United States Patent [19]

Whitehurst

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[54] **SORBENT FOR REMOVAL OF HEAVY METALS**

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[73] Assignee: Mobil Oil Corporation

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[21] Appl. No.: **444,609**

Related U.S. Application Data

[63] Continuation of Ser. No. 319,264, Dec. 29, 1972, abandoned.

[52] **U.S. Cl.** **208/251**; 208/253; 208/252

[51] **Int. Cl.**..... **C10g 17/00**

[58] **Field of Search**..... 208/251 R, 253, 252, 290, 208/297, 299

[56] **References Cited**

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[57] **ABSTRACT**

A novel use for sorbents involving the removal of heavy metals from liquid solutions has been discovered. More specifically, it has been discovered that these sorbents remove alkyl lead moieties from gasoline. The sorbents are comprised by a suitable substrate bonded to a metal by means of organic or inorganic cation exchanger functional groups.

5 Claims, 4 Drawing Figures

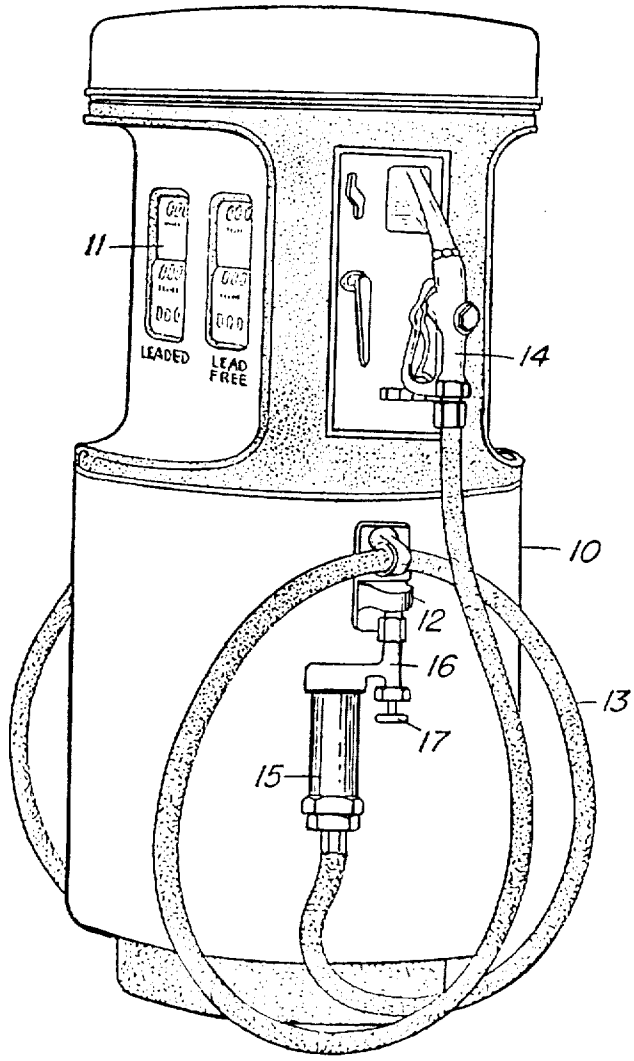
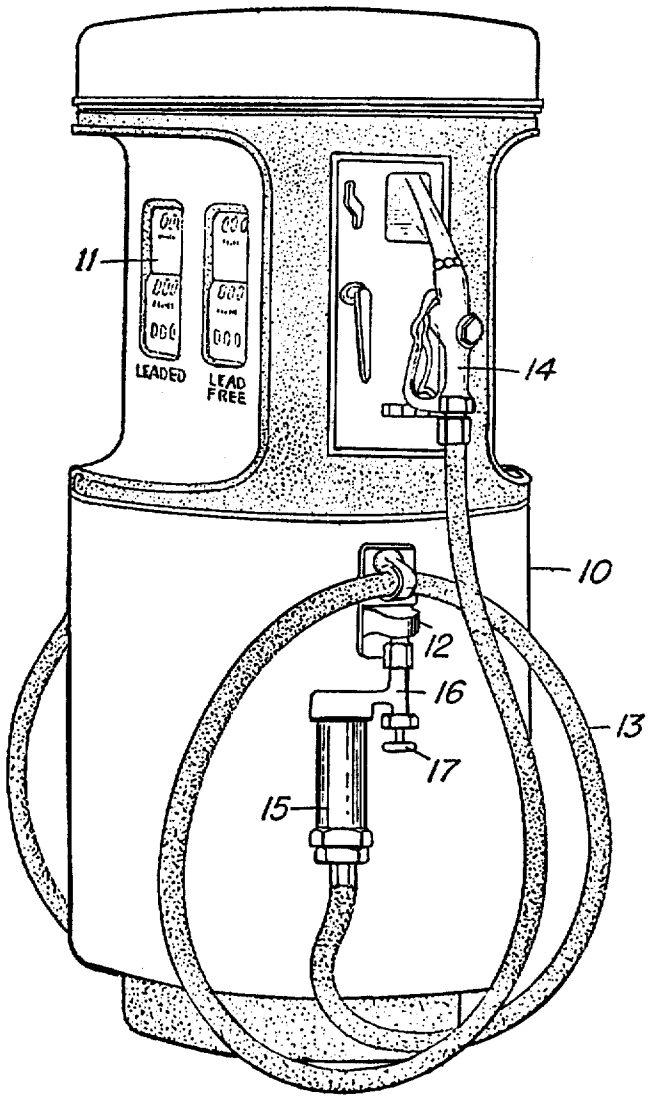


FIG. 1



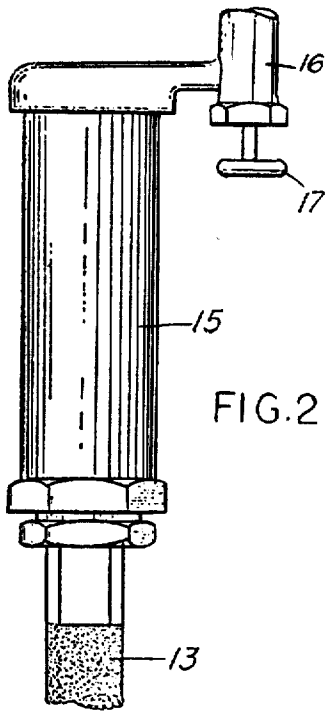


FIG. 2

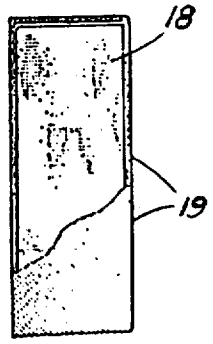
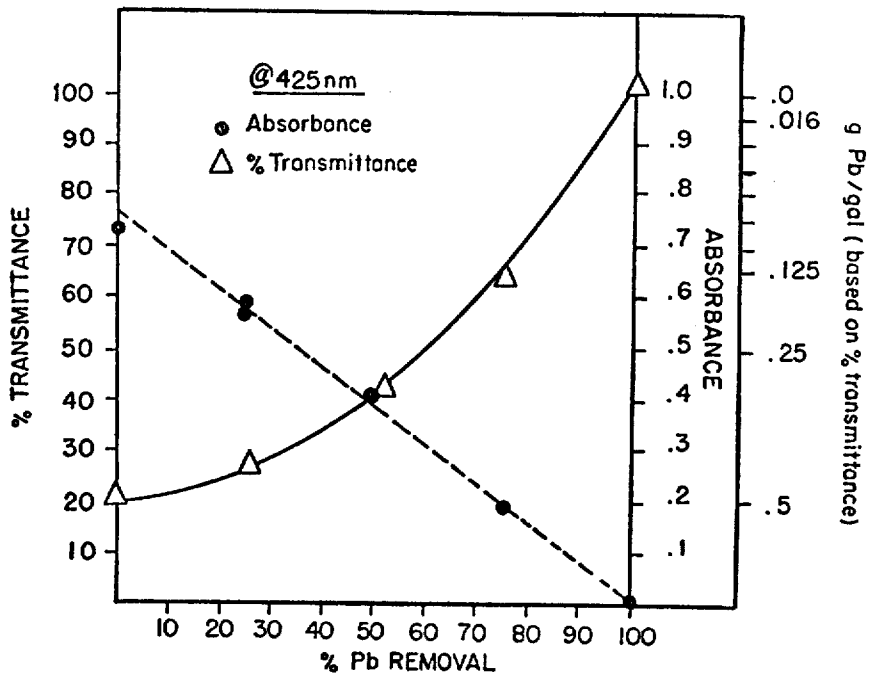


FIG. 3

FIGURE 4


@425nm
Absorbance
% Transmittance
% TRANSMITTANCE
100
90
80
70
60
50
40
30
20
10
ABSORBANCE
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
g Pb/gal (based on % transmittance)
.0
.016
.125
.25
.5
10 20 30 40 50 60 70 80 90 100
% Pb REMOVAL

SORBENT FOR REMOVAL OF HEAVY METALS

CROSS-REFERENCE TO RELATED APPLICATION

This case is a continuation of U.S. Pat. application Ser. No. 319,264 filed Dec. 29, 1972 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention deals with the removal of metals from compositions containing such metals as organic or inorganic compounds. It more particularly refers to removal of lead from gasoline. The need for the removal of metals is evidenced by the fact that their presence in hydrocarbon charge stocks conducted to catalytic cracking and catalytic reforming process units is known to poison and shorten the life of the catalyst with which such metal contaminated stocks come into contact.

It is also desirable to remove trace metals from lubricating oils or to recover soluble metal catalysts from reactor effluents or polymer solutions. The removal of heavy metals such as mercury, silver, calcium and the like from the water effluents of chemical or photographic plants is also highly desired from an ecological standpoint.

Unburned hydrocarbon, carbon and carbon monoxide emissions are regarded by many as representing a substantial source of air pollution. These engine emissions are subject to photo-chemical reaction in the atmosphere, providing what has been termed smog, which is an irritant of lachrymal and respiratory system tissues.

The incompletely oxidized carbon, e.g. carbon monoxide and unburned hydrocarbons, present in engine exhaust are the result of incomplete combustion of the hydrocarbon fuel in the engine combustion chamber. Complete oxidization of such carbon monoxide and/or hydrocarbons transforms such to carbon dioxide and water, probably in the form of steam due to the high combustion temperature. Neither carbon dioxide nor steam is considered a harmful emission.

Various means have been employed to reduce or eliminate carbon monoxide and unburned hydrocarbon emissions. One approach has been to pass the conbustible exhaust through a catalytic converter located in the engine's exhaust system where the carbon monoxide and hydrocarbons are catalytically oxidized, usually by the introduction of supplemental air, to carbon dioxide and water.

It is known that residues of alkyl lead from combustion of leaded gasoline tend to poison catalysts available for oxidizing unburned hydrocarbons and carbon monoxide in an engine exhaust. Such poisoning severely shortens the useful life of exhaust combustion catalysts. It has thus been heretofore proposed that "lead free" gasoline be supplied for use in automobiles equipped with emission control devices which utilize catalysts to help further oxidize exhaust gases.

Under most proposals, small, trace amounts of lead would be allowed in "lead-free" gasoline. The Federal Government regulations require all gasoline sales outlets to furnish at least one grade of gasoline having less than 0.07 gram of lead per gallon to the public by July 1, 1974. On Feb. 23, 1972 the Environmental Protection Agency in a paper relating to the 1970 Clean Air Act Amendments offered for comment a requirement of 0.05 grams of lead per gallon of gasoline. Other proposals have been even more stringent.

The normal network of petroleum product distribution involves railroad tank cars, pipelines, water borne tankers, tank trucks and bulk storage tanks. For commercial operation these are presently set up to handle different products. For example, the same pipeline might be used to convey a shipment of regular grade gasoline, premium grade gasoline, distillate fuel and other light liquid products in succession. According to present procedures, that portion of the fluids carried by the pipeline which constitutes an intermingling of the two products at their interface is diverted to use with the lower grade product, thus avoiding degradation of the higher grade hydrocarbon.

However when leaded gasoline is followed by lead-free gasoline, not just the interface comprising in intermingling or the two products, but the entire leadfree shipment becomes degraded. When leaded gasoline, containing tetraethyl lead, tetramethyl lead or a mixture of transalkylation products of the two is contacted with the metal or other surfaces of transportation and storage facilities, a significant amount of lead is left deposited in scale and on these surfaces. Since alkyl lead components are infinitely soluble in light hydrocarbons such as gasoline, upon after using the same faculties for lead free gasoline, the latter product becomes contaminated with lead which may run as high as about 0.1 grams of lead per gallon or more. These amounts of lead are sufficient to impair the life of exhaust emission control oxidation catalysts and are in excess of the presently proposed allowable limits on lead content of lead free gasolines.

2. Description of the Prior Art

Techniques have heretofore been known for removal of dissolved or suspended heavy metal contaminants from liquid products.

In catalytic cracking and reforming operations, the use of guard chambers containing a variety of sorbents and/or catalysts intended to remove heavy metal contaminants from the charge stock before contact is made with the catalyst have been described. Catalytic hydrodesulfurization processes and catalysts remove some amount of heavy metal contamination from hydrocarbon streams processed thereby.

Systems for removal of lead from gasoline have also been proposed. Presently known techniques require considerable time or are non-selective in effecting removal from the gasoline not only of the lead but also of those additives which are desired to be retained, such as antioxidants, anti-icing additives, metal passivators, detergents and the like.

One previously proposed system for removing lead from gasoline is described in U.S. Pat. No. 2,368,261. There, acid activated clay, such as bentonite which had been previously treated with hydrochloric or sulfuric acid, is used. Leaded gasoline is percolated through the clay whereby up to 95 percent of the lead present is removed. Unfortunately, acid activated clays will also remove other gasoline additives which are required or desired for proper protection and functioning of automotive equipment.

Another approach is that described in U.S. Pat. No. 2,392,846. According to an example in this patent, a five gallon lot of leaded gasoline is treated with 20 ml. of stannic chloride followed by addition of 100 grams of activated carbon. This results in decomposition of the tetraalkyl lead and adsorption of the lead decomposition products on the activated carbon thus drastically

reducing the lead content. The gasoline is removed from the activated carbon by decantation. This is a very slow process which permits the processing of about 35 gallons of gasoline per hour. Unfortunately even in this system, the additives desired to be retained in the gasoline are also adsorbed by the activated carbon.

Both the processes described in the cited prior patents depend for effectiveness on a chemical conversion of the tetraalkyl lead. The lead compounds can be reacted with such materials as halogens, halogen acids, metal halides, metal salts, sulfur dioxide, carboxylic acids, metals in the presence of hydrogen etc. While alkyl leads are infinitely soluble in gasoline, the resulting decomposition products are not readily soluble in hydrocarbons and hence can be selectively adsorbed on high surface adsorbents.

The American Oil Company, in a paper presented at the May 9, 1972 meeting of the API Division of Refining noted that in a significant number of its stations it was presently unable to meet the 0.05 gram/gal. or even the 0.07 gram/gal. requirement using scrutinous control of their distribution system and segregation of products. The area of greatest potential contamination was that of the service station itself. The report would indicate that gasoline manufacturers with distribution systems more extensive than those of American, and relying only on distribution control to ensure that the unleaded gasoline will remain within specifications, face an extremely difficult and expensive undertaking.

It is a primary objective of this invention to provide means to remove heavy metals from liquid, particularly hydrocarbon, streams. It is a further objective of this invention to remove lead alkyls from gasoline. Other and additional objects of this invention will become apparent from a consideration of this entire specification including the claims and drawings.

SUMMARY OF THE INVENTION

In accordance with and in fulfillment of the aforestated objectives, an embodiment of this invention consists of utilizing a sorbent comprising a porous solid substrate having pores with a minimum pore diameter of about 10A. and a minimum surface area of about 10 m^2/g; the substrate being modified by a functional group of an organic or inorganic cation exchanger which acts as a bridging member between the substrate and a metal; the metal being a Group IB, IIB or IVA metal having an atomic number of at least 29 for the removal of heavy metals from non-aqueous liquid solutions, and more particularly for removing lead from gasoline. For purposes of this dislosure, the group designations referred to are as defined in *Lange's Handbook of Chemistry* at 58–61 (10th ed. 1967), the term "cation exchanger" is defined in *Ion Exchange* by F. Helfferich at 12–47 (1962).

The following metals work particularly well: copper (Cu), silver (Ag), mercury (Hg) and tin (Sn).

BRIEF DESCRIPTION OF THE DRWINGS

FIG. **1** of the drawings attached hereto represents a typical service station gasoline pump modified according to the present invention.

FIG. **2** is an enlarged view of the cartridge for containing the lead removal agent.

FIG. **3** is a view in fragmentary section of a cartridge for containing the lead removal agent.

FIG. **4** is an analytical curve illustrating amount of lead removal as a function of absorbance and transmittance.

DESCRIPTION OF SPECIFIC EMBODIMENTS

In a preferred embodiment, the sorbent is placed in a canister in the discharge hose of a service station gasoline pump. This preferred embodiment is more particularly described by making reference to FIGS. **1–3.**

As shown in FIG. **1,** a gasoline dispensing pump of conventional design includes a housing indicated generally at **10** within which are contained a motor driven pump and a metering device, not shown. The metering device drives, through suitable gearing, indicators within a panel **11** to report gasoline dispensed and price for the amount so dispensed. The fuel after passing through the metering device, is conducted to the outside of the housing through a pipe connection **12** and into a discharge hose **13** equipped with a valve nozzle **14.**

The modification to conventional dispensing pumps is a canister **15** connected to the fuel discharge **12** by a pipe **16** provided with a valve for which the operating handle is shown at **17.** Fuel from the pipe **16** is conducted to the top of canister **15** containing the lead removal agent from which it passes through a suitably prepared cartridge and is thence discharged to hose **13** and nozzle **14.**

A typical cartridge is shown in FIG. **3** as constituted by a gauze container **18** within a wire mesh supporting cage **19.** Disposed within the container gauze **18** is a mass of the lead removal agent of the type which characterizes this invention.

For the usual service station, a cartridge having a diameter of about 24 inches and length of about 12 inches should be adequate to reduce the lead content to acceptable levels for a working life of about one month. When it is desired to change the cartridge, valve **17** is closed, the hose **13** is drained and the canister **15** is removed by unthreading from the top portion thereof. It is thus a simple matter to replace the cartridge in a very short period of time and return the dispensing pump to duty.

As previously noted, this invention is to be utilized in non-aqueous solutions, as the presence of water limits the performance of the sorbent. Due to the fact that gasoline on occasion contains small amounts of water, it is contemplated that a deliquescent material may be placed in the upstream portion of the cartridge to prevent the sorbent from being rendered of limited performance due to the presence of water.

EXAMPLES 1–11

These tests consisted of contacting approximately three to six volumes of gasoline containing 2.5 grams of lead/gallon of gasoline with one volume of sorbent under ambient conditions followed by a lead analysis of the contacted gasoline.

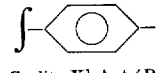
Following the contacting of the 2.5 grams of lead/gallon of gasoline fuel with the sorbent prepared as previously described, the lead content of the treated gasoline was analyzed as follows:

A 5 part by volume sample of gasoline was treated with 1 part by volume of a saturated solution of silver nitrate ($AgNo_3$) in absolute ethanol. After standing for ten minutes, the content of reduced silver in the sample was determined by turbidometric technique. These

measurements were done at 425 nm or 500 nm depending on the gasoline used. The measured transmission was compared with a standard analytical curve similar to the one illustrated by FIG. 4.

The percent lead removed by the sorbents is given in Table 1.

TABLE 1

Example number	Sorbent designation	Sorbent type	Percent Pb removal
1	AW		62
2	AM		64
3	BK		68
4	W		74
5	AF		79
6	X		81
7	AG		95
8	O		~100
9	AE	Zeolite-X] Ag^{+} (Pd^{+2})	24
10	AA	Zeolite-X] Sn^{+2} (Pd^{+2})	40
11	AD	Zeolite-X] Ag^{+}	83

Zeolite X is a substrate containing a cation exchanger functional group and may be chemically defined as a crystalline aluminosilicate having a prescribed crystalline form as described by A. G. Oblad, Oil & Gas Journal 70, 84, 1972.

What is claimed is:

1. A method for effecting the removal of heavy metal contaminants from solution in a substantially hydrocarbon solvent which comprises contacting said solution, in a flowing system, with a solid sorbent having a surface area of at least about 10 m^2/g, having pores of at least about 10 angstroms diameter and comprising a material selected from the group consisting essentially of carboxylic or sulfonic acid substituted organic cation exchange resin or a zeolite-X zeolite which has bonded thereto through its acid sites a metal of Groups IB, IIB or IVA of the Periodic Table having an atomic weight of at least 29.

2. The method as claimed in claim 1 wherein said metal is selected from the group consisting of Cu, Ag, Hg and Sn.

3. The method as claimed in claim 1 wherein said heavy metal contaminants are lead alkyl moieties and said substantially hydrocarbon solution is gasoline, and said contacting is carried out at about −50°C. to 100°C. and at space velocities of up to about 40 LHSV.

4. A method as claimed in claim 3 wherein said sorbent is located in a conduit means in a gasoline distribution system between a storage means and a dispensing means.

5. A method as claim in claim 4 including pumping said gasoline from said storage means through said conduit means to said dispensing means and sorbing said lead from said gasoline during said pumping.

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