June 21, 1966 A. B. STILES **3,257,163**

METHOD OF TREATING AUTOMOBILE EXHAUST GASES

Filed Feb. 12, 1965

FIG. 1

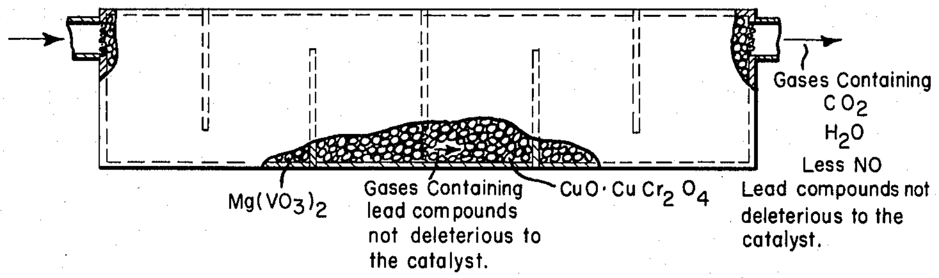
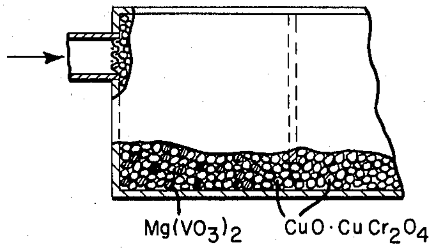


FIG. 2



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METHOD OF TREATING AUTOMOBILE EXHAUST GASES

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This application is a continuation-in-part of my copending application U.S. Serial No. 193,899, filed May 4, 1962, and now abandoned, which is in turn a continuation-in-part of application U.S. Serial No. 116,081, filed June 9, 1961, and now abandoned.

This invention relates to the treatment of automobile exhaust gases which contain such products as nitrogen 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 catalyst and a lead scavenger as follows,

- Scavenger:
  - Vanadium oxides, and vanadates of—
    - Alkali metals
    - Alkaline earth metals
    - Aluminum
    - Copper
    - Iron
    - Cobalt
    - Nickel
    - Manganese
    - Cerium
    - Chromium
- Catalyst:
  - Mangano-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 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. Where the scavenger and catalyst are placed in separate zones or beds, the exhaust gases are passed over both beds continuously throughout operation of the engine.

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

Alternatively the magnesium vanadate 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.

Exhaust gases can be mixed with extraneous air before entering the muffler in order to provide sufficient oxygen for complete combustion of the carbon monoxide and hydrocarbons. The air can be supplied by means of a pump or venturi or any other conventional means.

The scavengers do not remove all lead components 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 sequester most of the products of combustion of the lead compounds and the halogen compounds so that they have no effect on the catalyst.

Scavengers

The scavengers to be used are ammonium vanadate, vanadium pentoxide, vanadium tetroxide, and the vanadates of:

Sodium
Potassium
Lithium
Calcium
Barium
Strontium
Magnesium
Aluminum
Copper
Iron
Cobalt
Nickel
Manganese
Cerium
Chromium

It is to be noted that in the above list the ammonium vanadate is converted at relatively low temperature to vanadium oxides and is to be considered equivalent to vanadium pentoxide, vanadium tetroxide, and their mixtures.

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 particles in the range of about $\frac{1}{16}$ to $\frac{1}{2}$ 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 particles 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 aerogels.

Ordinarily from about 5 to 50% by weight of an alkali metal or alkaline earth metal 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 mangano-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 mangano-chromia-manganites have the following empirical chemical composition:

$$XCr_2O_n \cdot 2YMnO_m$$

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 can vary from 3:0.5 to 3:30. The atomic ratio, that of Y:X, is substantially the same and thus when Y equals 3, X can equal 0.5 to 30.

A mangano-chromia-manganite can be prepared having a ratio of Mn:Cr of 3:2 according to methods of Lazier U.S. Patent 1,746,782 and 1,964,001 and Wortz 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 a product having a ratio of 3:2 because a third of the chromium is not precipitated and is washed away.

The mangano-chromia-manganites can be prepared by procedures which are described in detail in the Howk 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 mangano-chromia-manganites of the desired Mn:Cr ratio.

CO-CATALYST

A co-catalyst can be included with the mangano-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 chromate 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: mangano-chromia-manganite can vary greatly and can range from, say, 10:1 to 1:10. About 1:1 is preferred.

INTERSPERSANTS

It is often desirable to add an interspersant to the catalyst aggregate as described in the above mentioned Howk and Stiles applications. The interspersants are refractories which have a melting point above 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 mangano-chromia-manganite apart. The refractory crystallites serve a similar function with crystallites of co-catalysts which are present.

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

(1) Aluminum oxide and hydroxide
(2) Titania
(3) Thoria
(4) Ceria
(5) Chromia
(6) Magnesia
(7) Calcium oxide and hydroxide
(8) Barium oxide and hydroxide
(9) Strontium oxide
(10) Zinc oxide
(11) Manganese oxide
(12) Silica
(13) Beryllia
(14) Zirconia
(15) Lanthana
(16) Hafnia

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

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

The amount of the interspersants can be widely varied and the total of the first interspersants can run from, say, 5 to 75% based upon the weight of mangano-chromia-manganite plus a co-catalyst if there is one. A second interspersant 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 interspersants can be found in the Howk 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) Alundum
(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 m.^{2}/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 m.^{2}/g. with pore dimensions of at least 60% less than 200 Angstroms. Mangano-chromia-manganite catalysts employing such preferred supports are described and claimed in U.S. application Serial No. 109,483, 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.

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.

The catalyst containing the alkali metal vanadate or vanadium oxide, 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 vanadium compound. 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, chromates, 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 manganates such as ammonium manganate. The preparation of catalysts will be illustrated further in the examples.

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

The catalysts, together with co-catalysts and interspersants if any, can be pilled or tableted as can the mangano-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 1/100 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 chloroplatinic 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 exhaust 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-slurry composed of 20 parts by weight magnesium oxide as the nitrate and 117 parts by weight ammonium metavanadate in 500 parts by weight water at 90° C. for 10 minutes.

(5) The granules are drained, then calcined at 400° C. for one hour.

Use of lead scavenger and lead catalysts

The catalyst and scavenger as prepared above are charged into a muffler-reactor as shown in FIGURE 1. The catalyst is placed in the 3 down-stream cells. The lead scavenger is placed in equal weight in the 3 up-stream cells. The exhaust gases when first contacting the lead scavenger are freed of a portion of the lead which would otherwise poison and slowly deactivate the catalyst in the down-stream cells. A large part of the lead is not absorbed by the scavenger nor by the catalyst but this lead does not greatly affect the catalyst.

Although the lead scavenger does not primarily function as a catalyst, it has appreciable activity for the oxidation and abatement of the noxious components of automotive engine exhausts, particularly when the scavenger is comparatively new.

The scavenger and catalyst above described are also employed as shown in FIGURE 2 of the drawing. Equal parts by weight of the granules of magnesium metavanadate and of the platinum catalyst are mixed and charged into the first section of the catalytic muffler as illustrated in FIGURE 2. The remainder of the muffler is filled with the platinum catalyst.

The exhaust gases from an internal combustion engine are mixed with air and introduced into the converter. The lead compounds contained in the gases are substantially removed as they pass through the first section. The exhaust gases are passed over both the scavenger section and the catalyst section continuously throughout operation of the engine.

A similar catalytic muffler charge can be made by using the mixture of granules in two, three, or all of the sections.

A similar catalyst charge is prepared using the precious metal catalyst described but supporting the magnesium vanadate 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% SiO_2–12% Al_2O_3, 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-slurry composed of 170 parts by weight ammonium metavanadate in 500 parts by weight water at 90° C. for 10 minutes.

(4) The granules are drained, then are calcined at 400° C. to convert the ammonium vanadate to V_2O_5.

Use of the scavenger and catalyst

The catalyst as prepared above is placed in the last three cells and the scavenger in equal weight is placed in the first three cells of the reactor-muffler shown in FIGURE 1. Exhaust gases are passed over both the scavenger and the catalyst continuously throughout the operation of the engine to which such a reactor-muffler is attached.

The scavenger and catalyst particles are intermixed in equal parts by weight and charged into the first cell of a muffler 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 a 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 by 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 CrO_3, and 40 parts by weight Al_2O_3 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 prepared in Step 1 to cause complete precipitation as indicated 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 pilling lubricant and pilled in a pharmaceutical machine to form ⅛" x ⅛" cylinders, whereas the third part is extruded as a moist paste to produce ⅛" x ⅛" 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 sodium metavanadate in 500 parts by weight water at 75° C. for 10 minutes.

(8) The impregnated granules are dried at 175° C. for 1 hour.

Use of the scavenger and catalyst

The scavenger is charged to the first three cells and an equal weight of catalyst is charged to the last three cells in FIGURE 1. Exhaust gases are passed over both the scavenger and the catalyst continuously throughout the operation of an engine to which such a muffler-reactor is attached.

The scavenger and catalyst particles are intermixed in equal parts by weight and charged into the first cell of a muffler 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 5, 6 and 7 above can be supported upon finely pulverized and porous silica-alumina, 150–325 mesh, that is it passes 150 and is retained on 325.

EXAMPLE 8

Preparation of the catalyst

(1) A solution-slurry is prepared composed of 59 parts by weight of nickel as the nitrate and 100 parts by weight CrO_3 in 1,000 parts by weight of water at 45° C. together with 40 parts by weight of pigment-grade titanium dioxide.

(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 is calcined at 400° C. for one hour.

(4) The powder obtained from Item 3 is kneaded in such a way that 100 parts by weight of the powder and 16.4 parts by weight of Ce_2O_3 as the nitrate are charged to a kneading machine together with sufficient water to form a uniform thick paste.

(5) The paste is dried and calcined at 400° C. for one hour.

(6) The calcined paste is converted to pills having ⅛" x ⅛" dimensions as right cylinders.

(7) The pills are heat treated at 500° C. for three hours.

Preparation of the scavenger

(8) 250 parts by weight of silica-alumina in the form of ⅛" x ⅛" cylinders and having a surface area of 40 square meters per gram and having 50% of the pores

less than 400 A. in diameter is immersed in a solution-slurry composed of 9 parts by weight of Al as the nitrate and 117 parts by weight of ammonium metavanadate and 50 parts by weight water at 90° C.

(9) The impregnated cylinders are drained, then calcined at 300° C. for one hour.

Use of the scavenger and catalyst

The scavenger as above prepared is charged to the first of ten equal cells in a muffler-reactor. The catalyst is charged to the down stream 9 equal cells so that the weight relationship between the scavenger and catalyst is 1 to 9.

The scavenger and catalyst can also be mixed and used as shown in FIGURE 2 of the drawings. Equal parts by weight of the catalyst and scavenger can be charged to the first section as illustrated in FIGURE 2 with catalyst in the remaining section. Instead the mixture can be used in two, three, or even more of the sections.

A similar catalyst charge can be prepared using the scavenger in very finely divided form. Thus equal parts by weight can be charged into one, two, three or more cells of a mixture into which the scavenger is supported upon activated alumina, 150–325 mesh.

EXAMPLE 9

Catalytic mufflers are charged as described in Example 8 with the exception that 59 parts by weight of cobalt replaces the nickel of Item 1.

EXAMPLE 10

Catalytic mufflers are charged as described in Example 8 with the exception that 113 parts by weight of cadmium replaces the nickel specified in Item 1.

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

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 ⅛" x ⅛" 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-slurry composed of 31 parts by weight of copper as the nitrate and 117 parts by weight of ammonium metavanadate in 500 parts by weight of water at 90° C. for 10 minutes.

(8) The granules are then dried and calcined at 300° C. for one hour.

Use of the scavenger and catalyst

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

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

The catalyst can be mixed with the lead scavenger in more finely divided form. Thus the catalyst as prepared in Items 7 and 8 can be supported upon diatomaceous earth having particle size 150–325 mesh.

EXAMPLE 17

(1) 250 parts by weight, 4–8 mesh, activated alumina of the type used in Example 1 is immersed in a solution composed of 30 parts by weight cobalt and 6.9 parts by weight zirconium dioxide, both as nitrates, in 500 parts by weight water at 80° C.

(2) The impregnated alumina is drained, then calcined at 400° C. for one hour.

Preparation of the scavenger

(3) 250 parts by weight of 4–8 mesh granular silica alumina having a surface area of 40 square meters per gram and having 50% of the pores smaller than 400 A. in diameter is immersed in a solution-slurry composed of 117 parts by weight ammonium metavanadate and 25 parts by weight titanium dioxide as a colloidal dispersion in 500 parts by weight water at 90° C. for 10 minutes.

(4) The impregnated granules are drained, then calcined at 300° C.

Use of the scavenger and catalyst

The scavenger and catalyst as above prepared are charged as shown in FIGURE 1.

The scavenger and catalyst particles can instead be intermixed in equal parts by weight and charged into the first cell of the muffler 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 Item 3 and 4 above can be supported upon pulverized silica gel, particle size 30–80 microns.

EXAMPLE 18

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 17 but with 32 parts by weight of copper as the nitrate used together with the ammonium metavanadate in Step 3.

EXAMPLE 19

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and just as described in Example 17 except that 9 parts by weight of aluminum as the nitrate is used together with the ammonium metavanadate in Step 3.

EXAMPLE 20

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and just as described in Example 17 with the exception that 30 parts by weight of cobalt as the nitrate is used together with the ammonium metavanadate in Step 3.

EXAMPLE 21

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 17 with the exception that 30 parts by weight of nickel as the nitrate is used together with the ammonium metavanadate in Step 3.

EXAMPLE 22

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 17 except that 35 parts by weight of cerium as the nitrate is used together with the ammonium metavanadate in Step 3.

EXAMPLE 23

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 17 with the exception that 17 parts by weight of chromium as the nitrate is used together with the ammonium metavanadate in Step 3.

EXAMPLE 24

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 17 with the exception that 166 parts by weight of Na_3PO_4 replaces the ammonium metavanadate in Step 3.

EXAMPLE 25

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 17 with the exception that 150 parts by weight of K_2HPO_4 is used instead of the ammonium metavanadate in Step 3.

EXAMPLE 26

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 17 with the exception that 174 parts by weight of K_2SO_4 is substituted for the ammonium metavanadate in Step 3.

EXAMPLE 27

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 17 with the exception that 142 parts by weight of Na_2SO_4 is substituted for the ammonium metavanadate in Step 3.

EXAMPLE 28

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 17 with the exception that 135 parts by weight of $Ni_3(PO_4)_2$ is substituted for the ammonium metavanadate in Step 3.

EXAMPLE 29

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 17 with the exception that 150 parts by weight of $NiSO_4$ is substituted for ammonium metavanadate in Step 3.

EXAMPLE 30

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 17 with the exception that 121 parts by weight of $NaVO_3$ is substituted for the ammonium metavanadate in Step 3.

EXAMPLE 31

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 17 with the exception that 138 parts by weight of KVO_3 is substituted for the ammonium metavanadate in Step 3.

EXAMPLE 32

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as described in Example 17 with the exception that 130 parts by weight of $Mg(VO_3)_2$ is substituted for the ammonium metavanadate in Step 3.

EXAMPLE 33

Preparation of the catalyst

(1) 250 parts by weight of 4–8 mesh activated silica gel having a surface area of 330 square meters per gram and having 50% of the pores finer than 100 A. in diameter is immersed in a solution-slurry containing 63 parts by weight of copper as the nitrate and 10 parts by weight of titanium dioxide as a colloidal dispersion in 500 parts by weight water at 60° C. for 10 minutes.

(2) The granules are calcined at 350° C. for one hour.

Preparation of the scavenger

(3) 250 parts by weight of 4–8 mesh activated alumina of the type used in Example 1 is immersed in a solution-slurry of 68 parts by weight of barium as the nitrate and 117 parts by weight of ammonium metavanadate in 500 parts by weight water at 90° C. for 10 minutes.

(4) The granules are drained, then calcined at 350° C. for one hour.

Use of the scavenger and catalyst

The scavenger and catalyst as thus prepared are charged to a muffler-reactor as shown in FIGURE 1.

The scavenger and catalyst particles can instead be intermixed in equal parts by weight and charged into the first cell of a muffler-reactor 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 activated alumina, 100–170 mesh.

EXAMPLE 34

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 33 except that 59 parts by weight of nickel replaces the copper in Item 1.

EXAMPLE 35

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 33 except that 56 parts by weight of iron as the nitrate replaces the copper.

EXAMPLE 36

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 33 except that 59 parts by weight of cobalt as the nitrate replaces the copper.

EXAMPLE 37

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 33 except that 113 parts by weight of cadmium as the nitrate replaces the copper.

EXAMPLE 38

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 33 except that 65 parts by weight zinc as the nitrate replaces the copper.

EXAMPLE 39

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 33 except that 105 parts by weight of bismuth as the nitrate replaces the copper.

EXAMPLE 40

Catalytic mufflers are charged as shown in FIGURES 1 and 2 and as just described in Example 33 except that 70 parts by weight of cerium as the nitrate replaces the copper.

EXAMPLE 41

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-slurry composed of 30 parts by weight of nickel as the nitrate and 117 parts by weight of ammonium metavanadate in 500 parts by weight water at 90° C. for 10 minutes.

(4) The impregnated granules are drained, then calcined at 350° C. for one hour.

Use of the scavenger

The scavenger as thus prepared is charged to the upstream 9 cells of a muffler reactor compartmented into 10 cells having equal volume. 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 42

Catalytic mufflers are charged as described in Example 41 except that 30 parts by weight of nickel is used to replace the cobalt specified in Step 1.

EXAMPLE 43

Catalytic mufflers are charged as described in Example 41 except that 32 parts by weight of copper replaces the cobalt in Step 1.

EXAMPLE 44

Catalytic mufflers are charged as described in Example 41 except that 28 parts by weight of iron replaces the cobalt in Step 1.

EXAMPLE 45

Catalytic mufflers are charged as described in Example 41 except that 33 parts by weight of zinc replaces the cobalt in Step 1.

EXAMPLE 46

Catalytic mufflers are charged as described in Example 41 except that 34 parts by weight of cerium replaces the cobalt in Step 1.

EXAMPLE 47

Catalytic mufflers are charged as described in Example 41 except that 51 parts by weight of bismuth replaces the cobalt in Step 1.

I claim:

1. In a process for treatment of automobile exhaust gases produced by burning leaded gasoline the steps comprising adding air to said gases and passing them continuously throughout operation of the automobile into contact with a scavenger selected from the group consisting of the vanadates of alkali metals, alkaline earth metals, aluminum, copper, iron, cobalt, nickel, manganese, cerium, and chromium and a catalyst selected from the group consisting of mangano-chromia-manganite; oxides, chromites, 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.

2. In a process for treatment of automobile exhaust gases produced by burning leaded gasoline the steps comprising adding air to said gases and passing them continuously throughout operation of the automobile first into contact with a scavenger selected from the group consisting of the vanadates of alkali metals, alkaline earth metals, aluminum, copper, iron, cobalt, nickel, manganese, cerium and chromium and thereafter into contact with a catalyst selected from the group consisting of mangano-chromia-manganite; oxides, chromites, 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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