AUTOMOTIVE POLLUTION CONTROL CATALYSTS AND DEVICES

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FOREWORD

The detailed, descriptive information in this book is based mainly on U.S. patents issued since the early 1970s that deal with automotive pollution control catalysts and devices.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced, technically oriented review of these timely topics.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring our new durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book. A short bibliography of important U.S. Government publications on this subject is also to be found at the end of the volume.

15 Reasons Why the U.S. Patent Office Literature Is Important to You —

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source.

2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."

3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.

4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.

5. Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.

6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.

7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.

8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.

9. Can aid in process design by providing a selection of alternate techniques A powerful research and engineering tool.

10. Obtain licenses — many U.S. chemical patents have not been developed commercially.

11. Patents provide an excellent starting point for the next investigator.

12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.

13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.

14. Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.

15. It is a creative source of ideas for those with imagination.

CONTENTS AND SUBJECT INDEX

INTRODUCTION

The automobile as a major source of air pollutants is currently receiving national attention. Strict standards have been legislated on automotive exhaust emissions and these are leading to significant technological developments ranging over new engine design and modifications, development of catalytic converters for exhaust treatment and formulation of new fuels and additives to reduce levels of emission components. The adoption of certain of these technological alternatives has already occurred and others will be introduced within the next two to ten years.

The number of automobiles involved, their relationship to major population centers and the complexity of the impacts that result from each technological alternative suggests a need for careful evaluation before-the-fact of the consequences which are likely to occur (5).

Gaseous waste products resulting from the burning or combustion of hydrocarbonaceous fuels, such as gasoline and fuel oils, comprise hydrocarbons, carbon monoxide and oxides of nitrogen as products of combustion or incomplete combustion and, when discharged directly to the atmosphere, pose a serious health problem.

While exhaust gases from other hydrocarbonaceous fuel burning sources such as stationary engines, industrial furnaces, and the like, contribute substantially to air pollution, the exhaust gases of automobile engines are a principal source of pollution. In recent years, with the ever growing number of automobiles powered by internal combustion engines, the discharge of waste products therefrom has been of increasing concern, particularly in urban areas, and the control thereof has become exceedingly important. Of the various methods which have been proposed for reducing the hydrocarbons, carbon monoxide and nitrogen oxides emissions, the incorporation of a catalytic converter in the exhaust system holds the most promise of meeting the increasingly rigid standards set by responsible governmental agencies.

This topic was covered by this publisher in an earlier volume, *Catalytic Conversion* *of Automobile Exhaust,* by J. McDermott, Park Ridge, N.J., Noyes Data Corp. (1971). At that time, however, such devices were only in the R&D stage. Now that they are required equipment on most automobiles and that catalyst sales alone are nearing the billion dollar level (with total device sales double or triple that), it seemed time to survey the practical aspects of catalyst, hardware and control devices for automotive pollution control.

It should be emphasized that this volume is a report on the state of the art as of mid 1977. In a technical area like emission control technology, in which the rate of change can potentially be rapid, new developments may require modifications of conclusions that were made previously.

The technology is complex in itself but beyond that lie the facts that

(1) huge investments in existing automotive production facilities can be threatened by change
(2) profit margins and sales in the dominant auto industry can be affected by the addition of legally required pollution control equipment which can raise prices with no obvious advantages seen by the purchaser and
(3) political implications of the two preceding items make legislative action uncertain and unpredictable.

Further legislation may impact the effects and implementation of the basic legal document dictating catalytic converter development, The Clean Air Act of 1970. Thus, passage of the Energy Policy and Conservation Act, PL 94-163, has created a new set of requirements for the industry that have impacted and will continue to impact on the development of future emission control systems. Mandated fuel economy goals will require that fuel economy become a high priority design constraint. Because of time, budget and manpower limitations, this may stretch out the development period for advanced emission control systems.

Up until the fuel economy legislation was passed, the manufacturers were working toward a voluntary 40% improvement in fuel economy by 1980 with the assumption that a 5-year freeze in the emission standards would be granted. The concrete fact that the manufacturers now know is that instead of a voluntary program their fuel economy is now subject to mandatory controls (1).

The manufacturers' primary emphasis now is on fuel economy, not solely on emissions. The manufacturers have to apportion their technical effort where they feel that it will do them the most good.

With fixed total resources, effort that was directed toward achieving more stringent emission control is bound to lose out to work toward improving fuel economy, especially since the same engineering staffs are generally involved (1).

The uncertainty as to what the emission standards would ultimately be has been stated by the manufacturers to be a problem for a long time, and is clearly a reason why the development progress has not been as rapid as desirable. Because of the demand on their manpower caused by the fuel economy legislation, and the fact that they cannot commit the resources to fully develop emission control systems for all of their models for every possible future standard, manufacturers have not been able to put concentrated effort into designing and developing the fleets of vehicles needed to determine how to meet any given future standard.

Additional reasons that development progress has slowed down could involve new regulatory requirements. EPA has proposed that the manufacturers meet new evaporative emission standards, and assembly line test requirements.

Further EPA has proposed that those manufacturers that produce Light Duty Trucks (LDT) meet more stringent LDT standards for an expanded vehicle class that includes for the first time trucks with gross vehicle weights in the 6,000 to 8,500 pound GVW range. All of these new regulations will require expanded development and testing to insure compliance. The same engineering staffs are generally involved in all of these activities.

THE PROBLEMS

Pollutants

The composition of the exhaust from internal combustion engines is characterized by the presence of unburned fuel hydrocarbons, both saturated and unsaturated, carbon monoxide, nitrogen oxides and hydrogen. In addition, to these noxious entities, the exhaust of internal combustion engines also contains measurable quantities of water vapor.

A typical diesel exhaust also contains partial oxidation products such as organic acids, aldehydes and ketones. These materials may be present in some of the exhaust from other types of internal combustion engines but are typical of the exhaust of diesel motors. In addition, the exhaust from internal combustion engines also frequently contains unburned carbonaceous solids.

The air in most cities contains substantial quantities of both oxides of nitrogen and the products of incomplete combustion of organic fuels. In the presence of sunlight, photolysis of the oxides of nitrogen leads to the formation of measurable quantities of ozone. The ozone, in turn, reacts with various organic pollutants to form compounds which can cause the many undesirable manifestations of smog, such as eye irritation, visibility reduction and plant damage.

When meteorological conditions prevent the rapid dispersion of pollutants a smog condition results. Furthermore, it is now known that in many cities a major portion of organic pollutants are derived from unburned or partially burned gasoline in auto exhaust.

The instantaneous composition of vehicular exhaust is a function of many factors, including parameters relating to engine design, and tuning, and driving mode, as well as fuel composition. Thus, it is difficult to specify a typical exhaust composition. Generally speaking, however, when present day automobile engines are started cold, carbon monoxide levels of about 5 to about 15 volume percent, along with the hydrocarbon levels of about 5,000 to about 15,000 parts per million are not unusual.

Carbon monoxide and hydrocarbon levels fall rapidly after engine start to levels of about 3% and 1,000 ppm respectively in about the first 100 seconds of engine operation. As the engine continues to warm to normal operating temperatures, exhaust compositions containing about 1 to about 2% carbon monoxide and several hundred parts per million hydrocarbon are oftentimes observed with present day automobiles.

Nitrogen oxide evolution with present automobile engines is closely tied in part to engine tuning and driving mode. For example, with very lean and very rich air to fuel ratios, nitrogen oxide emissions are relatively low. In between, higher emissions are observed. In addition, relatively higher NO_x emissions result from high speed driving modes. Generally, NO_x emissions are less than 0.3 to 0.4% on a volume basis, and on the average around 0.15%. Otherwise expressed in terms of grams per vehicle mile (GVM), baseline emissions for the various pollutants are shown in Table 1.

TABLE 1: NATIONAL EXHAUST EMISSIONS, LIGHT DUTY VEHICLES

Pollutant	Baseline Emissions, GVM*
Exhaust HC	17.0**
Exhaust CO	121.9**
Exhaust NO_x	5.4***

*Baseline emissions apply to pre-1968 models.
**1972-75 test cycle.
***1968-71 test cycle.

Source: Reference (3)

To place motor vehicle emissions in some perspective as a national problem, it is interesting to examine the data in Table 2. They indicate the magnitude of automotive emissions as a contributor to total pollution, a fact which undoubtedly led to the provisions of the Clean Air Act of 1970.

TABLE 2: PERCENTAGE OF NATIONAL EMISSIONS IN 1969

	CO	HC*	NO_x*
Motor vehicles	64.7	45.7	36.6
Other forms of transportation	9.0	7.2	10.5
Fuel combustion in stationary sources	1.2	2.4	42.0
Industrial processes	7.9	14.7	0.8
Solid waste disposal	5.2	5.3	1.7
Miscellaneous	12.0	24.7	8.4
Total	100.0	100.0	100.0

*In addition, emissions of HC and NO_x from motor vehicles and other sources undergo complex chemical reactions in the atmosphere and contribute to the formation of photochemical oxidants associated with urban smog.

Source: Reference (3)

Figures 1, 2 and 3 show the expected decrease in the various pollutants with effective automotive exhaust treatment (3). These figures were based on the original 1970 Clean Air Act provisions which called for major reductions in pollutants by 1975. On April 11, 1973, the Administrator granted the extension requested by U.S. automakers for meeting the statutory 1975 standards, imposing somewhat less stringent interim standards instead. As will be discussed further under The Legislative Requirements, the timetable keeps changing and the rigid 1978 requirements have become 1980 requirements by action of Congress in August 1977. Thus the trends in Figures 1 to 3 are indicative but the timing has been stretched.

FIGURE 1: REDUCTION IN HC EMISSIONS FROM MOTOR VEHICLES IN THE U.S., 1965-90

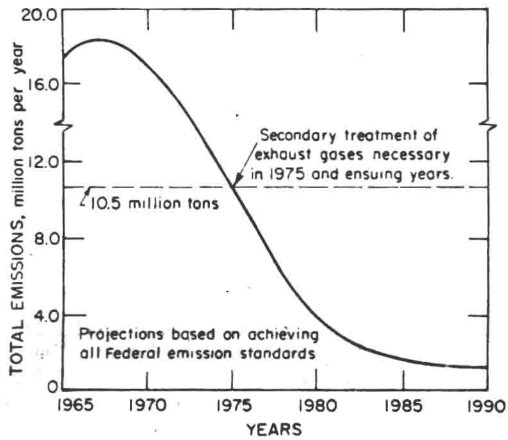
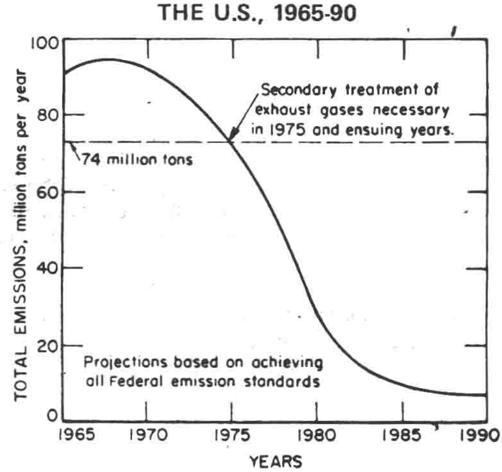
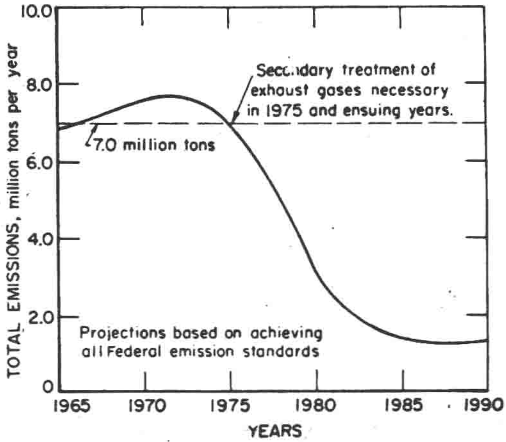


FIGURE 2: REDUCTION IN CO EMISSIONS FROM MOTOR VEHICLES IN THE U.S., 1965-90



Source: Reference (3)

FIGURE 3: REDUCTION IN NO_x EMISSIONS FROM MOTOR VEHICLES IN THE U.S., 1965-90



Source: Reference (3)

Vehicle Operating Environment

It has been known for many years that a catalytic converter can be a very effective means for reducing automotive exhaust pollution. The extremely severe temperature environment of an exhaust path, coupled with vibrations, especially those produced by the opening of the engine exhaust valves, makes it necessary that the converter be very rugged if it is to have any degree of longevity. A wide disparity in driving habits and owner attention to engine maintenance makes it necessary to design converters for the worst possible operating conditions.

Fuel Additive Effects

Lead, which in past years has been added to gasoline in the form of alkyl lead derivatives, such as tetraethyl lead (TEL) and tetramethyl lead (TML), to increase the octane number of gasoline most economically, is inimical in varying degree to catalysts. It is a particularly inhibitory poison in the case of platinum, and is undesirable from the standpoint of this catalyst's longevity even in trace concentrations as low as 0.05 g/gal (3). Thus, if catalytic converters are to be used, virtually lead-free gasoline will be required.

Ecological considerations will be an additional stimulus encouraging the ultimate removal of all lead from gasoline. However, lead probably will continue in limited use as an additive in one grade of gasoline until automobiles requiring leaded fuel are off the road. Complete removal of lead from motor fuel probably will not occur until near the end of this century, when virtually all pre-1975 vehicles requiring leaded gasoline will have been retired. The lowering of the octane level of gasolines as a result of the elimination of lead additives will require at least a partial restoration of the elimination of the octane level by increasing the high octane hydrocarbon components. While lead has not been banned as an additive (it has not been proven to be a major contributor to human blood level), there are definite plans to phase lead out of gasoline although Congress or EPA could change their minds on this (5).

Du Pont has developed a catalyst which appears to be somewhat resistant to poisoning by lead (1). Briefly, the catalyst is a perovskite-based catalyst in which some of the active materials are held in a lattice in such a way that lead cannot easily poison them. The catalyst can be formulated as an oxidation, reduction, or 3-way catalyst. Some of the positive points of this catalyst type are said to be its thermal stability at high temperatures, high activity, and resistance to poisoning. However, they need to be run somewhat hotter than more conventional oxidation catalysts, and tests run to date (by Chrysler, for example) show relatively low HC efficiency.

Although such catalysts have been investigated to permit the use of leaded fuels, some uses of this catalyst type that are compatible for both leaded and unleaded fuel are worthy of mention. First, if the temperature capabilities are significantly better than current catalysts they could be used as start catalysts or as a manifold-mounted (inside the exhaust manifold) oxidation catalyst.

Good resistance to high temperatures and poisoning is required of this type of system which has great potential for helping solve the HC warm-up problem. Second, this catalyst type could be used as a 3-way or a NO_x catalyst. In fact, if the stabilizing properties of the lattice are good enough to prevent ruthenium (Ru) from being lost, this could be a significant advance in NO_x catalyst technology, because Ru is an excellent NO_x catalyst material that has defied successful stabilization in an active form to date. (It tends to form a volatile and toxic oxide.) NO_x catalysts also need high temperature stability, so that perovskite catalyst may find its best application as a NO_x catalyst. Of course, more testing is needed to more properly assess the potential of this promising new technology.

Because of potential industry interest in lead-tolerant catalysts, data from two automobile manufacturers on the effect of lead on HC emissions should be mentioned. GM and Honda reported data on the effects of leaded fuel on HC emissions at no accumulated mileage. That is, the results reported are not a durability effect, they are a combustion effect. The results are shown in Table 3.

TABLE 3: EFFECT OF LEADED FUEL ON HC EMISSIONS (NO ACCUMULATED MILES)

Source	Fuels	% Reduction in HC*
GM	1.5 g/gal leaded	28
	1.0 g/gal leaded	23
	0.5 g/gal leaded	9
Honda	3.15 g/gal leaded	20

*% reduction in HC attributable to removal of lead from fuel.

Source: Reference (1)

According to GM, the lead acts as an HC oxidation inhibitor. This data along with the now recognized lack of improvement in fuel economy as compression ratio is raised, if emissions are held constant, might suggest less manufacturer interest in lead-tolerant catalysts.

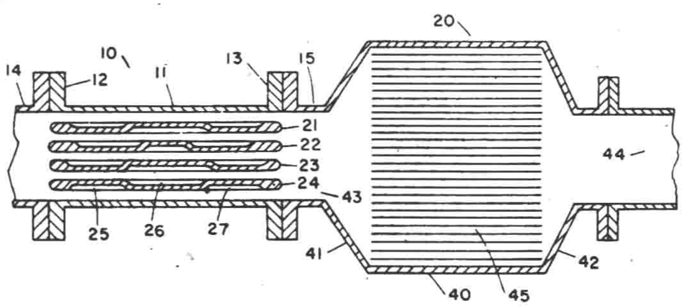
In attempts to provide antiknock action without the use of lead (which has doubtful environmental effects in addition to its poisoning effects on converter catalysts) organomanganese compounds have been developed as alternative antiknock compounds for gasoline.

Cyclopentadienyl manganese compounds are excellent antiknocks in gasoline used to operate spark ignited internal combustion engines. Not only are these compounds effective antiknock agents, but it has also been claimed that they do not adversely affect the activity of catalysts used to decrease the amount of undesirable constituents in engine exhaust gas. Under some operating conditions it has been found that, although the manganese antiknocks do not lessen the activity of the exhaust gas catalyst, they can interact in some manner at the surface of the catalyst bed leading to a reduction in the size of the openings into the bed thereby causing an increase in exhaust back pressure.

Because of their not yet precisely defined effect on catalyst HC conversion efficiency (CO activity does not appear to be harmed), but more because it is not yet absolutely certain that these manganese compounds and their combustion products are benign, it is difficult to make projections for their widespread use, although they probably are tempting octane boosters for those refiners lacking a a little bit of octane to get to 91 RON, or for those who desire to increase their octane to increase customer satisfaction (1).

A scheme developed by *L.M. Niebylski; U.S. Patent 3,996,740; December 14, 1976; assigned to Ethyl Corp.* is one in which the useful life of a catalyst being used in an engine exhaust system to lower the undesirable constituents in the exhaust gas of an engine being operated on gasoline containing a cyclopentadienyl manganese antiknock is greatly prolonged by providing an exhaust system having a plurality of substantially parallel proximately spaced vanes in the exhaust flow path upstream from the catalyst. The vanes have elongated recesses in their surface. Such a vane unit is shown coupled to a catalytic converter in Figure 4.

FIGURE 4: VANED INLET DEVICE FOR CATALYTIC CONVERTER TO DECREASE MANGANESE INTERFERENCE



Source: U.S. Patent 3,996,740

Vane unit **10** is constructed of conduit member **11**, which in this case is tubular and has flanges **12** and **13** at each end. Flange **12** is adapted to connect through pipe **14** to the outlet of the engine exhaust manifold. Flange **13** is adapted to connect to inlet portion **15** of catalytic converter **20**. Located within member **11** are parallel vanes **21, 22, 23** and **24**. These vanes are substantially parallel, one to another, and are aligned with the longitudinal axis of member **11**. Elongated recesses **25, 26** and **27** are milled in both surfaces of each vane. In this preferred embodiment these elongated recesses are aligned with the longitudinal axis of member **11**.

Catalytic converter **20** is constructed of cylindrical housing **40** having frusto-conical end members **41** and **42** forming inlet **43** and outlet **44**. Located within cylindrical housing **40** is honeycomb monolithic ceramic catalyst unit **45**. In operation, hot exhaust gas from the engine is conducted by exhaust pipe **14** into conduit member **11**. It passes through the space between vanes **21, 22, 23** and **24** and then into converter **20**. It passes through catalyst bed **45**, which in this instance is a honeycomb monolithic ceramic supported platinum catalyst. The treated exhaust exits at outlet **44** and after passing through a conventional muffler (not shown) is exhausted to the atmosphere.

The possible new inorganic additives, conceived as replacements for lead include manganese, nickel, phosphorus (already in use) and boron. Manganese and nickel are of interest because they contribute antiknock properties. Phosphorus, a good corrosion inhibitor, and boron result in more efficient fuel combustion. Maximum limits for these elements and lead in gasoline have been proposed as follows (5).

	g/gal
Mn	0.1
Pb	0.05
B	0.01
Ni	0.0075
P	0.005

The implications of such additions need to be explored relative to their (1) possible formation and emission of more toxic organometallics, e.g., nickel carbonyl, (2) smog production and health effects, should they be emitted with exhaust, (3) effects on operation of catalytic converters, and (4) ultimate disposal or recycle with respect to final disposition of spent catalytic converters. It would be foolhardy (and contrary to Clean Air Acts) to solve a HC, CO or NO_x problem by mere replacement with a technological alternative having similar or worse impact on the environment. Indeed, in 1977, California banned the use of manganese antiknock additives in that state.

THE LEGISLATIVE REQUIREMENTS

The Clean Air Act of 1970 (Public Law 91-604) as amended, required that automobiles produced in 1975 and therafter be provided with antipollutive measures to control automotive exhaust emissions. On April 11, 1973, however, the Administrator of EPA granted an extension requested by U.S. automakers, as noted earlier, extending the deadline for meeting the 1975 standards as originally formulated.