spacer plate is installed between the carburetor base and intake manifold. This plate uses a round electrical heating unit which replaces the square heating unit used on the gasoline-fueled engine.

Table 9 (cont'd)

Modifications Made to the Model Year 1983
Gasoline-Fueled Escorts to Convert Them to Methanol-Fueled

Engine

Basic Engine:

The engine that powers the methanol vehicle is the same basic design as the Escort's gasoline-fueled 1.6L high-output (HO) engine.

The compression ratio has been increased from 8.8:1 to 11.8:1. This was accomplished by installing the piston from a European 1.3L Ford engine in the 1.6L block. Each piston has been fitted with a special top compression ring which is barrel faced and hard chromed steel. Piston rings two and three are standard.

A 1984 head gasket that will withstand higher compression pressures is used to replace the standard gasoline head gasket. This head gasket uses a stainless steel fire ring and special backing material.

The base 1.6L camshaft (pink color code) is used in place of the HO camshaft (yellow color code).

Engine Oil:

A unique engine oil containing a special additive must be used with methanol-fueled engines. The recommended oil is marked for methanol engines only.

Ignition

Distributor:

The distributor is a modified, solid-state unit. Its operation is the same as the standard unit; the advance curves have been modified. The major difference is less mechanical advance.

Spark Plugs:

The spark plugs used in the methanol-fueled engine are two heat ranges colder than the spark plugs in the gasoline powered 1.6L engine. This is necessary to prevent engine damage due to preignition.

Tests on Aged Catalysts

Baseline (i.e., without a catalyst) FTP and HWY tests were first run on the Toyota Cressida to compare to the zero-mile vehicle baseline emissions measured in 1984. The Toyota Cressida was then used to test the aged catalyst efficiency of the six catalysts returned from California. FTP and HWY tests were performed for each catalyst with HC, CO, NOx, MPG, and aldehydes measured over each test in the sequence.

The need to replace fuel injectors in the Cressida continued. Table 10 gives a listing of the dates unscheduled, non-routine maintenance was performed on the Toyota Cressida for the period July 1, 1984 to September 30, 1987. New injectors were installed twice during this phase of the project in July 1984 and again in August 1986.

Bag-by-bag FTP and highway baseline results for the period August 8, 1986 to September 23, 1987 are presented in Appendix B. The data for HC in this appendix show that the average baseline FTP emissions for HC for the tests run November 7 to 14, 1986 are essentially double what they were for the period August 8 to October 28, 1986. At this point Toyota replaced the fuel injectors. Baseline HC emissions with this set of injectors were about the same as those for the period August 8 to October 28, 1986, but CO was lower and NOx higher.

Test results for the aged catalysts are presented in Tables 11 and 12. Table 11 gives FTP results for the catalysts; Table 12 gives the HWY results.

Comparison of New and Aged Catalyst Efficiencies

Tables 13 and 14 compare percent conversion efficiency for the new and aged catalysts for the FTP and HWY tests respectively. Because of the shifting of the baseline emission data, percent conversion gives a better indication of the performance of the catalyst than the actual emission levels achieved by the catalyst. The zero-mileage (i.e., new) efficiencies in this table are the same as presented previously.

Emission levels as measured on the Cressida are likely to differ from those in the Escorts for two reasons:

1. Engine-out emissions from the Cressida for HC and CO are low; and

2. The two cars have different engine-out emission and exhaust gas temperature characteristics.

Table 10

Unscheduled Maintenance on the Toyota Cressida*

July 1, 1984 to September 30, 1987

Date	Comments
July 3, 1984	Toyota installed new injectors and a new pulsating damper valve
November 27, 1984	New battery installed
August 4, 1986	New battery installed
August 18, 1986	Car stalled when put into gear when started cold for LA-4
August 19, 1986	Toyota representative observes test and agrees car needs repair
August 29, 1986	Toyota installed new fuel injectors
September 10, 1986	Stalling problem only marginally improved, caution must be exercised to keep car from stalling shortly into the FTP
November 13, 1986	Several stalls at idle
November 14, 1986	Engine seems to be running rough at cruise
August 8, 1987	Toyota replaced fuel filter and fuel injectors.
September 24, 1987	Car stalled 22 times during FTP preparation.
September 28, 1987	Car returned to Toyota.

* Unscheduled maintenance on the Toyota for the period February 1, 1984 to June 30, 1984 was previously reported in Reference 2.

Table 11

Aged Oxidation Catalyst FTP Emissions

Catalyst Formula	Sample No.	Test No.	Date	HC	CO	CO_2	NOx	MPG	HCHO (mg/mi)
				(g/mi)					
3Pt:2Pd(20)	4	864996*	08/19/86	0.35	3.9	387	0.83	10.4	152.8
		864998	09/10/86	0.54	4.8	370	0.89	10.9	124.6
		865000	09/12/86	0.55	4.7	369	0.88	10.9	83.8
3Pt:2Pd(20)	5	870165	10/09/86	0.53	5.5	376	0.97	10.7	94.5
		870167	10/10/86	0.54	5.5	377	0.90	10.6	140.8
Pd(20)	6	870177	10/29/86	0.39	5.5	377	0.73	10.6	366.7
		870451	10/30/86	0.36	5.4	379	0.71	10.6	164.4
		875295*	09/24/87	0.24	0.49	3[illegible]7	2.31	10.6	400.7
Pd(20)	1	879453*	10/31/86	0.51	5.7	387	0.89	10.4	187.8
		870506*	11/04/86	0.47	7.0	397	0.80	10.1	125.4
Pd(20)	1	871339	09/15/87	0.40	.50	383	1.92	10.6	521.0
		871340	09/16/87	0.36	.64	381	2.03	10.7	611.5
		871341	09/17/87	0.41	.73	380	2.10	10.7	632.7

Aged Three-Way Catalyst FTP Emissions

Catalyst Formula	Sample No.	Test No.	Date	HC	CO	CO_2	NOx	MPG	HCHO (mg/mi)
				(g/mi)					
3Pt:2Pd(20)	3	870169	10/16/86	0.32	4.6	380	0.57	10.6	68.9
		870171	10/21/86	0.32	4.7	385	0.57	10.5	53.6
Pd(20)	2	870535	11/05/86	0.31	5.9	391	0.59	10.3	51.5
		870527	11/06/86	0.36	6.9	421	0.54	9.5	53.6
Pd(20)	2	871334	08/25/87	0.33	2.9	388	1.36	10.4	156.7
		871335	09/04/87	0.23	2.8	391	1.59	10.4	105.8
		871336	09/09/87	0.31	2.9	381	1.29	10.6	103.3

* Essentially a void test, not used in data analysis (injectors changed).

Table 12

Aged Oxidation Catalyst HWY Emissions

Catalyst Formula	Sample No.	Test No.	Date	HC (g/mi)	CO (g/mi)	CO_2 (g/mi)	NOx (g/mi)	MPG	HCHO (mg/mi)
3Pt:2Pd(20)	4	864997*	08/10/86	0.02	2.9	334	0.51	12.2	4.3
		864999	09/10/86	0.04	5.1	322	0.38	12.5	4.9
		865001	09/12/86	0.04	5.1	321	0.37	12.5	2.3
3Pt:2Pd(20)	5	870166	10/09/86	0.05	5.8	334	0.42	12.0	3.4
		870168	10/10/86	0.05	5.4	331	0.40	12.1	0.0
Pd(20)	6	870438	10/29/86	0.02	5.2	329	0.34	12.2	4.7
		870452	10/30/86	0.02	5.4	333	0.36	12.1	VOID
Pd(20)	1	870454*	10/31/86	0.04	6.1	341	0.43	11.7	3.5
		870507*	11/04/86	0.03	6.2	322	0.34	12.4	2.3

Aged Three-Way Catalyst HWY Emissions

Catalyst Formula	Sample No.	Test No.	Date	HC (g/mi)	CO (g/mi)	CO_2 (g/mi)	NOx (g/mi)	MPG	HCHO (mg/mi)
3Pt:2Pd(20)	3	870170	10/16/86	0.02	3.1	332	0.27	12.2	0.2
		870172	10/21/86	0.01	2.6	333	0.27	12.2	0.0
Pd(20)	2	870536	11/05/86	0.02	5.2	348	0.26	11.6	1.0
		870528	11/06/86	0.02	5.6	359	0.26	11.2	2.4

* Essentially a void test, but used in data analysis (injectors changed).

Table 13

Comparison of Percent Conversion for New and Aged Catalysts on FTP Test

Catalyst Formula		3Pt:2Pd(20)			Pd(20)		
Aging and Testing Mode		TWC	OX	OX	TWC	OX	OX
Sample Number		3	4	5	2	1	6
Efficiency for:							
HC	Aged	78	57	63	77	70	82
	New	76	73	73	71	72	72
	Difference*	+2	−16	−10	−6	+4	+10
CO	Aged	63	66	57	62	92	73
	New	68	96	96	78	92	92
	Difference	−5	−30	−39	−16	0	−19
NOx	Aged	70	51	50	45	17	58
	New	75	35	35	85	36	36
	Difference	−5	+16	+15	−40	−19	+22
Ald.	Aged	82	67	65	71	N/A	30
	New	87	7	7	86	17	17
	Difference	−5	+60	+58	−15	N/A	+13

Table 14

Comparison of Percent Conversion for New and Aged Catalysts on HWY Test

Catalyst Formula		3Pt:2Pd(20)			Pd(20)		
Aging and Testing Mode		TWC	OX	OX	TWC	OX	OX
Sample Number		3	4	5	2	1	6
Efficiency for:							
HC	Aged	97	90	91	97	95	97
	New	98	97	97	98	97	97
	Difference*	−1	−7	−6	−1	−2	0
CO	Aged	76	60	52	69	65	70
	New	88	99	99	88	99	99
	Difference	−12	−39	−47	−19	−34	−29
NOx	Aged	83	73	74	82	74	76
	New	86	44	44	97	43	43
	Difference	−3	29	30	−15	+31	+23
Ald.	Aged	100	98	99	99	99	98
	New	97	76	76	96	81	81
	Difference	3	22	23	3	18	17

* Difference is aged minus new.

The percent conversion for the aged catalysts were determined by calculating the average emissions for each catalyst on the FTP and HWY tests, and then comparing these values with the average of the baselines immediately before and immediately following the tests for that catalyst. For example, the HWY tests for sample 4 run on September 10 and September 12, 1986 and compared to the "before" tests run August 8 and August 12, 1986 and also to the "after" runs on October 3 and October 8, 1986.

Appendix C shows the effect of the shifts in the baseline data on the percent conversion date of the aged catalysts. For some cases, this effect is relatively small. For example, sample 3 on the FTP test had a percent conversion range for HC of 76 to 80. For many cases, the effect is much larger (e.g., 58 to 71 for CO on sample 3 on the FTP test).

The highest tailpipe formaldehyde emission levels (and lowest percent conversions) occurred on the FTP zero-mileage runs in the oxidation mode (17 and 7 percent compared to TWC mode results of 86 and 87 percent for the Pd(20) and 3Pt:2Pd(20) catalysts, respectively).

When operated as oxidation catalysts, the aged Pd(20) catalysts perform somewhat better than their counterparts with the 3Pt:2Pd(20) formula, particularly on the FTP. The differences between the results for the two formulas are smaller when the catalysts are operated in the TWC mode.

Deterioration Factors

To further compare the catalysts, deterioration factors were calculated for each of them. Table 15 gives DF* for each of the six catalysts for HC, CO, NOx, and HCHO, and compares these values with the actual DF for HC, CO, and NOx for gasoline-powered light-duty vehicles. In calculating DF* several assumptuions were made:

1. Differences between the mileage accumulation in California and the AMA mileage accumulation route were ignored;

2. Maintenance differences were not accounted for;

3. Engine-out emissions were assumed to be constant over 50,000 miles; and

4. An expodential extrapolation of the form:

$$\text{Efficiency}_i = \text{Efficiency}_o \text{ EXP (k miles/1000)}$$

was used to calculate emissions at 4,000 and 50,000 miles. This is the same extrapolation method as was used in reference 4.

5. Because the <u>exact</u> number of miles each catalyst was aged was unavailable, the odometer readings when the catalysts were removed for shipment to Ann Arbor were used as an assumed number of miles aged. This represents a "best case" scenario.

Under these assumptions, the formula for DF* becomes:

$$DF^* = \frac{(1 - EFF_{50})}{(1 - EFF_4)}$$

Where, EFF_{50} and EFF_4 are the extrapolated catalyst efficiencies at 4,000 and 50,000 miles, respectively.

A value of "1" was used in Table 15 for those cases where no deterioration in catalyst efficiency occurred. The data in this table shows relatively good agreement between catalyst types and modes. For example the 3Pt:2Pd catalyst, when operated in Oxcat mode (samples 4 and 5), had DF* values of 2.2 and 2.0 for HC, and 5.3 and 4.6 for CO.

The agreement between DF* and DF for a gasoline car is of order of magnitude quality. Analysis of this data is complicated by three factors:

1. The number of samples is small;

2. Little is known about how, when, and where the fleet vehicles were driven; and

3. The condition of the EPA test vehicle varied greatly despite the relatively small number of miles it was driven during the test period.

<u>Conclusions</u>

After 12,000 to 14,000 miles of fleet use on the road aging:

1. Both catalyst types tested showed evidence of deterioration in their ability to convert CO in both three-way and oxidation modes;

2. There is little evidence of any change in the ability of either catalyst type to convert HC; and

3. When tested in the three-way mode, both catalyst types show degradation in their ability to convert NOx.

Table 15

FTP Deterioration Factors By Catalyst

Sample Number	Formula	Mode	HC	CO	NOx	HCHO
3	3Pt:2PD(20)	TWC	1	1.4	1.6	2.0
4		OX	2.2	5.3	1	1
5		OX	2.0	4.6	1	1
2	Pd(20)	TWC	1	2.5	3.1	3.1
1		OX	1.2	1.0	1.4	NA
6		OX	1.3	4.3	1.1	1
Gasoline car:	DF		1.3	1.2	1.1	NA

References

1. "Low Mileage Catalyst Evaluation With a Methanol-Fueled Rabbit - Second Interim Report," Wagner, R. and L. Landman, EPA/OAR/OMS/ECTD/CTAB/84-3, May 1984.

2. "Interim Report on Durability Testing of Low Cost Catalysts for Methanol-Fueled Vehicles," Wagner, R. and L. Landman, EPA/OAR/OMS/ECTD/CTAB-84-4, August 1984.

3. "Evaluation of Catalysts for Methanol-Fueled Vehicles Using a Volkswagen Rabbit Test Vehicle," Piotrowski, G., J. D. Murrell, and K. Hellman, Proceedings from Methanol: An Alternate Fuel, ASME Joint Conference on the Introduction and Development of Methanol as an Alternate Fuel, pp. 90-95, Columbus, OH, June 1986.

4. "Aftermarket Catalyst Durability Evaluation," Bruetsch, R., J. P. Cheng, and K. Hellman, SAE Paper 861555.

APPENDIX A

Maintenance of Escort/License Plate Number 0868570

VIN 1FABP137XDW237349*

Date	Odometer Reading	Comments
06/24/84**	3144	Lube, oil, filter
08/09/84	3493	Tow in (mechanical)
08/22/84	3632	Air conditioning water leak
01/14/85	6222	Lube, oil, filter, add antifreeze
04/05/85	9233	Lube, oil, filter, add antifreeze
05/22/85	10058	Tow in (no reason given)
09/11/85	12087	12,000-mile service
03/12/86	12493.8	Catalyst removed for shipment to Ann Arbor

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* This vehicle was used to age sample 4, a 3Pt:Pd(20) catalyst, in oxidation mode.

** First entry in maintenance records.

APPENDIX A (cont'd)

Maintenance of Escort/License Plate Number 0868571

VIN 1FABP137XDW237350*

Date	Odometer Reading	Comments
06/27/83	N/A	Accepted for delivery
02/21/84	N/A	Tow in (no reason given)
05/03/84**	3126	Lube and oil change
12/26/84	6579	Lube, oil, filter, checked brakes, wipers
03/11/85	9242	Add antifreeze
04/30/85	9801	Replace fuel filter
07/11/85	9811	Replace fuel pump
08/19/85	10798	Fix flat tire
10/15/85	12345	12,000-mile service
11/08/85	12937	Detail and check body fenders, glass wipers, decals, upholstery
11/26/85	N/A	Detail exterior
03/12/86	13306.3	Catalyst removed for shipment to Ann Arbor

* This vehicle was used to age sample 1, a Pd(20) catalyst, in oxidation mode.

** First entry in maintenance records with mileage recorded.

APPENDIX A (cont'd)

Maintenance of Escort/License Plate Number 0868572

VIN 1FABP137XDW237359*

Date	Odometer Reading	Comments
06/20/83	N/A	Predelivery inspection
06/27/83	03	Accepted for delivery
02/16/84	439	Inspected
05/24/84	2899	Lube, oil, filter
06/12/84	3365	Inspected
09/24/84	4431	Fix driver's door
12/17/84	6018	Lube, oil, filter
04/11/85	9061	Lube, oil, filter, clean air filter
07/27/85	11833	12,000-mile service
08/06/85	11833	Change locks (key lost)
10/11/85	13088	Replace ash tray
03/12/86	14249.2	Catalyst removed for shipment to Ann Arbor

* This vehicle was used to age sample 3, a 3Pt:2Pd(20) catalyst, in three-way mode.

APPENDIX A (cont'd)

Maintenance of Escort/License Plate Number 0868573

VIN 1FABP137XDW237378*

Date	Odometer Reading	Comments
12/14/84**	6762	Add antifreeze
02/02/85	7956	Tow in--out of gas
05/09/85	9645	Lube, oil, filter, change oil filter
05/24/85	10089	Tow in--mechanical
10/01/85	N/A	12,000-mile service
03/12/86	12732.0	Catalyst removed for shipment to Ann Arbor

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* This vehicle was used to age sample 2, a Pd(20) catalyst, in three-way mode.

** First entry in maintenance records with mileage recorded.

APPENDIX A (cont'd)

Maintenance of Escort/License Plate Number 0868574

VIN 1FABP137XDW237386*

Date	Odometer Reading	Comments
06/27/83	4	Accepted for delivery
01/31/84	73	Inspected
05/15/84	3073	Inspected
05/16/84	3079	Lube, oil, filter
05/30/84	9344(?)	4,000-mile service, lube, oil, filter remove front wheels
06/06/84	N/A	Vehicle in accident, but not damaged
12/10/84	6143	Lube, oil, filter, add transmission fluid, antifreeze
05/04/85	9221	Lube, oil, filter, add antifreeze, clean air filter
09/20/85	12009	12,000-mile service
03/12/86	13247.9	Catalyst removed for shipment to Ann Arbor

* This vehicle was used to age sample 6, a Pd(20) catalyst, in oxidation mode.

APPENDIX A (cont'd)

Maintenance of Escort/License Plate Number 0868575

VIN 1FABP1379DW237405*

Date	Odometer Reading	Comments
06/27/83	3	Accepted for delivery
04/03/84	N/A	Vehicle misfueled with gasoline; clean, drain, and flush gasoline from tank
04/18/84	1330	Fix arm rest
05/22/84	1968	Inspect
06/07/84	N/A	Accident--fender, hood, frame damaged
07/03/84	2545	Lube, oil, filter
02/15/85	5823	Lube, oil, filter, clean air filter, adjust brakes
07/18/85	9331	Lube, oil, filter
08/26/85	10171	Needs fuel pump
08/26/85	10171	Replace fuel filter
09/20/85	10172	Replace electric fuel pump
03/12/86	11809.4	Catalyst removed for shipment to Ann Arbor

* This vehicle was used to age sample 5, a 3Pt:2Pd(20) catalyst, in oxidation mode.

APPENDIX B

Toyota Cressida Baseline (No Catalyst)

FTP Results

Date (ODO KM)	Test	Odometer (km)	HC (g/mi)	CO (g/mi)	CO_2 (g/mi)	NOx (g/mi)	HCHO (g/mi)	MPG
8/8/86	864992	5314.7						
	Bag 1		2.00	17.7	419	2.59	395.7	
	Bag 2		1.01	15.4	351	1.23	321.2	
	Bag 3		0.85	13.0	345	1.98	261.4	
(5314.7)	Average		1.17	15.2	363	1.72	312.4	10.5
8/12/86	864994	5376.3						
	Bag 1		2.33	20.0	432	2.66	392.8	
	Bag 2		1.09	17.2	351	1.27	374.0	
	Bag 3		.96	14.8	343	1.94	200.9	
(5376.3)	Average		1.31	17.2	366	1.74	324.5	10.4
10/3/86	865003	5832.7						
	Bag 1		2.42	14.0	415	2.74	435.9	
	Bag 2		1.06	10.4	340	1.41	288.1	
	Bag 3		.97	10.1	341	2.16	241.3	
(5832.7)	Average		1.31	11.0	356	1.89	305.7	10.9
10/8/86	865005	5905.6						
	Bag 1		2.38	14.5	418	2.84	467.5	
	Bag 2		1.08	11.3	344	1.37	273.0	
	Bag 3		.99	10.2	342	2.11	246.8	
(5905.6)	Average		1.32	11.7	358	1.88	303.9	10.8
10/23/86	870173	6273.4						
	Bag 1		2.56	17.2	426	2.73	437.4	
	Bag 2		1.33	13.2	349	1.44	315.2	
	Bag 3		1.20	12.2	346	2.11	500.6	
(6273.4)	Average		1.54	13.7	364	1.89	391.5	10.5
10/28/86	870175	6368.5						
	Bag 1		2.84	18.3	421	2.71	344.0	
	Bag 2		1.42	13.6	346	1.43	362.1	
	Bag 3		1.23	12.3	342	2.09	235.3	
(6368.5)	Average		1.66	14.2	360	1.87	323.0	10.6
11/7/86	870529	6800.3						
	Bag 1		3.31	24.8	419	2.42	338.6	
	Bag 2		2.49	28.2	347	1.20	436.7	
	Bag 3		1.82	22.1	342	1.86	431.9	
(6800.3)	Average		2.46	25.8	360	1.63	415.3	10.1
11/13/86	870531	6862.9						
	Bag 1		3.49	26.7	416	2.38	504.9	
	Bag 2		2.69	28.8	342	1.09	360.1	
	Bag 3		1.81	22.6	336	1.84	338.8	
(6862.9)	Average		2.61	26.7	355	1.56	393.6	10.2

APPENDIX B (cont'd)

Toyota Cressida Baseline (No Catalyst)

FTP Test Results

Date	Test	Odometer (km)	HC (g/mi)	CO (g/mi)	CO_2 (g/mi)	NOx (g/mi)	HCHO (g/mi)	MPG
11/14/86	870533	6924.5						
	Bag 1		3.45	26.2	414	2.29	470.7	
	Bag 2		2.59	28.6	341	1.03	379.7	
	Bag 3		1.77	22.0	340	1.81	331.4	
(6924.5)	Average		2.52	26.3	356	1.51	390.0	10.2
08/18/87	871328							
	Bag 1		2.31	7.69	404	3.22	590.5	
	Bag 2		0.66	7.25	375	3.28	636.1	
	Bag 3		1.08	6.33	347	2.92	392.3	
(7137.0)	Average		1.12	7.69	373	3.17	560.9	10.6
08/19/87	871330							
	Bag 1		2.34	9.99	406	3.16	523.0	
	Bag 2		1.15	7.31	379	1.19	480.4	
	Bag 3		0.97	6.75	348	3.15	380.6	
(7200.7)	Average		1.35	7.71	376	2.48	462.0	10.5
08/20/87	871332							
	Bag 1		2.25	10.15	403	3.34	1798.2	
	Bag 2		1.08	7.33	373	1.81	577.1	
	Bag 3		0.94	6.43	345	2.96	399.4	
(7211.7)	Average		1.28	7.66	372	2.43	778.8	10.6
09/10/87	871337							
	Bag 1		2.37	10.79	398	3.45	219.9	
	Bag 2		1.11	6.97	360	1.83	307.2	
	Bag 3		0.93	6.24	338	2.90	271.4	
(7415.9)	Average		1.31	7.56	362	2.45	279.2	10.9
09/11/87	871338							
	Bag 1		2.24	10.6	397	3.35	236.6	
	Bag 2		0.1	7.4	359	1.81	305.3	
	Bag 3		0.92	6.2	337	2.88	4.4	
	Average		1.29	7.7	361	2.42	209.1	10.9
09/22/87	871342							
	Bag 1		2.17	10.6	394	3.39	604.0	
	Bag 2		1.13	7.6	362	1.81	509.2	
	Bag 3		0.94	6.6	331	2.89	445.6	
(7569.7)	Average		1.29	7.9	360	2.43	511.6	10.9
09/23/87	871343							
	Bag 1		2.24	10.3	394	3.46	445.5	
	Bag 2		1.15	7.9	362	1.74	448.4	
	Bag 3		0.95	6.6	330	2.85	382.2	
(7592.0)	Average		1.32	8.1	360	2.40	430.3	10.9

APPENDIX B (cont'd)

Toyota Cressida Baseline (No Catalyst)

Highway Test Results

Date	Test No.	HC (g/mi)	CO (g/mi)	CO_2 (g/mi)	NOx (g/mi)	MPG	HCHO (mg/mi)
08/08/86	864993	0.31	14.1	318	1.24	12.1	191.6
08/12/86	864995	0.37	15.7	317	1.23	12.0	181.8
10/03/86	865004	0.47	10.4	315	1.54	12.4	181.8
10/08/86	870164	0.51	11.1	316	1.51	12.3	182.3
10/23/86	870174	0.61	12.9	321	1.61	12.0	203.1
10/28/86	870176	0.60	12.8	318	1.54	12.1	210.0
11/7/86	870530	0.88	22.5	322	1.36	11.4	251.0
11/13/86	870532	0.80	22.5	324	1.42	11.4	285.2
11/14/86	870534	0.91	21.7	317	1.28	11.6	270.8
08/18/87	871329	0.62	5.5	292	2.69	13.6	52.7
08/19/87	871331	0.61	5.9	305	2.89	13.0	172.7
08/20/87	871333	0.59	5.8	298	2.81	13.3	N/A

APPENDIX C

Effect of Baseline Changes On Percent Conversion On HWY Test

Catalyst Formula	Sample Number	Test and Aging Mode	Baseline Comparison	Percent Conversion HC	CO	NOx	Ald.
Pd(20)	1	OX	Before*	70	92	17	-141
			After**	70	92	17	-25
Pd(20)	6	OX	Before	77	61	62	25
			After	85	79	54	34
3Pt:2Pd(20)	4	OX	Before	56	71	49	67
			After	59	58	53	66
3Pt:2Pd(20)	5	OX	Before	59	52	50	61
			After	67	61	50	67
Pd(20)	2	TWC	Before	77	63	48	80
			After	77	62	42	50
3Pt:2Pd(20)	3	TWC	Before	76	59	70	80
			After	80	67	70	83

* Compared to baseline tests made before catalyst was tested.

** Compared to baseline tests made after catalyst was tested.

APPENDIX C (cont'd)

Effect of Baseline Changes On Percent Conversion On FTP Test

Catalyst Formula	Sample Number	Test and Aging Mode	Baseline Comparison	Percent Conversion HC	CO	NOx	Ald.
Pd(20)	1	OX	Before*	94	52	75	99
			After**	96	72	72	99
Pd(20)	6	OX	Before	97	59	78	98
			After	98	76	74	98
3Pt:2Pd(20)	4	OX	Before	89	66	70	98
			After	92	53	75	98
3Pt:2Pd(20)	5	OX	Before	90	48	73	99
			After	92	56	74	99
Pd(20)	2	TWC	Before	97	58	84	99
			After	98	76	81	99
3Pt:2Pd(20)	3	TWC	Before	97	74	82	100
			After	98	78	83	100

* Compared to baseline tests made before catalyst was tested.

** Compared to baseline tests made after catalyst was tested.