4. McConnell, R. J., and McDonnell, T. F. Fuel and lubricant effects on oxidizing catalysts. SAE Paper 730597 (1973).
5. Aykan, K., Mannion, W. A., Mooney, J. J., and Hoyer, R. D. Durability of monolithic auto exhaust oxidation catalysts in the absence of poisons. SAE Paper 730592 (1973).
6. Hetrick, S. S., Hills, F. J. Fuel lead and sulfur effects on aging of exhaust emission control catalyst. SAE Paper 730596 (1973).
7. Giacomazzi, R. A., and Homfeld, M. F. The effect of lead, sulfur, and phosphorus on the deterioration of two oxidixing bead-type catalysts. SAE Paper 730595 (1973).
8. Environmental Protection Agency. Regulation of fuels and fuel additives. Federal Register, 38 (No. 6, Part III): 1257 (January 10, 1973).
9. Sorensen, L. L. C., and Nobe, K. Effect of lead on oxidation activity of copper oxide–alumina catalyst. Environ. Sci. Technol. 6: 239 (1972).
10. Coordinating Research Council. 1971 Octane number requirement survey. Report No. 448 (November 1971).
11. Coordinating Research Council. Influence of leaded and unleaded fuels on octane requirement increase in 1971 model cars (phase I: 1970–71 CRC road testing program). Report No. 451 (September 1972).
12. Pierson, W. R., Hammerle, R. H., and Kummer, J. T. Sulfuric acid aerosol emissions from catalyst-equipped engines. SAE Paper 740287 (1974).
13. Beltzer, M., Campion, R. J., and Petersen, W. L. Measurement of vehicle particulate emissions. SAE Paper 740286 (1974).
14. Kerley, R. V., and Felt, A. E. Gasoline fuel. U.S. Pat. 3,038,792 (June 12, 1962).
15. Cordera, F. J., Foster, H. J., Henderson, B. M., and Woodruff, R. L. TEL scavengers in fuel affect engine performance and durability. SAE Paper 877A (1964).

mometer endurance results. The solid line shows the catalytic activity for hydrocarbon oxidation when a 1975-type "unleaded" fuel, containing 0.05 g lead/gal is used. This shows a slow deterioration in catalyst activity which is typical of prototype 1975 automotive units. It is the average for five catalyst samples; best expressed by the expotential equation: (standard deviation $\sigma =$ 2.97).

$$Y = 67.86 + 15.16\, e^{-x/100} \qquad (1)$$

A test run of 300 hr (cyclic test, alternating between idle and moderately heavy engine load) is equivalent to about 25,000 miles of vehicle operation.

The dotted line shows the catalyst activity loss, using a fuel containing 1.5 g lead/gal, with no scavenger. The small loss in activity is comparable to that with "unleaded" fuel. The equation for lead–no-scavenger fuel is given in eq. (2).

$$Y = 67.80 + 16.92\, e^{-x/100} \qquad (2)$$

with $\sigma = 2.40$. The data indicate that the two fuels produce equivalent catalyst performance, and that the individual points with lead-no-scavenger fuel show comparable variance.

As yet, we have run no extended mileage car tests with a leaded fuel containing no scavenger.

The use of commercially leaded fuels is attractive for several reasons. The elimination of lead has several adverse supply effects (*10,11*): (a) less efficient conversion of petroleum to gasoline with an adequate octane rating; (b) a progressive increase, with extended mileage, in octane need for cars running on unleaded fuel; (c) loss of the broad availability of fuel for 1975 vehicles because of the restricted availability of unleaded fuel. The continued use of leaded fuel would improve the gasoline supply and simplify the problem of the automobile owner in finding fuel for his 1975 catalyst-equipped car.

There is some concern that the wide use of catalysts to minimize vehicle emissions will increase the formation and discharge of SO_3 (sulfate) to the atmosphere. Evidence has been cited that a catalyst increases the sulfate emission (*12,13*).

We find that both catalytic and noncatalytic vehicles emit some SO_3 when running on unleaded fuel. Leaded fuel, however, reduces the emissions of SO_3 on noncatalyst cars. For example, vehicles equipped with either catalyst or noncatalyst systems emit as SO_3 an average of 14.7% of the sulfur present in the fuel when running extended mileages on unleaded fuel. However, similar noncatalyst vehicles running on leaded fuel emit, on the average, only 6% of the sulfur as SO_3.

The analysis of exhaust deposits from both noncatalyst and catalyst vehicles suggests that a portion of the lead forms inert lead sulfate with exhaust SO_3. The lead sulfate is principally retained in the exhaust system, as are most lead compounds. This result suggests that the broad present use of leaded fuel is actually minimizing sulfate emission from present vehicles.

Those conversant with the function of the scavenger in leaded fuel (*14,15*) suggest that its elimination would produce some problems of spark plug fouling and engine exhaust valve durability. The ethylene dibromide part of the scavenger mix is actually the most effective for preventing these problems. However, the use of ethylene dichloride only would involve appropriate and more costly metallurgical changes. These modifications may make it possible to use a single, leaded fuel for both catalyst and noncatalyst vehicles. Much further engineering and vehicle testing is necessary.

REFERENCES

1. Weaver, E. E. Effects of tetraethyl lead on catalyst life and efficiency in customer type vehicle operation. SAE Paper 690016, p. 128 (1969).
2. Yolles, R. S., Wise, H., and Berriman, L. P. Study of catalytic control of exhaust emissions for Otto cycle engines, PB193533. Stanford Research Institute Report prepared for NAPCA, HEW, Contract No. CPA 22-69-115 (1970).
3. Neal, A. H., Wigg, E. E., and Holt, E. L. Fuel effects on oxidation catalysts and catalyst-equipped vehicles. SAE Paper 730593 (1973).

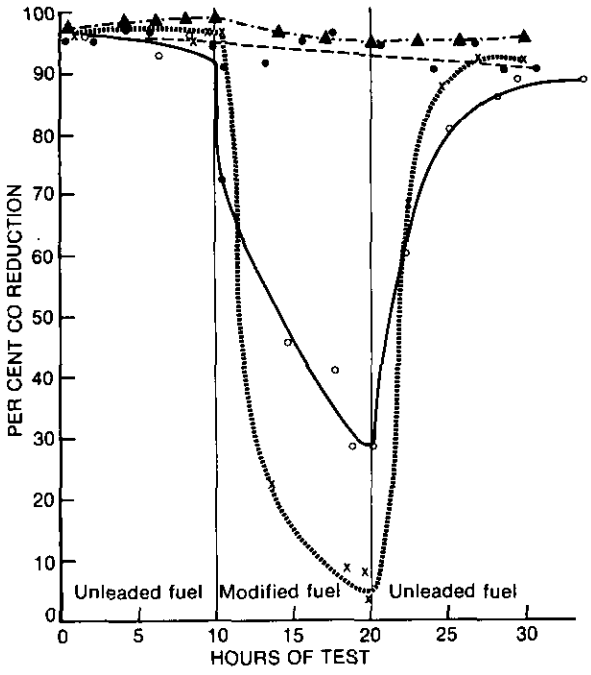

FIGURE 1. Multicylinder engine dynamometer studies of the effects of various modified fuels on the ability of noble metal catalysts to remove carbon monoxide emissions. The modified fuels contain: (—○) 3 g Pb/gal with motor mix scavengers; (--●) 3 g Pb/gal without scavengers; (--×) no lead, but containing ethylene dichloride and ethylene dibromide in the amount normally used with 3 g Pb/gal; (•-▲) 2 g Pb/gal with 1.0 theory ethylene dichloride.

Scavengers are normally added with the tetraethyllead during the production of commercial leaded fuel. This scavenger typically consists of sufficient ethylene dichloride to form lead chloride with the lead present (1.0 theory), plus half as much additional ethylene dibromide (0.5 theory). This combination of tetraethyllead and scavengers is termed "motor mix". These organic halides are soluble in the gasoline and form volatile lead halides during engine combustion. These volatile halides carry the lead out of the combustion chamber, to minimize the accumulation of lead on spark plugs, exhaust valves, and combustion chamber walls.

When fuel containing no lead, but only the mixed scavenger is burned, the catalyst shows an even more severe inactivation (Fig. 1). Again, the recovery of catalyst activity on pure gasoline, (no lead, no scavenger) compared with use of a fuel containing only scavengers, is prompt and nearly complete.

When leaded fuel is used, but with no scavenger, there is only a small loss in activity (Fig. 1). Similarly, a leaded fuel containing only the ethylene dichloride portion of the scavenger again exhibits little loss in activity. A small permanent loss is encountered with both fuels.

Through a series of studies on synthetic gases, and on single cylinder and multicylinder engine dynamometer measurements, we have identified the ethylene dibromide part of the scavenger as the component which inactivates platinum–palladium oxidation catalysts. The use of either ethylene dichloride alone or no scavenger in leaded fuel results in only a small catalyst inactivation. This effect is similar for both carbon monoxide and hydrocarbon oxidation by the catalyst.

Figure 2 presents more extended dyna-

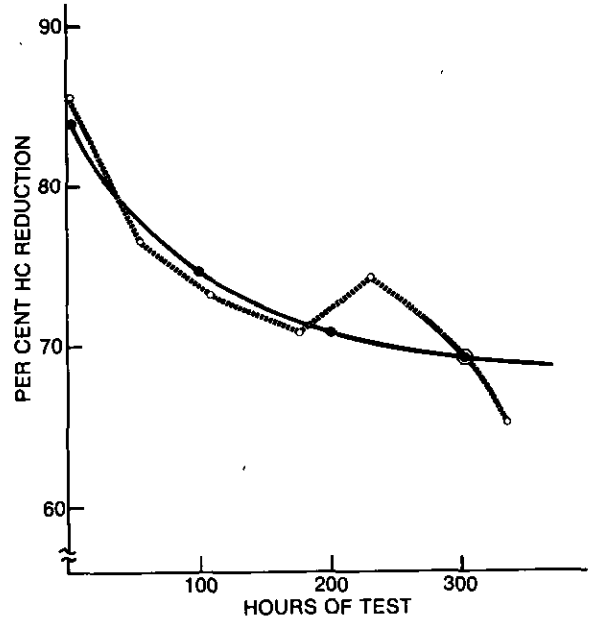

FIGURE 2. Multicylinder engine endurance tests, comparing platinum-palladium catalyst deterioration on (——) 1975-type "unleaded" fuel containing 0.05 g Pb/gal as motor mix, vs. (---) modified fuel containing 1.5 g Pb/gal without scavengers. Catalytic hydrocarbon removal is measured.

Environmental Health Perspectives
Vol. 10, pp. 113–116, 1975

Operation of Platinum—Palladium Catalysts with Leaded Gasoline

by D. Maxwell Teague,* Leo. B. Clougherty,* and Anthony N. Speca*

The effect of various fuel additives on the ability of platinum–palladium catalytic converters to remove the carbon monoxide and hydrocarbon components of automotive exhaust has been examined. Engine dynamometer studies suggest that these catalysts may be successfully used in conjunction with fuels of relatively high tetraethyllead concentrations, provided the ethylene dibromide portion of the scavenger is excluded.

It has been amply demonstrated that the use of leaded fuel rapidly inactivates a noble metal oxidation catalyst used to control hydrocarbon and CO emissions in a motor vehicle (*1–7*). This limits their use to unleaded fuel. For this reason, the Federal government has mandated the availability in the U.S. of unleaded fuel, containing no more than 0.05 g/gal of lead (*8*). This limitation applies to both base metal, as well as precious metal oxidation catalysts, containing platinum and palladium, of the type expected to be generally used in 1975 model vehicles.

In view of the advantages of using leaded fuel in all vehicles, we have some interesting and significant results to report regarding the possibility of operating catalytic vehicles on leaded fuel. This information is of a preliminary nature, based on laboratory and dynamometer tests. No "on the road" vehicle studies have, as yet, been made. Because of the social and economic issues involved, the Chrysler Corporation is making this new knowledge on the subject immediately available to the various industries and to the government for further study.

The effect of using a noble metal catalytic converter with an engine running on fuel containing various additives was examined via engine dynamometer tests. The dynamometer test, to stabilize catalyst performance, consists of an initial 10 hr running on fuel containing no added lead antiknock. This is followed by 10 hr of operation on the same fuel containing the additive in question. A final 10 hr of operation, again on unleaded fuel, measures the extent of permanent deterioration.

Figure 1 shows that when standard leaded gasoline is used as the modified fuel, there is an abrupt loss in catalytic CO removal from 95% to 30%. A subsequent 10 hr of operation again on unleaded fuel shows a fairly rapid, but not complete, recovery of catalytic activity back to 88% removal.

In view of the rapid recovery of the catalyst, it appeared unlikely that the deposition of solid lead compounds, which occurs during operation of catalysts on leaded fuel (*5,6,9*), is the cause of the large activity loss. Thus, another mechanism was sought.

* Chrysler Corporation, Box 1118, Detroit, Michigan 48231.