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METHOD AND APPARATUS FOR TREATING EXHAUST GASES OF INTERNAL COMBUSTION ENGINES

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FIG. 1

CuO - CuCr₂O₄
NiO - NiCr₂O₄
XₘCr₂O₄ - ₂YₘnOₘ

EXHAUST GASES CONTAINING ADDED AIR

K₂SO₄

GASES CONTAINING LEAD COMPOUNDS NOT DELETERIOUS TO THE CATALYST.

FIG. 2

K₂SO₄

CuO - CuCr₂O₄
NiO - NiCr₂O₄
XₘCr₂O₄ - ₂YₘnOₘ

GASES CONTAINING CO₂, H₂O, LESS NO, LEAD COMPOUNDS NOT DELETERIOUS TO THE CATALYST.

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METHOD AND APPARATUS FOR TREATING EXHAUST GASES OF INTERNAL COMBUSTION ENGINES

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The application is a continuation-in-part of my co-pending application Serial No. 193,899, filed May 4, 1962, and now abandoned, which is a continuation-in-part of my co-pending application Serial No. 116,061, filed June 9, 1961, and now abandoned.

This invention relates to the treatment of automobile exhaust gases which contain such noxious and undesirable products as nitric oxide, carbon monoxide, and hydrocarbons and products of combustion of alkyl lead antiknock compounds. This invention is more particularly directed to the treatment of such gases with both a lead sensitive catalyst and a scavenger as follows:

Scavenger:
Sulfates of—
Ammonium
Sodium
Potassium
Lithium
Magnesium

Catalyst:
Manganese-chromia-manganite
oxides, chromites, and manganites of—
Copper
Iron
Cobalt
Nickel
Cadmium
Zinc
Bismuth
Cerium
Platinum
Rhodium
Palladium
Ruthenium

In the drawings:
FIGURE 1 illustrates an embodiment in which automobile exhaust gases are passed first through a scavenger and thereafter through a catalyst, and
FIGURE 2 represents a modification in which the scavenger is mixed with the catalyst.

According to the present invention the catalysts above tabulated are protected from the deleterious effect of the combustion products of alkyl lead and of the halogen compounds often included in leaded gasolines. The scavengers listed can be used for a preliminary treatment of the exhaust gases before they pass to the catalyst but it is not imperative that there be separate zones.

In FIGURE 1 there is illustrated a modification of the invention in which a typical scavenger, potassium sulfate, is placed in the first section of a catalytic muffler. Gases must first pass through this before reaching the second section which contains, illustratively, manganese-chromia-manganite.

Alternatively the potassium sulfate pellets can be mixed with the catalyst pellets in at least one or two sections of the muffler and as specifically shown the first section contains the mixture while the remaining sections do not.

The scavengers do not remove all lead compounds from the automobile exhaust gases and apparently considerable quantities of lead compounds pass through the scavenger to the catalyst. However the scavengers listed seem to remove or to render innocuous the products of combustion of the lead compounds and the halogen compounds so that they are no longer deleterious to the catalyst.

SCAVENGERS

The scavengers to be used are the sulfates of:
Ammonium
Sodium
Potassium
Lithium
Magnesium

The scavengers or mixtures of them can be utilized in any form in which they supply sufficient surface to the gases being treated without at the same time creating excessive resistance to gas flow. In general the products should be in the form of particles, pellets, granules, rods, or other appropriate shapes. Most preferred is to have the particles in the range of about \( \frac{1}{8} \) to \( \frac{1}{4} \) inch in largest cross section. While not usually preferred, the scavengers can be in the form of even smaller discrete particles. Thus the scavengers either as such or preferably supported as below described can be used in the form of particles down to 25 microns in largest dimension. Below this figure the particle are very apt to fuse to the catalyst surface and to become almost a part of the catalyst.

It will often be found most advantageous to support the scavengers upon or to mix them with suitable carriers because of the tendency of some of them to melt under the conditions of high temperature operation sometimes encountered in treatment of automobile exhaust gases. The compounds can be supported upon or mixed with any of the carriers listed below and additionally there can be used inert materials which do not melt at the temperatures reached and which do not decompose or react. Thus there can be used various clays such as bentonite, diatomaceous earth, finely divided silica, or silica aerogel.

Ordinarily from about 5 to 50% by weight of a sulfate scavenger should be applied to a support. More or less can be used but if too little is used the activity and capacity drop and the volume of the equipment required becomes unreasonable. Eighty or even nearly one hundred percent of the scavenger can be used on the carrier. The advantage of using a carrier to reduce fusion will be in part lost with very large amounts of scavenger.

The catalysts to be used in conjunction with the scavengers mentioned will be listed below by sections:

THE MANGANO-CHROMIA-MANGANITE CATALYSTS

The manganese-chromia-manganite catalysts to be used according to the invention are described and claimed as such and with co-catalysts, interspersants, and supports in copending Howk and Stiles applications Serial No. 109,483, filed May 19, 1961 and Serial No. 59,263, filed September 29, 1960, and reference can be had to such applications for further details. A general description should be sufficient here.

The manganese-chromia-manganites have the following empirical chemical composition:

\[ XCr_2O_4/2YMnO_3 \]

in which \( n \) can be 2, 3, and 6 and \( m \) can be 1, 1.33, 1.5, 2, and 2.5. The Mn:Cr weight ratio will vary from 3:0.5 to 3:30. The atomic ratio, that of \( Y:X \), is substantially the same and when \( Y = 3 \), \( X \) can equal 0.5 to 30.

A manganese-chromia-manganite can be prepared having a ratio of \( \text{Mn:Cr} \) of 3:2 according to the methods of Lazer U.S. Patents 1,746,782 and 1,964,601 and Wurtz U.S. Patent 2,108,156. In these and other prior suggestions of manganese chromites it is proposed that equimolecular amounts of the manganese compound and the chromium compound be used which in aqueous solutions results in
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a product having a ratio of 3:2 because a third of the chromium is not precipitated and is washed away.

The manganese-chromia-manganite can be prepared by procedures which are described in detail in the Hawk and Stiles applications above mentioned. Generally, it can be said that they are prepared by reacting appropriate salts of manganese and chromium in aqueous solution. Thus, manganese nitrate and chromic acid anhydride are dissolved in water and ammonia is added to make a precipitate. The products of high manganese ratio can be prepared by adjusting the amounts of components, but a high chromium product can be made when a hexavalent chromium salt is used as a chromium source only by adding further chromium compound, such as ammonium chromate, to the precipitate thus prepared after filtration. Alternatively, the appropriate proportion of suitable salts such as manganese nitrate with chromium nitrate can be precipitated or fused together to give manganese-chromia-manganite of the desired Mn:Cr ratio.

CO-CATALYST

A co-catalyst can be included with the manganese-chromia-manganite and there can be used, for example, such co-catalysts as those described in Patent No. 1,964,001. Thus one or more of the following can be added as the carbonate or can be added as a basic carbonate or oxide:

- Copper
- Nickel
- Zinc
- Iron
- Cadmium
- Cobalt
- Tin
- Bismuth

The co-catalysts can, of course, be added as other compounds depending upon the specific treatment and processing conditions used.

The weight ratio of co-catalyst:manganese-chromia-manganite can vary greatly and can range from, say, 10:1 to 1:10. About 1:1 is preferred.

INTERSPERSONS

It is often desirable to add an interpersant to the catalyst aggregate as described in the above mentioned Hawk and Stiles applications. The interpersants are refractories which have a melting point about 1000°C. and more preferably above 1600°C. The crystallite size of the refractory should be such that its crystallites keep the crystallites of the manganese-chromia-manganite apart. The refractory crystallites serve a similar function with crystallites of co-catalysts which are present.

The interpersants which can be used include such water-insoluble precipitates as:

- Aluminum oxide and hydroxide
- Titanium oxide
- Thoria
- Ceria
- Chromia
- Magnesia
- Calcium oxide and hydroxide
- Barium oxide and hydroxide
- Strontium oxide
- Zinc oxide
- Manganese oxide
- Silica
- Beryllia
- Zirconia
- Lanthana
- Hafnia

Aluminum hydroxide, which is present as oxide in the final product, is preferred. Manganese oxide and chromia are listed as interpersants to be added in amounts exceeding those which would be present in the manganese-chromia-manganite of the ratios described.

It is to be noted that the interpersants can be added in the first precipitation of formation of the catalyst aggregate and a second interpersant can be added after the catalyst aggregate has been formed and especially after it has been heat-treated or calcined. The interpersants can be heat-decomposable products or they can be introduced in the form of solids or dispersions.

The amount of the interpersants can be widely varied and the total of the first interpersants can run from, say, 5 to 75% based upon the weight of manganese-chromia-manganite plus a co-catalyst if there is one. A second interpersant can range in amount from 0.5 up to 50% or even more by weight of the weight of the catalyst aggregate to which it is added.

Further details of the introduction of co-catalysts and interpersants can be found in the Hawk and Stiles applications previously mentioned.

SUPPORTS

Supports suitable for use according to the present invention include various refractory bodies customarily used for this purpose in the art. There can be used for example:

- (1) Porous ceramic spheres, tablets, or rings which have a softening or melting point in excess of 1200°C.
- (2) Etched nickel, Nichrome, and inconel wire
- (3) Alumina
- (4) Pumice
- (5) Diaspore
- (6) Bauxite
- (7) Periclase
- (8) Zirconia
- (9) Titania
- (10) Diatomaceous earth
- (11) Calcium sulfate
- (12) Barium oxide
- (13) Calcium oxide
- (14) Activated alumina granules

The preferred refractory supports are:
- Bauxite
- Zirconia
- Titania
- Activated alumina

It is preferred that the surface area be at least 10 m²/g. with pore dimensions such that 40% are less than 200 Angstroms. It is even more preferred that the surface area be at least 80 m²/g. with pore dimensions of at least 60% less than 200 Angstroms. Manganese-chromia-manganite catalysts employing such preferred supports are described and claimed in U.S. application Serial No. 101,943, filed May 19, 1961. The catalyst support can be washed with water or with weak acids followed by washing with water as covered in a copending application of the assignee of the present case, Gilby U.S. application Serial No. 108,763, filed May 9, 1961, and now abandoned.

The amount of catalyst applied to a support can be widely varied in accordance with usual practices but ordinarily will run from 1 to about 20% by weight based upon the weight of refractory. Less catalyst does not ordinarily give adequate activity and more catalyst is wasteful.

As described in said Hawk and Stiles application above, the gases supplied to the manganese-chromia-manganite catalyst are the exhaust gases from motor vehicles and other internal combustion engines to which has been added an appropriate amount of air for the customary oxidation reaction. It is also indicated that in some situations it may be desired not to add air in a first stage in which reduction occurs, air being added later to effect oxidation.

The catalyst containing the sulfate whether tableted or supported as described can be calcined, if desired, at a temperature which does not go so high as to result in sintering of the catalyst components including the sulfate. Temperatures from about 250 to 800°C. will be satisfactory and the times can run from a few minutes up to 30 minutes or an hour. Such calcination will be
particularly desirable if there are heat-decomposable components in the catalyst.

THE OXIDE, CHROMITE, AND MANGANITE CATALYSTS

The catalysts used for the invention can be chromium oxide and oxides, chromites, and manganites of copper, iron, cobalt, nickel, cadmium, zinc, bismuth, and cerium and mixtures of these.

The oxides of the metals named can be in any stage of oxidation and after the oxides are applied, or formed, in catalysts of the invention the oxide will resonate from one valence state to another. Ordinarily the oxides will be prepared in a catalyst for sale in the highest valence state because this is convenient.

The oxides will ordinarily be prepared by a reduction of a decomposable compound. Thus copper nitrate, carbonate, acetate, formate, hydroxide, or the like can be heated to form the oxide. The same salts of the other metals can similarly be used.

The chromites and manganites of the metals named can be formed by heating the basic metal chromate. The manganite can be formed by metathesis or preferably by heating and decomposition such as by heating a nitrate of the metal in the presence of suitable manganites such as ammonium manganite. The preparation of catalysts will be illustrated further in the examples.

The co-catalysts and the interspersants described above can be used with the oxide chrome and manganite catalysts in the proportions described above.

The catalysts, together with co-catalysts and interspersants if any, can be piled or tableted as can the manganato-chromia-manganite catalysts. Alternatively and preferably they will be supported upon a refractory support such as one of those listed above and in the proportions above listed.

PRECIOUS METAL CATALYSTS

The precious metal catalysts used can be platinum, rhodium, palladium, ruthenium and their mixtures, and with the catalysts listed above.

The metals are usually applied as finely divided or colloidal metals upon the surfaces of appropriate carriers.

The preparation of such catalysts is conventional but will be illustrated hereinafter.

The refractory support can be used as a carrier and any of those listed above is satisfactory. The amount of the precious metal to use upon a carrier is well understood. Generally from about 1/300 of 1% to 1% by weight is used based upon the weight of carrier. More can of course be used but this is expensive and if much less is used the activity is too low.

The amount of the scavengers to be used can be widely varied. If too little is used then they will become relatively ineffective after too short a time. If too much is used, too great a resistance to flow of gases may become involved and the weight, volume, and cost of the material may become excessive. In general the ratio of the weight of scavenger to the weight of catalyst including support will range from 10:1 to 0.1:1. Generally about equal amounts by weight are preferred. It is to be noted that when the catalyst particles are mixed with particles of scavenger the mixture can extend throughout the catalytic bed or can be confined to individual sections. As illustrated in the drawing only the first section contains the scavenger. The amount of scavenger illustrated in FIGURE 2 is intended to be approximately 1/12:1 for the ratio of scavenger to catalyst.

In order that the invention may be better understood reference should be had to the following illustrative examples.

EXAMPLE 1

Preparation of the catalyst

(1) 250 parts by weight of activated alumina, 4-8 mesh size, having a surface area of 200 square meters per gram and having 60% of the pores less than 600 A. in diameter is immersed in a solution consisting of 5 parts by weight platinum as chloroplatonic acid in 500 parts by weight water at 50° C. for 15 minutes.

(2) The granules, after draining, are placed in a tube which permits hydrogen to enter at one end and exhausted at the other. Hydrogen humidified to 60% at 75° C. is passed over the catalyst for one hour at 75° C. to reduce the metal and to control migration of the precious metals to a peripheral location on the granules.

(3) The catalyst is finally heated to 200° C. in the same hydrogen flow for one hour.

Preparation of the lead scavenger

(4) 250 parts by weight of activated alumina, of the type used for the catalyst preparation above, is immersed in a solution-sulfur compound of 80 parts by weight of sodium sulfate in 500 parts by weight water at 90° C. for 10 minutes.

(5) The granules are drained, then dried at 150° C. for ten hours.

Use of lead scavenger and lead catalyst

The lead scavenger and catalyst described above is employed as shown in FIGURE 2. The lead scavenger is placed in the 3 down-stream cells. The lead catalyst is placed in equal weight in the 3 upstream cells. The exhaust gases entering the converter and the lead compounds contained in them are made relatively innocuous by the scavenger as they pass through the first scavenger section.

A similar catalytic muffler charge can be made by using the mixture of scavenger in two, three, or all of the sections. A similar catalyst charge is prepared using the precious metal catalyst described but supporting the sodium sulfate upon the activated alumina as in Items 4 and 5 above such that most of the alumina is in the range of 40-80 microns in largest dimensions. This scavenger is used in a weight equal to the weight of the catalyst and is charged as shown in FIGURE 2 into one or more sections of the muffler.

EXAMPLE 2

Preparation of the catalyst

(1) 250 parts by weight of silica-alumina, 88% SiO₂-12% Al₂O₃, 4-8 mesh, having 40 square meters per gram surface area and 50% of the pores smaller than 400 A. in diameter is immersed in a solution composed of 5 parts by weight palladium as palladium chloride in 500 parts by weight water at 40° C. for 10 minutes.

(2) The granules, after draining, are placed in a closed tube and hydrogen humidified to 50% at 70° C. is passed over the catalyst for one hour, then the temperature is increased to 250° C. for an additional hour.

Preparation of the scavenger

(3) 250 parts by weight of silica-alumina, 4-8 mesh, of the type used in the preparation above is immersed in a solution composed of 120 parts by weight ammonium sulfate in 500 parts by weight water at 90° C. for 10 minutes.

(4) The granules are drained, then dried at 150° C.
Use of the scavenger and catalyst

The scavenger as prepared above is charged to the first three cells and an equal weight of catalyst is charged to the last three cells in Figure 1.

The scavenger and catalyst particles are intermixed in equal parts by weight and charged into the first cell of a muller as shown in FIGURE 2. The mixture can be placed in two, three, or all of the cells.

The catalyst granules can be mixed with the lead scavenger in more finely divided form. Thus the scavenger as prepared in Items 3 and 4 above can be supported upon pulverized diatomaceous earth having a particle size in the range of 25–70 microns.

EXAMPLE 3

Catalytic mufflers are charged as shown in FIGURES 1 and 2, and as described in Example 2 but replacing palladium with an equal weight of ruthenium.

EXAMPLE 4

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 2 but replacing palladium with an equal weight of a 50–50 mixture of platinum and rhodium.

EXAMPLE 5

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 2 but replacing palladium with an equal weight of a 50–50 mixture of palladium and rhodium.

EXAMPLE 6

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 2 but replacing palladium with an equal weight of a 50–50 mixture of platinum and palladium.

EXAMPLE 7

(1) A solution-slurry is prepared composed of 63 parts by weight of copper as the nitrate, 100 parts by weight CrO₃, and 40 parts by weight A₁₂O₃ as the hydrate in 0.5 micron and smaller particle size in 1,000 parts by weight water at 40° C.

(2) A concentrated solution of ammonium carbonate is slowly added to the solution-slurry of paragraph one to effect complete precipitation as determined by a test of the supernatant liquid.

(3) The precipitate is filtered, then calcined at 400° C. for one hour.

(4) The calcined powder is kneaded in a machine of the type used in the bakery industry in proportion such that 100 parts by weight of the powder obtained in Item 3 above and 40 parts by weight of magnesium oxide as the acetate and water are mixed to make a uniform, thick paste.

(5) The kneaded paste is calcined at 450° C. for one hour.

(6) The calcined paste is divided into three equal parts. The first part is granulated and screened to 8–14 mesh, the second part is mixed with a pill lubricant and pill in a pharmaceutical machine to form ¼” x ¼” cylinders, whereas the third part is extruded as a moist paste to produce ¼” x ½” cylinders.

Preparation of the scavenger

(7) 250 parts by weight of activated bauxite, 4–8 mesh, having a surface area of 130 square meters per gram and having pores such that 75% are less than 600 A. in diameter is immersed in a solution-slurry of 100 parts by weight of lithium sulfate in 500 parts by weight water at 75° C. for 10 minutes.

(8) The impregnated granules are dried at 175° C. for 1 hour.
EXAMPLE 11
Catalytic mufflers are charged as described in Example 8 with the exception that 65 parts by weight of zinc replaces the nickel.

EXAMPLE 12
Catalytic mufflers are charged as described in Example 8 with the exception that 56 parts by weight of iron replaces the nickel.

EXAMPLE 13
Catalytic mufflers are charged as described in Example 8 with the exception that 140 parts by weight of bismuth replaces the nickel.

EXAMPLE 14
Catalytic mufflers are charged as described in Example 8 with the exception that 55 parts by weight of tin replaces the nickel.

EXAMPLE 15
Catalytic mufflers are charged as described in Example 8 with the exception that 32 parts by weight of copper replaces one-half of the nickel.

EXAMPLE 16
As in FIGURES 1 and 2 of the drawings:
(1) A solution-slurry is prepared composed of 16.15 parts by weight of manganese, 3.2 parts by weight copper, 3.0 parts by weight nickel, all as the nitrates, plus 20 parts by weight Al₂O₃ as the hydrate of the type used in Step 1 of Example 7 and 30 parts by weight CrO₃ in 100 parts by weight water at 40° C.
(2) Anhydrous ammonia is added to the solution-slurry of Step 1 to effect complete precipitation as determined by a test of the supernatant liquid.
(3) The precipitate is filtered, then is ignited at 400° C. for one hour.
(4) The powder is kneaded in such a way that 100 parts by weight of powder obtained in Item 3 is mixed with 20 parts by weight CrO₃ as (NH₄)₂CrO₄ plus water to make a uniform thick paste.
(5) The kneaded paste is calcined at 400° C. for two hours.
(6) The calcined powder is pilled to form cylinders 1/8" x 3/8".

Preparation of the scavenger
(7) 250 parts by weight of 4-8 mesh activated alumina of the type used in Example 1 is immersed in a solution comprising 100 parts by weight of potassium sulfate in 500 parts by weight water at 50° C. for 10 minutes.
(8) The granules are dried at 175° C.

Use of the scavenger and catalyst
The scavenger and catalyst as above prepared are charged to a muffler-reactor as shown in FIGURE 1.

Preparation of the catalyst
(1) A solution-slurry is prepared composed of 16.3 parts by weight manganese, 18.9 parts by weight copper, both as the nitrates, plus 15 parts by weight Al₂O₃ as alumina hydrate having a particle size finer than one micron, and 35 parts by weight CrO₃ in 1,000 parts by weight water at 40° C. for 10 minutes.
(2) Anhydrous ammonia in gaseous form is added to the solution-slurry of Step 1 to effect complete precipitation as determined by a test of the supernatant liquid.
(3) The precipitate is filtered, then is ignited at 400° C. for one hour.
(4) The ignited filter cake is kneaded in such a way that 100 parts by weight of the powder from Item 3 plus 10 parts by weight of CrO₃ as ammonium chromate are mixed together with water to make a thick paste.
(5) The paste is then dried and calcined at 400° C. for one hour.
(6) The ignited paste is mixed with sufficient water to permit extrusion and forming into 1/8" x 3/8" cylinders which are then dried at 150° C. for one hour.

Preparation of the scavenger
(7) 250 parts by weight of 8-16 mesh activated alumina of the type used in Example 1 having a particle size of 8-14 mesh is immersed in a solution composed of 80 parts by weight of sodium sulfate in 500 parts by weight water at 70° C. for 10 minutes.
(8) The granules are dried, then calcined at 200° C. for one hour.

Use of the scavenger and catalyst
The scavenger and catalyst as prepared above are charged as in FIGURE 1.

EXAMPLE 18
Preparation of the catalyst
(1) A solution-slurry is prepared composed of 2.75 parts by weight manganese, 3.2 parts by weight copper, 3.0 parts by weight nickel, and 31.2 parts by weight chromium, all as the nitrates, together with 20 parts by weight alumina as finely divided hydrate of the type used in Step 1 of Example 7 in 100 parts by weight water at 60° C.
(2) A concentrated aqueous solution of ammonium carbonate is added to completely precipitate the metals in Item 1 as determined by a test of the supernatant liquid.
(3) The slurry is filtered and the filter cake is calcined at 400° C. for one hour.
(4) The ignited powder is kneaded in such a way that 100 parts by weight of powder from Item 3 plus 10 parts by weight of magnesium oxide as the nitrate and sufficient water are mixed to form a uniform thick paste.
(5) The paste is calcined at 350° C. for one hour.
(6) The ignited paste is formed into 1/8" x 3/8" cylinders.

Preparation of the scavenger
(7) 250 parts by weight of activated alumina, 4-8 mesh size, of the type used in Example 1 is immersed in a solution of 100 parts by weight of ammonium sulfate in 500 parts by weight of water at 90° C. for 10 minutes.
(8) The granules are then dried.

Use of the scavenger and catalyst
The scavenger and catalyst as thus prepared are charged as in FIGURE 1.

Preparation of the catalyst
(1) A solution-slurry is prepared composed of 16.3 parts by weight manganese, 18.9 parts by weight copper, both as the nitrates, plus 15 parts by weight Al₂O₃ as alumina hydrate having a particle size finer than one micron, and 35 parts by weight CrO₃ in 1,000 parts by weight water at 40° C. for 10 minutes.

EXAMPLE 19
(1) 250 parts by weight, 4-8 mesh, activated alumina of the type used in Example 1 is immersed in a solution
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EXAMPLE 24
Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 21 except that 59 parts by weight of cobalt as the nitrate replaces the copper.

EXAMPLE 25
Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 21 except that 113 parts by weight of cadmium as the nitrate replaces the copper.

EXAMPLE 26
Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 21 except that 65 parts by weight of zinc as the nitrate replaces the copper.

EXAMPLE 27
Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 21 except that 105 parts by weight of bismuth as the nitrate replaces the copper.

EXAMPLE 28
Catalytic mufflers are charged as shown in FIGURES 1 and 2 as just described in Example 21 except that 70 parts by weight of cerium as the nitrate replaces the copper.

EXAMPLE 29
Preparation of the catalyst
(1) 250 parts by weight of 4–8 mesh activated alumina of the type used in Example 1 is immersed in a solution composed of 30 parts by weight cobalt, 27.5 parts by weight manganese, and 4 parts by weight magnesium oxide all as the nitrates in 500 parts by weight water at 90° C. for 15 minutes.
(2) The impregnated granules are drained, then calcined at 500° C. for one hour.

Preparation of the lead scavenger
(3) 250 parts by weight of 8–14 mesh activated alumina of the type used in Example 1 is immersed in a solution of 100 parts by weight of magnesium sulfate in 500 parts by weight water at 90° C. for 10 minutes.
(4) The impregnated granules are drained then dried.

Use of the scavenger
The scavenger as thus prepared is charged to the upstream 9 cells of a muffler reactor compartmented into cells having equal volumes. The catalyst was charged to the remaining down-stream cell. The catalyst and scavenger can be mixed as generally described above and can be charged to a catalytic muffler of the type shown in FIGURE 2.

The lead scavenger in more finely divided form can be applied to the catalyst granules. Thus the scavenger as prepared above can be supported upon activated bauxite, 150–325 mesh, and mixed in equal proportions by weight with the catalyst granules. The mixture can be charged as in FIGURE 2 to one, two, three or more of the cells and can be charged to all of them using more or less of the scavenger.

EXAMPLE 30
Catalytic mufflers are charged as described in Example 29 except that 32 parts by weight of nickel is used to replace the cobalt specified in Step 1.

EXAMPLE 31
Catalytic mufflers are charged as described in Example 29 except that 28 parts by weight of copper replaces the cobalt in Step 1.

EXAMPLE 32
Catalytic mufflers are charged as described in Example 29 except that 28 parts by weight of iron replaces the cobalt in Step 1.
EXAMPLE 33
Catalytic mufflers are charged as described in Example 29 except that 33 parts by weight of zinc replaces the cobalt in Step 1.

EXAMPLE 34
Catalytic mufflers are charged as described in Example 29 except that 34 parts by weight of cerium replaces the cobalt in Step 1.

EXAMPLE 35
Catalytic mufflers are charged as described in Example 29 except that 35 parts by weight of bismuth replaces the cobalt in Step 1.

What is claimed is:
1. In an apparatus for treatment of automobile exhaust gases resulting from use of leaded fuel; a scavenger and a catalyst, the scavenger serving to remove from the exhaust gases the lead compounds deleterious to the catalyst, the scavenger and the catalyst being selected from the following group:

   Scavenger:
   - Sulfates of:
     - Ammonia
     - Sodium
     - Potassium
     - Lithium
     - Magnesium

   Catalyst:
   - Manganese-chromia-manganite oxides, chromites and manganites of:
     - Copper
     - Iron
     - Cobalt
     - Nickel
     - Cadmium
     - Zinc
     - Bismuth
     - Cerium
     - Platinum
     - Rhodium
     - Palladium
     - Ruthenium

2. In a process for treatment of automobile exhaust gases produced by burning leaded gasoline the step comprising passing said gases into contact with a scavenger selected from the group consisting of the sulfates of ammonia, sodium, potassium, lithium, and magnesium, and passing the gases into contact with a catalyst selected from the group consisting of manganese-chromia-manganite oxides, chromium, manganites of copper, iron, cobalt, nickel, cadmium, zinc, bismuth and cerium and precious metal catalysts selected from the group consisting of platinum, rhodium, palladium and ruthenium.

3. In a process for treatment of automobile exhaust gases produced by burning leaded gasoline the step comprising first passing said gases into contact with a scavenger selected from the group consisting of sulfates of ammonia, sodium, potassium, lithium, and magnesium, and thereafter passing the treated gases into contact with a catalyst selected from the group consisting of manganese-chromia-manganite oxides, chromium, manganites of copper, iron, cobalt, nickel, cadmium, zinc, bismuth and cerium and precious metal catalysts selected from the group consisting of platinum, rhodium, palladium and ruthenium.

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